20 al 22 de noviembre de 2019

Edificio CINC. Ciudad de la Cultura

Santiago de Compostela-Galicia (España)

Colegio Oficial de Químicos de Galicia

Sociedade Portuguesa de Química

Asociación de Químicos de Galicia

XXV ENCONTRO GALEGO-PORTUGUÉS DE QUÍMICA

20 al 22 de noviembre de 2019

Edificio Cinc. Ciudad de la Cultura

Santiago de Compostela-Galicia (España)

Colegio Oficial de Químicos de Galicia

Sociedade Portuguesa de Química

Asociación de Químicos de Galicia

XXV ENCONTRO GALEGO-PORTUGUÉS DE QUÍMICA.
Noviembre 2019

Coordinador Editorial
Cristina Díaz Barral
Manuel Rodríguez Ménez

Edita
Colegio Oficial de Químicos de Galicia
Rúa Lisboa, nº 10, Local 31E – Edificio Área Central Fontiñas.
15707 Santiago de Compostela (A Coruña)
www.colquiga.org

Tirada
50 Ejemplares y 250 en formato digital

Imprime
OCERO
Sada (A Coruña)

Depósito Legal
VG699-2017

ISBN
978-84-09-16320-5

Este libro de comunicaciones y conferencias, presentadas en el XXV Encontro Galego-Portugués de Química, Colegio Oficial de Químicos de Galicia

Catalogación recomendada Libro de resúmenes del XXV Encontro Galego-Portugués de Química. Edificio Cinc. Ciudade da Cultura. Santiago de Compostela (España) 2019

© Colegio Oficial de Químicos de Galicia

Derechos reservados. Prohibida la reproducción de este libro por cualquier medio, total o parcialmente, sin permiso expreso del editor.

El coordinador editorial declara que el contenido de los resúmenes científicos es de la entera responsabilidad de los respectivos autores.

PRÓLOGO

Foi no ano 1985, cando se estableceu un vínculo entre os químicos do norte de Portugal e de Galicia organizando aquel I ENCONTRO GALEGO PORTUGUÉS DE QUÍMICA. Xa pasaron 34 anos daquel primeiro ENCONTRO que os profesores José Luis Costa Lima, José Luis Figueiredo, Gonzalo Vázquez Uña, Juan Vieites Bautista de Sousa, Pelayo Rubido Muñiz e José Varela Cardama puxeron en marcha.

Neste ano 2.019 os ENCONTROS GALEGOS PORTUGUESES acadan a súa vixésima quinta edición, coa mesma ilusión coa que aqueles pioneiros se puxeron en marcha e, tamén, coa mesma idea: Os ENCONTROS deben ser un punto de encontro entre os profesionais da química das dúas nacións irmáns.

En recordo daquel Primeiro ENCONTRO hoxe volvemos sobre os nosos pasos e reunímonos na cidade de Santiago de Compostela que nos veu nacer aquel 14 de novembro de 1985, pero este XXV ENCONTRO xa non é só un punto de reunión entre portugueses e galegos é, xa un espazo onde se xuntan persoas que teñen a química por profesión non só na península Ibérica senón, tamén, mais alá das nosas fronteiras. Como ten que ser, xa que a química é unha ciencia sen fronteiras.

A química é unha ciencia que abarca todas as facetas da vida e, tamén, sirve de base para outras disciplinas e, entre todas, poder facer unha sociedade mais xusta e próspera. Por iso é importante que as persoas que estean a traballar na química, xa sexa na vertente científica como na súa aplicación empresarial, teñan un punto de encontro onde poñer en valor o seu coñecemento, onde establecer vínculos de colaboración futura para un maior avance da química e, en definitiva, da sociedade.

Espero e desexo que este XXV ENCONTRO GALEGO PORTUGUÉS sexa rico en conclusións, que permitan mellorar a vida das persoas e aportar solucións aos graves problemas que temos neste planeta chamado Terra. Estou seguro que así será. Pois a cidade de Santiago de Compostela, meta de preregrinaxe e cidade que invita a reflexión é o mellor marco onde facer este Congreso e, de paso, render homenaxe a aquel primeiro ENCONTRO e aos seus promotores.

Finalmente so espero que os desexos cos que vides a este XXV ENCONTRO GALEGO PORTUGUÉS DE QUÍMICA se vexan cumpridos. Grazas por vir e grazas aos pioneiros daquel ENCONTRO GALEGO PORTUGUÉS DE QUÍMICA

Dr. Manuel Rodríguez Méndez
Decano Colegio Oficial de Químicos de Galicia.

ÍNDICE

INTRODUCCIÓN 7
LOCALIZACIÓN DEL XXV ENCONTRO GALEGO PORTUGUÉS DE QUÍMICA 8
INFORMACIÓN SOBRE EL CONGRESO 12
PROGRAMA DEL ENCONTRO 13
RELACIÓN DE CONFERENCIAS PLENARIAS 16
RELACIÓN DE COMUNICACIONES 17
CONFERENCIAS PLENARIAS 40
COMUNICACIONES ORALES 46
- QUÍMICA ALIMENTARIA 47
- QUÍMICA Y MEDIOAMBIENTE 63
- BIOQUÍMICA Y BIOTECNOLOGÍA 83
- CATÁLISIS Y FOTOCATÁLISIS 90
- ENSEÑANZA DE LA QUÍMICA 96
- ELECTROQUÍMICA 100
- QUÍMICA INDUSTRIAL E INGENIERÍA QUÍMICA 103
- NANOQUÍMICA E NANOTECNOLOXÍA 111
- QUÍMICA DE POLÍMEROS 121
- QUÍMICA ANALÍTICA 125
- QUÍMICA-FÍSICA 140
- QUÍMICA INORGÁNICA 152
- QUÍMICA ORGÁNICA 157
- QUÍMICA Y SALUD 168
- QUÍMICA TEÓRICA 200

COMUNICACIONES POSTER 205
- QUÍMICA ALIMENTARIA 206
- QUÍMICA Y MEDIOAMBIENTE 229
- BIOQUÍMICA Y BIOTECNOLOGÍA 259
- CATÁLISIS 268
- ENSEÑANZA DE LA QUÍMICA 276
- QUÍMICA INDUSTRIAL 279
- NANOQUÍMICA Y NANOTECNOLOGÍA 295
- QUÍMICA DE POLÍMEROS 303
- QUÍMICA ANALÍTICA 310

QUÍMICA FÍSICA 332
QUÍMICA INORGÁNICA 344
QUÍMICA ORGÁNICA 349
QUIMICA Y SALUD 365
QUÍMICA TEÓRICA 380
ÍNDICE DE AUTORES 383

INTRODUCCIÓN

Un año más se celebra este congreso que reune a los profesionales de la química de ambos lados del Miño. Este año se conmemora la 25ª Edición de este congreso internacional, en la misma ciudad donde nació y con la misma ilusión de la primera vez, aquel 14 de noviembre de 1985, cuando nos reunimos en Santiago de Compostela. Hoy lo hacemos con la convicción de haber superado las expectativas de aquellos pioneros que vieron necesario establecer un intercambio de conocimientos, que permitiese potenciar las relaciones interpersonales de los profesionales de la Química. Con el mismo espíritu, personas a ambos lados del Miño y de los 5 continentes, se reúnen para hablar de química.

Esta XXV edición del ENCONTRO GALEGO-PORTUGUÉS DE QUÍMICA ha sido organizada bajo los auspicios del Colegio Oficial de Químicos de Galicia, Asociación de Químicos de Galicia y Sociedade Portuguesa de Química.

COMISIÓN DIRECTIVA
Manuel Rodríguez Méndez (COLQUIGA)
José Luis Francisco Fuentes (COLQUIGA)
José Ramón Bahamonde (COLQUIGA)
José Luís Figueiredo (FEUP)
José Luís Costa Lima (FFUP)
Baltasar Romão de Castro (FCUP)

COMISIÓN CIENTÍFICA
Tomas Lindahl. Premio Nobel de Química 2015
Pilar Bermejo Barrera (USC)
José Manuel Andrede Garda (UDC)
José María Fernández Solis (UDC)
Artur Silva (UA)
Fernanda Proença (FCUP)
Joaquim Luis Faria (FEUP)

COMISIÓN ORGANIZADORA
José María Fernández Solis (UDC)
Manuel Rodríguez Méndez (COLQUIGA)
José Manuel Andrade Garda (UDC)
José Luis Francisco fuentes (COLQUIGA)
José Ramón Bahamonde Hernando (COLQUIGA)
María Pastora Bello Bugallo (USC)
Ana María Gayol González
Emilio Manuel Osende Bardanca (COLQUIGA)

La Comisión Organizadora del XXV Encontro Galego-Portugués de Química, desea manifestar su agradecimiento a las siguientes instituciones:

LOCALIZACIÓN DEL XXV ENCONTRO GALEGO PORTUGUÉS DE QUÍMICA

Santiago de Compostela é a capital da Comunidade Autónoma de Galicia. A súa zona antiga é Patrimonio da Humanidade dende o ano 1.985. Xunto con Xerusalem e Roma, Santiago é un centro de peregrinación do cristianismo. Dende a etapa medieval, chegase a Santiago dende diversas rutas de peregrinación, dende o centro de Europa a mais longa, ata a súa Catedral adeicada ao Apostolo Santiago. Centos de miles de peregrinos de todo o mundo veñen peregrinando ata a súa Catedral.

Santiago de Compostela ten unha población de case 96.456 habitantes (INE 2017), que pode duplicarse durante o curso universitario.

INFORMACIONES VARIAS

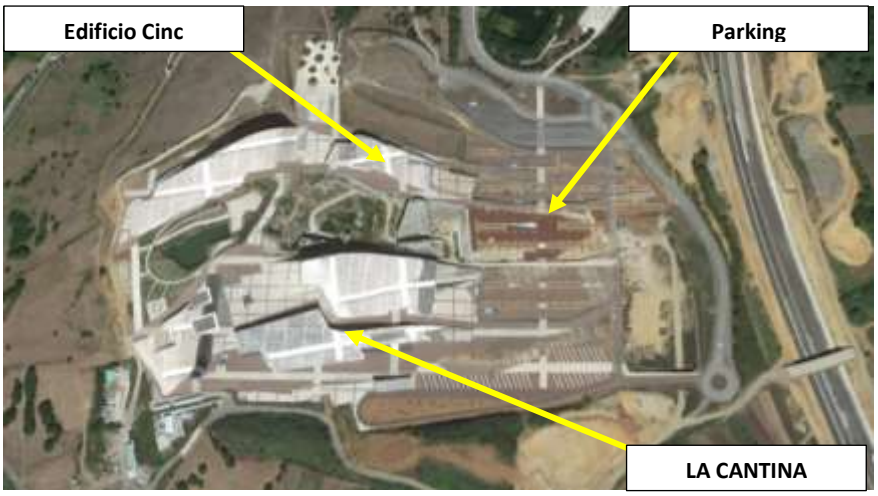
El Encontro se celebrará en el edificio Cinc, situado en la Cidade da Cultura de Galicia. En Monte Gaias, s/n, 15707 Santiago de Compostela.

LA CIDADE DA CULTURA DE GALICIA

Situada en Santiago de Compostela, la Cidade da Cultura de Galicia se yergue en la cima del monte Gaiás como un formidable hito arquitectónico del nuevo siglo dedicado al conocimiento y a la creatividad.

Diseñada por el arquitecto americano Peter Eisenman para acoger las mejores expresiones de la cultura de Galicia, España, Europa, Latinoamérica y el mundo, con objeto de conectar Galicia a las redes nacionales e internacionales de creatividad y

conocimiento. Sus singulares edificios, conectados por calles y plazas y dotados de un avanzado nivel tecnológico, configuran un espacio de excelencia para la reflexión y el debate.



PARA COMER LOS DÍAS DEL CONGRESO:

Todos los días hay un Catering en el edificio Cinc, de 13:30 a 15:00 h., para comer. Dentro de este edificio hay un servicio de cafetería y dentro de las instalaciones de la Cidade da Cultura está LA CANTINA, donde podréis comer (se recomienda ir a primera hora).

LA CANTINA

La Cantina es una taberna característica del rural gallego trasladada a este moderno y espectacular complejo. Esta es la propuesta que el estudio Nómada aplicó en la Cantina, que recibió el máximo galardón en los prestigiosos *Restaurant & Bar Design Awards* con el que se reconoce al restaurante mejor diseñado en todo el mundo.

Con un lenguaje contemporáneo, pero partiendo de la cultura popular gallega, la Cantina dispone de mesas alargadas y en paralelo bajo unos árboles esquemáticos que evocan las romerías a la sombra de las *carballeiras*.

Un largo mostrador que atraviesa la pared sirve y anexiona dos espacios: cafetería y comedor, imponiéndose el color geométrico y desinhibido usado tradicionalmente en las manifestaciones artísticas populares gallegas.

Además de servicio de cafetería en horario ininterrumpido, la Cantina cuenta con carta de comidas y un completo menú del día.

ACCESO A LA CIDADE DA CULTURA DE GALICIA.

POR AUTOPISTA. Es gratis

El acceso puede hacerse desde la autopista, el tramo de la autopista que rodea a Santiago de Compostela es gratis. Desde la autopista, en cualquier sentido, saliendo por la SALIDA 70 se accede directamente a la Cidade da Cultura de Galicia.

Desde la Ciudad de Santiago de Compostela

La Cidade da Cultura de Galicia es un complejo que ya forma parte de la ciudad de Santiago de Compostela y es uno de sus atractivos turísticos desde el que puede divisarse la Ciudad y su Catedral. Por ello, por la ciudad señalización que lleva a la Cidade da Cultura de Galicia.

Tiene una zona de aparcamiento muy amplio y en donde está señalizado el acceso a los diversos edificios. Las coordenadas GPS que llevan al parking son:

42º 51’ 15’’ N

08º 31’ 24’’ O

CONEXIONES EN BUS CON EL NÚCLEO URBANO DE SANTIAGO. LÍNEA 9:

- Itinerario de ida. Salidas desde Casas Novas (frecuencia: 60 min.). Desde las 8:00 h:

Casas Novas - Santa Isabel - Galeras - San Clemente - A Senra - Virxe da Cerca - Porta do Camiño - San Roque - Basquiños - Pastoriza - Anxo Casal - Rodríguez de Viguri - Fontiñas - Piscinas - Multiusos Fontes do Sar - Cidade da Cultura.

- Itinerario para salir de la Cidade da Cultura de Galicia (frecuencia: 60 min.). Hasta las 22:00 h:

Cidade da Cultura - Multiusos Fontes do Sar - Piscinas - Fontiñas - Concheiros - Campo da Angustia - Rúa de Bonabal - San Roque - Virxe da Cerca - A Senra - San Clemente - Galeras - Santa Isabel - Casas Novas.

INFORMACIÓN SOBRE EL CONGRESO

RECEPCIÓN

La oficina de información y la recepción para retirar la documentación del Encontro, estará localizada en el vestíbulo del Edificio CINC y estará abierta a las 11:00 horas del día de inicio del Encontro y permanecerá abierta durante todos los días de su celebración.

EQUIPAMIENTO DE PROYECCIONES

Las salas de conferencias están equipadas con ordenador y cañón de proyección. Cada orador deberá transferir el fichero de su presentación al ordenador de la sala que le corresponda, con la antelación suficiente. Siendo aconsejable se realice en la sesión anterior.

PRESENTACIONES ORALES

Las conferencias plenarias tendrán una duración de 45-50 minutos más 10 minutos para preguntas. La duración de las comunicaciones orales será de 10 minutos más 5 minutos para resolución de dudas. Se solicita a todos los oradores que cumplan el tiempo estipulado, a fin de evitar retrasos en el programa.

POSTERS

Deberán colocarse el primer día, primera sesión y retirarse el último, tras el acto de clausura, por los propios autores de la comunicación. Se solicita a los autores de los trabajos presentados, estén presentes junto a los mismos durante la sesión de discusión.

CENA DEL ENCONTRO

La cena del Encontro se celebrará el día 21 de noviembre a las 21:00 horas en el Comedor del Convento de San Francisco. La asistencia deberá confirmase en el momento de efectuar la acreditación y recogida de documentación. El coste es de 35 euros.

PROGRAMA DEL ENCONTRO

DÍA	hora	SALAS			
		PLENARIAS	A	B	C
		A			
20	10:00-12:00	**INSCRIPCIÓN Y RECEPCIÓN**			
	12:00-12:30	**SESIÓN DE APERTURA. Sala A**			
	12:30 -13:30	**CONFERENCIA PLENARIA APERTURA. Sala A**			
	13:30-15:00	COMIDA			
	15:00		QS01	QO01	QA01
	15:15		QS02	QO02	QA02
	15:30		QS03	QO03	QA03
	15:45		QS04	QO04	QA04
	PAUSA: 5 minutos				
	16:05		QS05	QO05	QA05
	16:20		QS06	QO06	QA06
	16:35		QS07	QO07	QA07
	16:50		QS08	QO08	QA08
	17:05-18:00	CAFÉ - POSTERS			
	18:00-18:45	**CP1**			
	18:45		QS09	QO09	ALM01
	19:00		QS10	EDU03	ALM02
	19:15		QS11	QO10	ALM03
	19:30		QS12	ELC01	ALM04
	19:45		QS13	ELC02	ALM05

día	hora	SALAS			
		PLENARIAS	A	B	C
		A			
21	10:00		QS14	NN01	AMB01
	10:15		QS15	NN02	AMB02
	10:30		QS16	NN03	AMB03
	10:45		QS17	NN04	AMB04
	PAUSA: 5 minutos				
	11:05		QS18	NN05	AMB05
	11:20		QS19	NN06	AMB06
	11:35		QS20	NN07	AMB07
	11:50		QS21	NN08	AMB08
	12:05-12:45	CAFÉ - POSTERS			
	12:45-13:30	**CP2**			
	13:30-15:00	ALMUERZO-COMIDA			
	15:00		QS22	NN09	AMB09
	15:15		QS23	BB01	AMB10
	15:30		QS24	BB02	AMB11
	15:45		QS25	BB03	AMB12
	BB04				
	16:05		QS26	BB04	AMB13
	16:20		QS27	BB05	AMB14
	16:35		QS28	QA12	AMB15
	16:50		ALM06	QA13	AMB16
	17:05-17:45	CAFÉ - POSTERS			
	17:45 - 18:30	**CP3**			
	18:30		ALM07	QF01	AMB17
	18:45		ALM08	QF02	AMB18
	19:00		ALM09	QF03	AMB19
	19:15		ALM10	QF04	IND01
	19:30		ALM11	QF05	IND02
	19:45				IND00
	21:00	CENA DEL ENCONTRO			

día	hora	SALAS			
		PLENARIAS	A	B	C
		A			
22	10:00		ALM12	QF06	IND03
	10:15		ALM13	QF07	IND04
	10:30		ALM14	QF08	IND05
	10:45		ALM15	QF09	IND06
	PAUSA: 5 minutos				
	11:05		ALM16	QF10	CAT01
	11:20		ALM17	QF11	CAT02
	11:35		ALM18	POL01	CAT03
	11:50		ALM19	POL02	CAT04
	12:05		ALM20	POL03	CAT05
	12:20-12:45	PAUSA- CAFÉ			
	12:45-13:30	**CP4**			
	13:30-15:00	ALMUERZO-COMIDA			
	15:00		ALM21	QI01	QT01
	15:15		ALM22	QI02	QT02
	15:30		ALM23	QI03	QT03
			PAUSA 5 minutos		
	15:50		ALM24	QI04	QA09
	16:05		QT04	EDU01	QA10
	16:20		BB00	EDU02	QA11
	PAUSA: 5 minutos				
	16:40	ACTO DE CLAUSURA			

RELACIÓN DE CONFERENCIAS PLENARIAS

CONFERENCIA APERTURA:

Prof. Dr. Tomas Lindahl

Premio Nobel de Química 2.015.

"Repair of endogenous DNA damage and cancer prevention"

CP 1 **Prof. Dra. María Eduarda Pereira.**

CESAM & LAQV-REQUIMTE, Department of Chemistry, University of Aveiro.

"Innovative Solution to Remove a Mixture of Potential Toxic Elements from Natural Waters"

CP 2 **Prf. Dr.D. Xosé Luis Legido Soto.**

Dpto. Física Aplicada. Catedrático Universidad de Vigo.

"Propiedades físicas de productos termales para usos terapéuticos"

CP 3 **Prof. Dr. Adrián M.T. Silva**

Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculty of Engineering, University of Porto

"Identification and Catalytic Degradation of Environmental Contaminants of European Union Concern"

CP 4 **Dra. Dña. María Covadonga Salgado Blanco**

Intecmar (Instituto Tecnolóxico para o Control do Medio Mariño de Galicia). Vilagarcía de Arousa.

"programa de control do medio mariño de galicia: a química na seguridade alimentaria"

RELACIÓN DE COMUNICACIONES

CONFERENCIAS PLENARIAS

CONFERENCIA DE APERTURA

Prof. Dr. Tomas Lindahl
"Repair of endogenous DNA damage and cancer prevention"

CP 1 **Prof. Dra. María Eduarda Pereira.**
"Innovative Solution to Remove a Mixture of Potential Toxic Elements from Natural Waters"

CP 2 **Prf. Dr.D. Xosé Luis Legido Soto.**
"Propiedades físicas de productos termales para usos terapéuticos"

CP 3 **Prof. Dr. Adrián M.T. Silva**
"Identification and Catalytic Degradation of Environmental Contaminants of European Union Concern"

CP 4 **Dra. Dña. María Covadonga Salgado Blanco**
"programa de control do medio mariño de galicia: a química na seguridade alimentaria"

COMUNICACIONES

Química Alimentaria.

ALM01 Otimização de processos de extração de antocianinas a partir de cálices de Hibiscus sabdariffa L. para obtenção de corantes alimentares naturais

ALM02 Extrato de Gomphrena globosa L. como corante natural em biscoitos: efeito em diferentes parâmetros físicos

ALM03 Caracterização fenólica e nutricional das infusões de cinco plantas aromáticas e suas propriedades bioativas

ALM04 Fatty acids profile in acorn gluten free bread

ALM05 Characterization of aroma compounds in barley and malt using a low-pressure assisted extraction procedure

ALM06 Irradiação UV-C de cogumelos para obtenção de vitamina D2

ALM07 Aplicação de frutos de Lonicera caerulea L. var. Kamtschatica no desenvolvimento de corantes alimentares com propriedades bioativas

ALM08 Prospeção da atividade antibacteriana de frutos e pedúnculos de Lycium barbarum L.

ALM09 Efeito dos polifenóis da couve como modeladores da alergia alimentar

ALM10 The use of seaweed in daily diets as a source of nutrients

ALM11 Análise comparativa dos frutos da Opuntia ficus-indica e O. robusta

ALM12 Carboximetilación del almidón de yuca ecuatoriano (*Manihot esculenta Crantz*) por modificación química Carboximetilación del almidón de yuca ecuatoriano

ALM13 Development of a natural ingredient from kiwi epicarp with potential application in the food industry

ALM14 Punica granatum L. bioresidues as a source of compounds with bioactive properties

ALM15 Modelling and optimization of the extraction process of pigments from seaweed from the Galician coast

ALM16 Optimización de la extracción de compuestos fenólicos a partir de 8 especies de algas comestibles de las costas de Galicia utilizando la metodología de superficie respuesta

ALM17 Thymus carnosus extracts as a source of phytochemicals for neuroprotection and anti-aging products

ALM18 Conteúdo Fenólico dos Azeites Virgem Extra Monovarietais Portugueses

ALM19 Influência do tamanho de gota e razão O/A na atividade antioxidante de galatos em sistemas emulsionados

ALM20 Ingredientes naturais como agentes conservantes: aplicação em formulações nutracêuticas

ALM21 Perfil fenólico e propriedades bioativas do epicarpo de jabuticaba

ALM22 Carboximetilación del almidón de yuca ecuatoriano (*Manihot esculenta Crantz*) por modificación química Carboximetilación del almidón de yuca ecuatoriano

ALM23 Complexation of resveratrol with γ-cyclodextrin for lemon juices enrichment: effects on stability and antioxidant activity

ALM24 Validation of a GC-MS method to quantify acrylamide in biscuits and the use of asparaginase for its mitigation

ALM25 Chemical characterization and antioxidant activity of sweet cherry by-products: stems and pits

ALM26 Atividade anti-inflamatória e imunomoduladora de extratos de Lentinula edodes

ALM27 Las algas como nueva materia prima para la obtención de pigmentos

ALM28 Efeito do silicato de cálcio na composição química de Pleurotus ostreatus var. Florida

ALM29 Caracterização e quantificação de açúcares presentes na abóbora de chila através de cromatografia iónica

ALM30 Soluções corantes baseadas em emulsões duplas incorporando extrato de Sambucus nigra L.: Desenvolvimento e teste em diferentes matrizes alimentares

ALM31 Nova estratégia de coloração de produtos lácteos usando extratos antociânicos de flores comestíveis

ALM32 Valorização de cladódios de opuntia ficus-indica (l.) Miller

ALM33 Propriedades bioativas de infusões potenciadas pela mistura de plantas

ALM34 Controlo da qualidade do teor de CO2 em água mineral engarrafada

ALM35 Effect of a biosurfactant from the corn-milling industry on anthocyanins extracted during winegrape skin maceration

ALM36 Biosurfactant obtained from a corn residual stream as agent for improving water solubility of copper oxychloride pesticide: a comparative study

ALM37 Influência do ciclo de crescimento no perfil fenólico e nas propriedades bioativas de Cynara cardunculus L. var altilis

ALM38 Distribuição e atividade antioxidante do hidroxitirosol e seus ésteres em sistemas emulsionados

ALM39 Evaluation of the prebiotic galacto-oligosaccharides addition in the traditional Portuguese cake “bolo-de-arroz”

ALM40 Fraccionamiento de polisacáridos sulfatados de Bifurcaria bifurcata

ALM41 Volatile, phenolic and fatty acid profiles of Portuguese almond cultivars

ALM42 Desenvolvimento e Aplicação de um Revestimento Conservante Natural para Fiambres; Perfil Físico-Químico e Estabilidade

ALM43 Otimização da extração de antocianinas a partir de epicarpos de jabuticaba e validação da capacidade corante do extrato numa matriz alimentar

ALM44 Influence of traditional extraction techniques on chemical composition of Mentha pulegium liqueurs

ALM45 Profiling of volatile carbonyl compounds in defective green coffee beans by means of a fan-assisted extraction process.

ALM46 Evaluación del perfil fenólico individual de *Calluna vulgaris* (L.) y de su potencial bioactivo

Química Ambiental

AMB01 Modeling circular economy on combined treatment of chemical adsorption by bentonite and sulfate radical thermal activation-catalyzed sodium percarbonate of red winery wastewater

AMB02 Procesos avanzados de oxidación para la degradación del plaguicida metomilo en aguas de drenes del sector de Uraca, región Arequipa, Perú

AMB03 Contaminación y Acumulación de metales tóxicos (As, Al, Pb, Fe) en agua, vegetales y plantas medicinales de mayor consumo en la ciudad de Arequipa Perú

AMB04 Superparamagnetic hybrid nanostructured materials for environmental decontamination

AMB05 Efecto de la concentración de metales en la actividad de un biorreactor de membrana enriquecido en bacterias N-damo

AMB06 Can the impact associated with critical rare elements be reduced trough living macroalgae?

AMB07 3D tuned porous carbon monoliths as catalysts in wet peroxide oxidation of paracetamol

AMB08 Influence of agro-environmental conditions on phenolic compounds and biological properties of grape (Vitis vinifera L.) stems

AMB09 Variación espacio-temporal de la concentración de Cr y Ni en suelos y sedimentos intermareales

AMB10 Lipofilização de antocianinas baseado na retenção de enzimas em membranas porosas

AMB11 Can the recycling of valuable europium from wastes be achieved through live macroalgae?

AMB12 Monitorização de Pesticidas como Poluentes Emergentes em Rios do Nordeste de Portugal

AMB13 Desenvolvimento de um sensor eletroquímico para a deteção de compostos fenólicos em águas

AMB14 Polymeric coatings containing new antifouling synthetic bile acid derivatives to prevent marine biofouling

AMB15 Pharmaceutical Drugs as Environmental Emerging Pollutants

AMB16 White winery wastewater treatment by coagulation/flocculation optimized by a Simplex Lattice Design and O3/Fe2+/UV process

AMB17 Evaluation of the potential of marine macroalgae for gadolinium removal from aquatic systems

AMB18 Asparagopsis armata: a nightmare for Azores coast biodiversity

AMB19 A new biotecnological-based iron-fertilizer formulation for environmental sustainable correction of chlorosis of soybean plants grown in calcareous soils

AMB20 Construcción de un micro-prototipo de sistema de electrocoagulación para funcionamiento en flujo continuo

AMB21 Elaboración de un montaje para hallar la curva de volumen de gases generados en un proceso de electrocoagulación

AMB22 A comparison of three digestion methods to extract microplastics from marine plankton samples

AMB23 Avaliação Do Potencial De Valorização Do Composto Para A Remoção De Paracetamol Em Águas

AMB24 Extracción y determinación de Cd, Pb, As y Sb en agua empleando redes metalo-orgánicas de la familia uio-66

AMB25 Metals concentrations and removal along the SBR Wastewater Treatment Plant of Torres Vedras, Portugal

AMB26 Metals sorption and partitioning coefficients in all matrices of the Torres Vedras SBR WWTP, Portugal

AMB27 Formas de hierro y aluminio en suelo rizosferico y no rizosferico desarrollado sobre cenizas volcánicas del Volcan Cotopaxi, Ecuador

AMB28 Adsorción y desorción de aniones fluoruro y vanadato por dos Andosoles africanos

AMB29 Sustainable Strategies And Tools For Wildfires Prevention And Control: A Dynamic Evaluation

AMB30 Concentraciones de actividad de isótopos de uranio en muestras de suelo de la Costa Norte de Galicia (NW España)

AMB31 Kinetic modelling of the hydrothermal carbonization of compost derived from Municipal Solid Waste

AMB32 Fotocatálise heterogénea usando UV-LEDs aplicada ao pós-tratamento de efluentes vinícolas

AMB33 Comparison of glyphosate and imidacloprid induced toxicity using two cell models

AMB34 Soil water interface monitoring: development of automatic analysis tools

AMB35 Aplicação de minerais aluminossilicatos em processos foto-Fenton no tratamento de efluentes vinícolas

AMB36 Mellora do sistema de xestión de RAEE de Galicia (España) no marco da economía circular

AMB37 Three-dimensional reduced graphene/BiOI aerogels for photocatalysis degradation of water pollutants

AMB38 Síntese de meso-diarilporfirinas "push-pull" para usar em células solares como sensibilizadores

AMB39 Comparison of cadmium binding by humic and fulvic acids extracted from compost samples of different feedstock

AMB40 Assessment of the potentialities of siderophores produced by Rhizobium radiobacter to cope with iron deficiency in plants grown in calcareous soils

AMB41 plastics in our oceans: management strategies and modeling

AMB42 Avaliação das potencialidades do uso da cinza de carvão para remediar a Drenagem Ácida de Mina. Caso de estudo: Mina de Benga. Provincia de Tete. Moçambique

AMB43 Seguimiento del tratamiento en una Depuradora de Aguas Residuales Urbanas (EDAR) mediante fluorescencia de matriz de excitación-emisión (fluorescencia EEM)

AMB44 Characterization of chemical composition and sources contribution study of atmospheric particulate matter (PM10) from a Western-Europe coastal city

AMB45 Evolution of equivalent black carbon concentrations in an urban background site and correlation between on-line and off-line data

AMB46 Characterization, acid-base properties and metal complexation of humic-like substances extracted from organic matter during the composting process

AMB47 Green technologies applied to revalorize agricultural wastes. Case study: Camellia sinensis

Bioquímica y Biotecnología

BB00 Intermediate molecular weight poly (ethylene glycol) inhibits protein aggregation

BB01 Avaliação do efeito de extratos da polpa de Cucurbita ficifolia Bouché no stresse oxidativo celular

BB02 Voláteis, α e β- ácidos em lúpulo: um estudo da planta à cerveja

BB03 Drought stress effects on cowpea polyphenolic composition and antioxidant activity

BB04 Oligomerización enzimática de rutina en sistemas acuosos bifásicos biocompatibles

BB05 L-asparaginase recovery through supported ionic liquid materials based on silica

BB06 Bioactive potential of aqueous extracts from basidiomycete strains

BB07 Comparison of methods for extraction of biomolecules from Phaeodactylum tricornutum

BB08 Bio-hybrid magnetic nanoparticles for the purification of immunoglobulin G

BB09 Isolation and characterization of bioactive compounds from Phaeodactylum tricornutum.

BB10 Optimization of ergosterol extraction from Pleurotus mushrooms using response surface methodology (RSM)

BB11 Cosmeceutical properties of p-hydroxybenzoic acid and use of microencapsulation technique to ensure controlled release

BB12 nanoestructuras magnéticas para la mejora de técnicas en bioquímica y biología molecular

BB13 Decolorization of dyes from textile effluents by laccase using ionic liquids

Catálisis

CAT 01 Bidirectional Synergy between POMs and ZIFs in POM@ZIF Nanocomposites for an Improved OER Electrocatalysis

CAT 02 Bifunctional CoxNiyP nanowires for electrocatalysis of the oxygen and hydrogen evolution reactions and energy-saving of overall water splitting using a bipolar membrane

CAT03 Wet peroxide oxidation of paracetamol using natural clay-based materials as catalysts.

CAT04 Why not Iron? Revisiting the carbene insertion reactions

CAT05 Solvent-free desulfurization system to produce low-sulfur diesel using hybrid monovacant Keggin-type catalyst

CAT06 Funcionalización de superficies mediante nanopartículas de TiO2

CAT07 Study of the Performance of Alkaline Ionic Liquids for the Catalysis of Biodiesel Production from Waste Cooking Oil

CAT08 Valorização de óleos alimentares usados através de processos de conversão em biodiesel catalisados por líquidos iónicos

CAT09 Esterification and transesterification of glycerol to glycerol acetates in the presence of carbon catalysts - synthesis of fuel additives

CAT10 Production and characterization of biodiesel obtained by transterification catalyzed by ionic liquid choline hydroxide

CAT11 Degradation of textile dyes in aqueous solutions using type-Fenton

CAT12 Hybrid nanomaterials for photocatalytic environmental applications

Educación y Enseñanza de la Química

EDU01 A ciência cidadã e as atitudes dos alunos face à disciplina de Físico-Química

EDU02 Experimentos comestibles ¿Se puede degustar la ciencia?

EDU03 Diseño de un Sistema Automático para la Manipulación de Gases en el Aula

EDU04 Práctica virtual de Laboratorio de Química: Determinación del calor de vaporización del agua

EDU05 ExpHerimentando: una propuesta constructivista basada en un enfoque CTS (Ciencia, Tecnología y Sociedad)

Elecroquímica

ELC01 Preparation of AuNPs nanocomposites for electroanalytical sensors development

ELC02 Síntesis de clústeres de platino fotoquímica

Química Industrial e Ingeniería Química

IND00 Adsorption dynamics of CO2/CH4/N2 mixtures in zeolite 4A for Biogas Upgrading

IND01 Fixed Bed Dynamics of Multicomponent Adsorption of Pentane and Hexane Isomers in ZIF-8

IND02 Supercritical CO_2 extraction as green technology for obtainig coffee oil

IND03 Lipofilização de antocianinas baseado na retenção de enzimas em membranas porosas

IND04 Optimization of Nanoemulsion Formulations using Saponin from Quillaja Bark, a Natural Surfactant

IND05 One-step conversion of Eucalyptus globulus wood into platform chemicals under microwave irradiation using biphasic systems.

IND06 Heavy Metals Removal on Leachate for Use as Fertilizers

IND07 Pyrolysis of leather wastes from the footwear industry – preliminary results

IND08 Analysis of the relevant aspects of ecodesign to a circular economy: application in Galicia

IND09 Modified carbon nanotubes for the purification of immunoglobulin g

IND10 Extraction of the bioactive compounds from the solid residue obtained by microwave extraction using Mastocarpus stellatus red seaweed as raw material

IND11 Alternativas para el tratamiento de madera de pino azulada

IND12 Natural creams formulated with green extracts from wild Acacia dealbata Link flowers and thermal spring waters

IND13 Obtención de fertilizantes líquidos a partir de material bioestabilizado

IND14 Poly(ionic liquid)-based materials for CO2 capture

IND15 Pyrolysis of leather wastes from the footwear industry - preliminary results

IND16 Optimization and characterization of the products obtained from Eucalyptus globulus wood in sequential hydrothermal stages

IND17 Green extraction for the recovery of high valuable compounds from model red seaweeds.

IND18 Pressurized ethanolic extraction of polyphenols from maqui (Aristotelia chilensis Stuntz) leaves

IND19 Towards the circularity of products: the case of a waste intermediate plant.

IND20 Optimización de la planta de lavado de pasta cruda de celulosa para la excelencia ambiental

IND21 Use of nettle leaves (Urtica dioica L.) extracts as cosmetic agent in topical cream formulation based on thermal spring waters

Nanoquímica y Nanotecnología

NN01 Nanomateriais versátiles baseados na magnetita para aplicacións teragnósticas.

NN02 Nuevos materiales poliméricos termoplásticos reforzados con micro y nanopartículas de celulosa

NN03 Development of polysaccharide-based nanosystems using marine-based polymers

NN04 Photophysical characterisation of post-modified carbon dots obtained from olive mill wastewaters, and sensing behaviour toward p-nitroaniline

NN05 P-doped glucose-derived carbon/carbon nanotube hybrids for supercapacitors application

NN06 Synthesis of carbon nanostructures by chemical vapour deposition over Ni Al co oxides using plastic solid waste as precursor

NN07 Study of the interaction between fluorescent Carbon dots and the fluorescent by-products that result from their synthesis

NN08 Energy Storage for Fashion Applications: Fluorescent Textile Supercapacitors

NN09 The intrinsic redox ability of Electrogenerated Hydrophilic Carbon Nanomaterial

NN10 Coffee Grounds of Vending Machines: A Sustainable Route for Synthesis of Luminescent Carbon Nanomaterials

NN11 Water-in-oil nanoemulsions based in natural extracts with antimicrobial and antioxidant properties

NN12 Influence of the starch dissolution approach in the green synthesis of starch-capped silver nanoparticles

NN13 influencia del tamaño de partícula sobre las propiedades magnéticas de nanopartículas de fe3o4

NN14 Silica-based aerogels reinforced with aramid fibers for thermal insulation at extreme temperatures

NN15 Biocompatible and macrophage-targeting mannosylated lipid nanoparticles for the treatment of tuberculosis

NN16 Lapatinib-loaded nanostructured lipid carriers for breast cancer therapy

Química de Polímeros

POL01 Remediación ambiental en vías férreas: captación de metales pesados a través del uso de polímero impresos iónicamente (IIPs)

POL02 poly(diphenylacetylene)s: optical properties and structural analysis

POL03 Cellulose based gel polymer electrolytes for energy storage

POL04 Study of the degradation mechanisms of PVC insulation on electric wires

POL05 Synthesis and Sensing Ability of New Fluorescent Oxacyclophane-Calix[4]arene-based Polymer

POL06 Materiais de base poliuretano com resistência à fadiga térmica incrementada para calçado de segurança

POL07 Analysis of the effect of temperature on durability of polymers used in the coating of electrical conductors.

POL08 Lignina: ¿es posible garantizar su calidad?

Química Analítica

QA01 Determinación de sustancias tóxicas en superficies elaboradas con caucho reciclado mediante GC-MS/MS

QA02 Electrochemical sensing of benzocaine for cocaine profiling via molecularly imprinted polymers

QA03 Determinación del contenido de elementos traza en zumos comercializados en españa y portugal

QA04 Application of FTIR (Fourier Transform Infrared Spectroscopy) for determination of nutritional and antinutritional parameters in bean samples

QA05 Development of a selective electrochemical sensor based on molecularly imprinted polymers (MIPs)

QA06 Comparative amperometric determination of mercury using ionophor chelator and enzyme inhibition approaches

QA07 Nanofibers for solid phase extraction. How can we use them?

QA08 Biogenic amines determination by ion-pair chromatography using potentiometric detection

QA09 Estudio de los niveles de elementos críticos tecnológicos (TCEs) en muestras de algas mediante ICP-MS

QA10 Biomimetic magnetic particles in Sensors and Biosensors

QA11 Estudo do perfil de aminas biogénicas em amostras biológicas recolhidas de vacas leiteiras

QA12 Identificación de compuestos volátiles y semivolátiles en mieles mediante microextracción en fase sólida miniaturizada (SPME) seguida de GC-MS

QA13 Method validation for quantification of metals in natural waters by ICP-OES

QA14 Exploiting flow-based systems for monitoring persistent inorganic pollutants (PIPs) in recreational waters

QA15 Correlación entre métodos espectrofotométricos y electroquímicos para la determinación de la capacidad antioxidante en frutos silvestres.

QA16 Determinación de plomo en plásticos (LDPE) mediante el análisis de emulsiones por ETAAS

QA17 Direct determination of lead in mussels, microalgae and microplastics by ultrasonic slurry sampling-ETAAS

QA18 Prediction of methane and propane in natural gas using mid-IR spectrometry and PLS

QA19 Differentiation of microplastic polymers by reflectance FT-mid IR spectrometry and principal components analysis (PCA)

QA20 Exploiting solid phase extraction in a sequential injection system for phosphate determination in fertilized soil leachates

QA21 Caracterização de Pigmentos de Algas da Galiza

QA22 Ranitidine selective electrode based on cucurbit[6]uril for pharmaceutical quality control

QA23 Persistência de resíduos de disparo (GSR) de armas longas

QA24 Validación de un método rápido y efectivo para la determinación de cloruro de benzalconio en formulaciones farmacéuticas

QA25 Optimización de un método MSPD-UAE-GC-QqQ-MS/MS para el análisis de compuestos orgánicos de estaño en sedimentos

QA26 Stabilization of herbicide oxadiazon through microencapsulation

QA27 Voltammetric behaviour of the psychoactive substance benzylpiperazine

QA28 New electroanalytical method for the determination of formaldehyde in wood-based products

QA29 Essential oils and their individual components: analytical challenges in cosmetics

QA30 Evaluation of phenolic compounds and antioxidant activity of medicinal plants with potential for kidney disease treatment

QA31 Determination of antibiotics in different wastewater samples by LC-MS/MS

QA32 Variables implicadas en el desarrollo de métodos de análisis por inyección de grandes volúmenes en Cromatografía de Gases utilizando la interfaz TOTAD

QA33 Desenvolvemento dun método analítico para a determinación de elementos críticos tecnolóxicos en sedimentos mariños.

QA34 Optimización Operacional del Proceso de Extracción Polifenólica a Partir de Residuos de la Industria Vitivinícola

Química Física

QF01 The solubility of amino acids in aqueous electrolyte solutions

QF02 Multicomponent Diffusion in Hydrocarbon Mixtures

QF03 Caracterización fotofísica del 6-amino-1,3-benzotiazol-2-carbonitrilo para su uso como sonda fluorescente

QF04 Polymorphism of cocrystals: A case study

QF05 Comportamiento de sistemas ternarios de sal sodica con surfactantes en función de la temperatura

QF06 Estudo da dinámica da transferencia protónica no 2-ciano-6-hidroxibenzotiazol

QF07 Exploring the role of surface chemistry of carbon xerogels in the oxygen reduction reaction

QF08 Investigation of Orientationally Disordered Solid Phases

QF09 Investigation on the solubility and other thermophysical properties of quaternary ammonium salts aqueous solutions

QF10 Assessment of the actual light dose in photoreactions and phototherapies

QF11 Activity coefficients at infinite dilution of water and organic compounds in methylimidazolium based ionic liquids

QF12 High pressure Taylor dispersion technique as a tool for the measurement of diffusion coefficients in supercritical carbon dioxide

QF13 Thermodynamic properties of 9-phenylacridine

QF14 A method for the kinetic study of DNA nitrogenous bases alkylation reactions

QF15 Viscosidad dinámica de mezclas n-alcano + 1-octanol en función de la temperatura

QF16 Thermochemical properties of anthranilate derivatives

QF17 Evaluation of the effects of substituents on reactivity of 2-aminobenzoxazole and 2-metil-6-nitrobenzoxazole

QF18 Thermodynamic study of 4,4'-DDD and 4,4'-DDA

QF19 Synthesis of Pharmaceutical Nanococrystals - a Preliminary Approach

QF20 Solubility of hesperetin or benzoic acid in eutectic solvents

QF21 Improvement of physical-chemical properties of gemfibrozil

QF22 High pressure Taylor dispersion technique as a tool for the measurement of diffusion coefficients in supercritical carbon dioxide

Química Inorgánica

QI01 Influence of UiO-66(Zr) preparation strategies in its catalytic efficiency for desulfurization processes

QI02 Copper and cobalt complexes as a structural model for the galactose oxidase active site

QI03 Mn(III) biomimetic models: catalase activity and kinetic studies of their reaction with H2O2 and TBHP

QI04 NMR study of the interaction of Ga(III) complexes with liposomes

QI05 Estudio de la influencia del ligando en la obtención de arquitecturas helicoidales o meso-helicoidales

QI06 Evaluation of the effect of tris(3-hydroxy-4-pyridinonate) Fe(III) chelates to treat Iron Deficiency Chlorosis

QI07 Resolución quiral de complejos de Co(II) y Zn(II) derivados de bistiosemicarbazonas

QI08 Superoxide dismutase activity and neuroprotective effects of manganese salen complexes

Química Orgánica

QO01 Understanding the Mechanism of Action of LpxK - a Key Therapeutic Target for Antibiotic Drug Discovery

QO02 Novas pirano-3-desoxiantocianinas e estudo das suas propriedades cromáticas

QO03 Chlorophyll derivatives bearing uracil-alditols: synthesis and antibacterial and antitumor properties

QO04 Synthesis of new tetrasubstituted imidazoles with potential biological activity

QO05 Combined ammonium and pyridinium phthalocyanines for bacteria photoinactivation

QO06 Síntesis de un Inhibidor de la Enzima 3beta-HSD por Conversión Directa del Grupo Metilcetona de la 16-DPA en Amida Secundaria

QO07 Estudo Mecanístico para a Transproteção de Aminas Terciárias usando Boc2O: Acesso a Ambos os Enantiómeros do Ácido 2-Azanorbornano-3-exo-carboxílico

QO08 Análogos Gémini de vitamina D: Síntesis total de UVB1

QO09 Micro y nanopartículas de celulosa para su uso en productos industriales estratégicos

QO10 Coumarin derivatives as versatile scaffolds towards potential GSK-3β inhibitors

QO11 The Boron Hot-Spot Methodology: Peptide Functionalization

QO12 Synthesis and characterization of porphyrin-cyclodextrin dyes

QO13 Síntese de pigmentos azuis derivados de piranoflavílios e estudo das suas formas de equilíbrio em solução aquosa

QO14 Enantiomeric Resolution and Chiroptical Properties of Calix[4]arene-based Chiral Receptors

QO15 New Synthetic Approaches for Fluorescent Inherently Chiral Calix[4]arenes

QO16 Síntesis de epímeros de análogos de segunda generación de vitamina D

QO17 Novel Penicillin-based Sulfones to Unlock Bacterial Resistance to Antibiotics

QO18 Serine-based surfactants: potential drug delivery and antimicrobial agents

QO19 Sulfuros quirais como catalizadores asimétricos

QO20 Asymmetric Synthesis of a promising [18F]F-DOPA precursor

QO21 Extração, isolamento e transformação química da lenhina proveniente da lenha da videira

QO22 Disarming P. aeruginosa by Modulators of the Master Regulator of Quorum Sensing LasR

QO23 New pathways for paroxetine synthesis and nitration of the sesamol group for antibody binding.

QO24 Design And Synthesis Of A Novel Family Of Serine-Derived Surfactants: The Serine Ester-Quats

QO25 Mass Spectrometry Study of a Boron Hot-Spot Technology Based in 3-Hydroxyquinolinones

Química y Salud

QS01 Flor de Aloe vera: composición fenólica y propiedades bioactivas

QS02 Hypoxia-activated triazene prodrugs for tumor-selective delivery

QS03 Bioactive Compounds in haemodialysis polysulfone membrane to reduce oxidative stress and inflammation in chronic kidney disease patients

QS04 Photodynamic inactivation of antibiotic resistant bacteria using cationic porphyrins

QS05 Phlorotannins from Fucus vesiculosus and their potential to prevent diseases of the modern civilization

QS06 Sin Comunicación

QS07 Ésteres alquílicos de homarina: uma nova classe de inibidores da acetilcolinesterase

QS08 Bioactive compounds in haemodialysis polysulfone membrane to reduce oxidative stress and inflammation in patients on dialysis

QS09 The photobiological role of the sulfur atoms introduction into squaric ring in indolenine-based squaraine cyanine dyes

QS10 Influência da viabilidade das sementes na composição química e propriedades bioativas de Cynara cardunculus L.

QS11 Can the elderberry anthocyanins overcome the mitochondrial dysfunction associated with degenerative brain diseases?

QS12 Antiproliferative and cytostatic combined effects of simvastatin and 5-fluorouracil in an in vitro cancer model

QS13 Curcumin Analogs: Evaluation as Potential Therapeutic Agents

QS14 Phthalocyanine loaded nanodroplets for Photoacoustic Tomography

QS15 The potential antidiabetic effect of flavonoids through inhibition of fructose 1,6-bisphosphatase

QS16 Photoinactivation of Escherichia coli through water-soluble ammonium-phthalocyanines

QS17 Biocompatible Indium phthalocyanine with near-infrared absorption as contrast agent for photoacoustic imaging

QS18 Chalcones as modulators of neutrophils' oxidative burst, in physiological and hyperglycemic conditions

QS19 Síntese de derivados de imidazole e avaliação do potencial anticancerígeno em linhas celulares do carcinoma de células renais

QS20 Interaction of dietary polyphenols with the endothelium: when nutrimetabolomics meets biophysics

QS21 Synaptosomes as membranar models to study the effects of carotenoids on lipid peroxidation

QS22 Photoactive Cellulose Supported Materials for Antimicrobial Photodynamic Therapy (aPDT)

QS23 Development of new anticancer metallodrugs

QS24 Novel 9-substituted-acridine derivatives as potential Acetylcholinesterase inhibitors

QS25 Discovery of azaaurones as potent antimycobacterial agents

QS26 Aspectos químicos y nutricionales del filete de *Aloe vera*

QS27 Automated Microwave-assisted Synthesis for PET Radiochemistry

QS28 Estudo da fase inicial de agregación do beta-amiloide

QS29 Nanopartículas lipídicas como transportadores de compostos derivados das antocianinas para aplicação tópica

QS30 Recubrimiento antibacteial de una superficie de Ti6Al7Nb para implantes biomédicos.

QS31 Use of Phenanthroline Derivatives in Chemotherapy Treatments for Cancer and as Alternative Therapeutics in the Era of Antibiotic Resistance: Interaction with DNA and Modulation of the Efficiecy

QS32 The effects of N-alkyl chain length on the physicochemical and in vitro phototherapeutic properties of squaraine cyanine dyes

QS33 Estudio comparativo de la citotoxicidad en células de cáncer de pulmón A549 del efecto del grupo funcional enlazado al anillo piridoxal del ligando en complejos de vanadio.

QS34 Estudio de la interacción de un compuesto de molibdeno con una hidrazona con el ADN y de sus efectos citotóxicos en la línea celular humana de cáncer de pulmón A549.

QS35 Brain activity of white wine polyphenols on Alzheimer's disease-like pathology: a first step toward a reliable therapeutic concept for brain degeneration

QS36 C5-Curcuminoids: a promising starting point for discovery of new dual inhibitors of p53-MDM2/X

QS37 Ingredients of permanent and temporary tattoos: current analytical perspective

QS38 Estudio de la interacción con ADN de hidrazonas derivadas de piridoxal y de su citotoxicidad sobre la línea celular A549

QS39 Estudio de potenciales aplicaciones antitumorales de complejos de vanadio (V) con ligandos derivados de 2,6-diformil-4-metilfenol.

QS40 Synthesis and characterization of cationic meso-substituted porphyrins for theranostic

QS41 Atividade antioxidante de derivados do hidroxitirosol em liposomas

QS42 Improved nucleophilic synthesis of 18FF-DOPA using microwave technology

QS43 New chalcone derivatives with antimitotic activity: synthesis, antitumor activity and chemosensitivity studies

Quimica Teórica

QT01 molUP: How to start a computational QM/MM study of an enzyme?

QT02 Using DFT and Semi-Empirical Methods as Alternative to QM/MM Approach to Study Biological Systems: Interaction of phenanthroline derivatives with duplex DNA and G-quadruplexes

QT03 Application of QM/MM Methods in the study of the reactivity of the enzyme Tryptophan Synthase

QT04 Estimación de datos termodinámicos en dímeros de lignina mediante química computacional

QT05 Automatization of a Nucleus-Independent Chemical Shift (NICS) Analysis as an Indicator of Aromaticity in Rings

QT06 Optimization of an in silico Virtual Screening Protocol for the Identification of Biofilm Formation Inhibitors in LasR

CONFERENCIAS PLENARIAS

Repair of endogenous DNA damage and cancer prevention

Prof. Dr. Tomas Lindahl
Premio Nobel de Química 2.015

Human cancer is generally associated with mutagenic changes in tumour suppressor genes and oncogenes. While some of those deleterious mutations may be caused by radiation and other environmental agents, a large proportion is likely to be due to unavoidable endogenous chemical DNA damage by hydrolysis, and oxidation, and minor alterations by reactive small molecules in the cell such as S-adenosylmethionine and formaldehyde. Note that a DNA single strand is less chemically stable than a protein chain. In consequence, DNA repair is required. Most spontaneous DNA lesions are corrected by the base excision repair pathway, but direct damage reversal also occurs of threatening mis-coding lesions such as O6 methylguanine. The relevant DNA repair mechanisms involving AP endonucleases and ten different DNA glycosylases recognising different lesions will be described. Thus, DNA in living cells which is the carrier of stable genetic information also exhibits slow turnover by base excision repair, with at least 10,000 damaged nucleotides replaced every day in all proliferating human cells.

CP 1

Innovative Solution to Remove a Mixture of Potential Toxic Elements from Natural Waters

Prof. Dra. Eduarda Pereira

CESAM & LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro

The contamination of water results in the presence of a wide variety of potential toxic elements. These elements lead at serious environmental and public health problems due to their toxicity, persistent character, bio-accumulation and bio-amplification along food chain.
In order to reduce its levels in waters, several techniques like sorption, flotation, ion exchange, membrane filtration and oxidation have been used. Among these techniques, sorption has been one of the most effective and simplest approaches. In this context, nanoscience has an important contribution in the development of new nanomaterials with high sorption capacity. However, in most cases, the application of a single nanomaterials as sorbent to reduce the levels of a wide variety of elements in natural waters is not effective, because nanomaterials are usually selective and cannot remove simultaneously all the contaminants. An innovative strategy to remove several toxic elements from waters is the application of a sorbent that is the combination of different nanomaterials.
So, a combination of different types of nanoparticles to obtain a sorbent able to remove simultaneously potential toxic elements such as Hg(II), Pb(II), As(V) and Cd(II) from contaminated water is the needed approach. Magnetic nanoparticles Fe_3O_4@SiO_2/SiDTC, Fe_3O_4@SiO_2/EDTA and $CoFe_2O_4$ have good performance in the removal of mono-elemental solution and their combination can achieve an efficiency of removal higher than 80% of several elements from contaminated waters even if they are used in saline waters. The dose of each nanoparticle in the sorbent mixture and the pH are among the important parameters in the multielementar sorption process.

CP2

Propiedades físicas de productos termales para usos terapéuticos.

Prof. Dr. José Luis Legido Soto
Dpto. Física Aplicada. Catedrático Universidad de Vigo.

El termalismo es hoy en día un sector económico en desarrollo en muchos países del mundo. En Galicia y Norte de Portugal existen numerosas fuentes de agua minero-medicinal utilizadas en centros termales con un fin terapéutico. Además del agua minero-medicinal en fase líquida en termalismo se emplean otros productos derivados como son los vapores que se pueden aplicar en forma de nebulizadores, aerosoles o estufas, así como, los peloides comúnmente conocidos como barros, limos, fangos o turbas.
Las propiedades físicas de los distintos productos termales son importantes para conocer los mecanismos de acción de algunas aplicaciones terapéuticas. Así, las propiedades térmicas como el calor específico, la conductividad térmica y la difusividad térmica van a influir en la forma de aplicación termoterápica y las propiedades mecánicas, como la densidad y la viscosidad, también van a intervenir en los procesos de balneación.
En este trabajo se realiza un estudio de las propiedades mecánicas y térmicas (densidad, viscosidad, calor específico, conductividad térmica y difusividad térmica) de las aguas minero-medicinales y los peloides termales

Identification and Catalytic Degradation of Environmental Contaminants of European Union Concern

Prof. Dr. Adrián M.T. Silva*

Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

**adrian@fe.up.pt*

We are facing new challenges with the spread of organic chemical micropollutants in water bodies. Priority substances (PSs) and contaminants of emerging concern (CECs) have been found in the aquatic environment, often up to µg L^{-1} levels. Water is a highly sensitive natural resource and alternatives to minimize water contamination are required, aiming at enhanced environmental and life quality in Europe. Directive 2013/39/EU, Decision 2015/495 and 2018/840 were launched to update the water framework policy in Europe, emphasizing the need to develop new water treatment technologies to deal with this problem [1-3].

An overview of the author's experience in the monitoring of these micropollutants and in the synthesis, characterization and application of active and stable catalysts, including catalytic membranes, for different water treatment technologies, will be discussed in this lecture. Special emphasis will be placed on the use of carbon materials and their respective functionalization, since carbon materials with no added metals can be used as active catalysts in some of these processes. The aim is to reveal how to perform a meticulous tailoring of the surface chemistry (surface oxidation and heteroatom doping) and texture (surface area, pore size, distance between adjacent sheets/stacks) of carbon materials with different dimensionalities (1D, 2D, 3D). The target is to oxidize EU-relevant organic chemical micropollutants at the same time considering water disinfection (eliminating antibiotic resistant bacteria and their genes), by generating highly reactive radicals from O_3, persulfate activation or H_2O_2, in the case of H_2O_2 added or photocatalytically generated in-situ [4-5].

Three major questions will be answered: Which is the best suited surface chemistry? What about textural properties? What type(s) of carbon material(s) should be implemented in each process?

Acknowledgements

This work was financially supported by project NORTE-01-0145-FEDER-031049 (InSpeCt) funded by FEDER funds through NORTE 2020 - Programa Operacional Regional do NORTE and by national funds (PIDDAC) through FCT/MCTES (PTDC/EAM-AMB/31049/2017). Scientific collaboration under project "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020" (NORTE-01-0145-FEDER-000006, NORTE 2020, Portugal 2020 Partnership Agreement, through FEDER) and project "Associate Laboratory LSRE-LCM" (UID/EQU/50020/2019 - FCT/MCTES - PIDDAC) is also acknowledged.

References

[1] A.R. Ribeiro, O.C. Nunes, M.F.R. Pereira, A.M.T. Silva, Environ. Int. 75 (2015) 33.
[2] M. Barbosa, F.F.N. Moreira, A.R. Ribeiro, M.F.R. Pereira, A.M.T. Silva, Water Res. 94 (2016) 257.
[3] J.C.G. Sousa, Ribeiro A.R., Barbosa M.O., M.F.R. Pereira, A.M.T. Silva, J. Hazard. Mater. 344 (2018) 146.
[4] M. Pedrosa, G. Drazic, P.B. Tavares, J.L. Figueiredo, A.M.T. Silva, Chem. Eng. J., 369 (2019) 223.
[5] A. Torres-Pinto, M.J. Sampaio, C.G. Silva, J.L. Faria, A.M.T. Silva, Appl. Catal. B: Environ. 252 (2019) 128.

CP4

Programa de control do medio mariño de galicia: a química na seguridade alimentaria

Dra. Doña Covadonga Salgado
Intecmar (Instituto Tecnolóxico para o Control do Medio Mariño de Galicia). Peirao de Vilaxoán s/n. 36611 Vilagarcía de Arousa.
csalgado@intecmar.gal

Creado por Lei no ano 2004 como Ente Público, o INTECMAR constitúe o instrumento oficial da Administración autonómica de Galicia, para o control da calidade do medio mariño e a aplicación das disposicións legais en materia de control técnico-sanitario dos produtos do mar.

O principal cometido do INTECMAR é dar cumprimento á lexislación vixente en materia de calidade da produción de moluscos e outros organismos mariños e contribuír a protexer e mellorar a calidade do medio mariño, polo que a súa actividade céntrase en facer o seguimento, o control e a investigación da calidade ambiental das augas costeiras de Galicia, especialmente no que se refire ás condicións oceanográficas (tanto físicas como químicas), fitoplancto, biotoxinas mariñas, contaminación química -metais pesados, compostos organoclorados e hidrocarburos- microbioloxía e patoloxía.

Para levar adiante este labor, o INTECMAR ten implantado un completo sistema de control, caracterizado por estar deseñado e ter capacidade para poder actuar sobre unidades de produción de reducido tamaño; por manter unha frecuencia de mostraxe moi intensa; por cubrir tódalas zonas de produción da costa galega; e por controlar tódolos grupos de especies sometidos a explotación comercial do marisqueo e da acuicultura.

Como laboratorio de control oficial de análises agroalimentarios, INTECMAR está acreditado segundo a norma UNE-EN ISO/IEC 17.025, "Requisitos xerais para a competencia dos laboratorios de ensaio e calibración", na que se recollen tódolos requisitos que debe cumprir un laboratorio de ensaio para demostrar que posúe un sistema de xestión e que é tecnicamente competente e capaz de xerar resultados tecnicamente válidos.

O Sistema de Xestión do INTECMAR, determinado polo conxunto da estrutura organizativa, autoridade, responsabilidades, procedementos, métodos de ensaio e recursos do laboratorio, está documentado en catro niveis: Manual de Calidade; Procedementos Xerais; Procedementos Específicos; Rexistros Técnicos e Rexistros de Calidade.

Os resultados do traballo desenvolvido no Instituto Tecnolóxico para o Control do Medio Mariño de Galicia transmítense ós distintos departamentos da Administración autonómica relacionados; ás entidades sectoriais do marisqueo e a acuicultura: Confrarías de Pescadores, Organizacións de Produtores e Asociacións Profesionais; e ponse á xeral disposición da sociedade.

A información que sobre o estado do medio mariño e as súas distintas zonas de produción de moluscos bivalvos se obtén no INTECMAR, pode ser consultada no sitio web www.intecmar.gal. Emprégase tamén o correo electrónico para enviar aos departamentos administrativos pertinentes e ás entidades sectoriais interesadas os informes preliminares de recontos de fitoplancto; e a estas mesmas entidades e ás empresas do sector que así o solicitaran, avisos rápidos de peches e aperturas de zonas de produción, acompañados das correspondentes resolucións.

COMUNICACIONES ORALES

QUÍMICA ALIMENTARIA

Otimização de processos de extração de antocianinas a partir de cálices de *Hibiscus sabdariffa* L. para obtenção de corantes alimentares naturais

Manuel Ayuso[1,2], Eliana Pereira[1], José Pinela[1], Custódio Lobo Roriz[1], M.A. Prieto[1,3], Maria Filomena Barreiro[4], Lillian Barros[1], Isabel C.F.R. Ferreira[1,*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; [2]Departamento de Biologia Aplicada de Plantas e Solo, Faculdade de Biologia, Universidade de Vigo, 36310, Vigo, Espanha; [3] Grupo de Nutrição e Bromatologia, Faculdade de Ciência e Tecnologia de Alimentos, Universidade de Vigo, Ourense Campus, E32004 Ourense, Espanha; Centro de Qualidade Alimentar, INIA, C/Universidad s/n, 42004 Soria, Espanha; [4]Laboratório de Engenharia de Separação e Reação - Laboratório de Catálise e Materiais (LSRE-LCM), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
**iferreira@ipb.pt*

A seletividade do consumidor na escolha de produtos alimentares contendo aditivos tem desafiado a indústria alimentar e os centros de investigação a encontrar novas fontes e métodos de extração eficientes para a produção sustentável de ingredientes de base natural com capacidade corante [1]. Nesta vertente, as plantas surgem como uma fonte promissora de pigmentos naturais bioativos com potencial aplicação no setor industrial. *Hibiscus sabdariffa* L. é um bom exemplo, pois trata-se de uma espécie cujo cálice detém uma elevada concentração de antocianinas [2]. Visando maximizar a recuperação destes compostos antociânicos a partir do cálice desta espécie para posterior utilização como corantes alimentares, este estudo foi delineado com o objetivo de otimizar dois métodos de extração, assistidos por calor (HE) e ultrassons (UE), utilizando a metodologia de superfície de resposta (RSM).

Para otimização, foi implementado um desenho compostos central de cinco níveis combinando três variáveis independentes, nomeadamente tempo (*t*), percentagem de etanol (*S*) e temperatura (*T*) ou potência (*P*) do ultrassons. Os teores das antocianinas delfinidina-3-*O*-sambubiósido e cianidina-3-*O*-sambubiósido foram quantificados por LC-DAD-ESI/MS^n e usadas como critérios de resposta para otimização por RSM. Os modelos teóricos foram ajustados através de uma equação polinomial de segunda ordem e as respostas maximizadas pelo método *Simplex* [3]. Após otimizar as condições para as variáveis *t*, *T* e *S* ou *P*, procedeu-se à otimização da razão sólido/liquido (*S/L*) para HE e UE.

Os modelos desenvolvidos foram ajustados com sucesso aos dados experimentais e utilizados para determinar as condições ideais de extração. A UE foi mais eficiente, permitindo recuperar 23,83 mg de antocianinas por cada g de material vegetal seco e obter 51,76 mg desses pigmentos por cada g de extrato ao aplicar as condições de processamento ótimas: t = 26,1 min, P = 296,6 W e S = 39,1% etanol. A quantidade de antocianinas obtida através da extração UE foi cerca de 3 vezes superior à quantidade obtida por HE. Quanto à razão *S/L*, o incremento desta quarta variável aumentou os rendimentos de extração de antocianinas, atingindo um máximo ao utilizar 200 g/L [3].

Os resultados demonstram que *H. sabdariffa* é uma fonte de antocianinas viável para produzir corantes de base natural, através de uma metodologia economicamente exequível à escala industrial.

Agradecimentos
Os autores agradecem à Fundação para a Ciência e Tecnologia (FCT, Portugal) e ao Fundo Europeu de Desenvolvimento Regional (FEDER), no âmbito do Programa PT2020, pelo apoio financeiro ao CIMO (UID/AGR/00690/2019) e ao FEDER, através do POCI-COMPETE2020 e da FCT, pelo suporte financeiro ao LA LSRE-LCM (POCI-01-0145-FEDER-006984); pela bolsa de doutoramento de Custódio Lobo Roriz (SFRH/BD/117995/2016), e pelos contratos de J. Pinela e L. Barros ao abrigo do CEEC institucional. Trabalho financiado por FEDER, através do Programa Operacional Regional Norte 2020, no âmbito do Projeto NORTE-01-0145-FEDER-023289 (DeCodE) e do projeto Mobilizador Norte-01-0247-FEDER-024479 (ValorNatural). Também agradecem ao programa FEDER-Interreg España-Portugal pelo apoio financeiro através do projeto 0377_Iberphenol_6_E e ao TRANSCoLAB (0612_TRANS_CO_LAB_2_P).

Referencias

[1] M. Carocho, L. Barros, J.C.M. Barreira, ... I.C.F.R. Ferreira, Food Chemistry, 207 (2016) 51.
[2] I. Jabeur, E. Pereira, L. Barros,...I.C.F.R. Ferreira, Food Research International, 100 (2017) 717.
[3] J. Pinela, M.A. Prieto, E. Pereira,…I.C.F.R. Ferreira, Food Chemistry, 275 (2019) 309

Extrato de *Gomphrena globosa* L. como corante natural em biscoitos: efeito em diferentes parâmetros físicos

Manuel Ayuso[1,2], Custódio Lobo Roriz[1,3], Eliana Pereira[1], Sandrina Heleno[1], Márcio Carocho[1], Patricia Morales[3], Lillian Barros[1], Isabel C.F.R. Ferreira[1,*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; [2]Departamento de Biologia Aplicada de Plantas e Solo, Faculdade de Biologia, Universidade de Vigo, 36310, Vigo, Espanha; [3]Dpto. Nutrición y Ciencia de los Alimentos. Facultad de Farmacia. Universidad Complutense de Madrid (UCM), Madrid, Spain.
**iferreira@ipb.pt*

Nos últimos anos, consumidores e indústria têm procurado corantes naturais que sejam seguros e, simultaneamente, associados a efeitos benéficos para a saúde. Existem alguns corantes naturais autorizados pela EFSA, no entanto, não conseguem satisfazer todas as necessidades da indústria pela sua instabilidade, nomeadamente a alterações de temperatura, pH, luminosidade entre outros fatores [1]. Assim, a comunidade científica tem-se debruçado no estudo de matrizes naturais para obtenção de agentes com diferentes funções, nomeadamente função corante [2]. Entre as moléculas naturais com capacidade corante encontram-se as betacianinas, compostos pigmentados, com elevado poder corante, obtidas preferencialmente a partir de beterraba (tonalidades na gama dos vermelhos). Neste sentido, o presente trabalho visa a utilização de flores de *Gomphrena globosa* L. (perpétua roxa), como fonte de betacianinas para potencial aplicação na indústria alimentar [3]. As flores de *G. globosa* foram sujeitas a uma extração assistida por ultrassons previamente otimizada (t = 22 min, P = 300 W, Et = 0% e S/L = 5 g/L), obtendo-se 47 ± 5 mg gonfrenina/g de extrato. Os extratos obtidos foram liofilizados e incorporados em biscoitos para avaliação das suas características físicas nomeadamente: a) cor, com recurso a um colorímetro para análise das coordenadas L* = Luminosidade, a* = vermelho/verde e b* = amarelo/azul; b) textura, através de um texturómetro, analisando os parâmetros de dureza, adesividade, elasticidade, coesão, mastigabilidade e resiliência. Estes parâmetros foram analisados ao longo de um tempo de prateleira de 30 dias e comparados com: i) biscoitos sem corante, ii) biscoitos com extrato corante liofilizado; iii) biscoitos com extrato de corante comercial (E162). De acordo com os resultados obtidos nos parâmetros de avaliação de cor, verificou-se que o extrato de *G. globosa* liofilizado apresentou resultados mais promissores em termos de estabilidade (L *56; a *25.5; b *4.3), mantendo uma coloração rosa após a cozedura e durante os 30 dias de análise, enquanto que, o corante comercial E162 (L *60.7; a *23,2; b *18,1) sofreu alterações na capacidade corante, provocadas pela cozedura, no entanto, apresentou também grande estabilidade ao longo dos 30 dias de análise. Nos parâmetros de textura avaliados, as mudanças gerais na textura foram resultado de uma interação significativa entre o tipo de corante e a passagem do tempo. A dureza dos biscoitos diminuiu devido à retrogradação, enquanto os parâmetros de adesividade, elasticidade, coesão e resiliência aumentaram, mas não de uma forma significativa. Desta forma, com o decorrer deste trabalho foi possível concluir que o extrato obtido a partir de flores de *G. globosa*, é uma fonte de betacianinas com potencial para aplicação na indústria alimentar como corante natural. De realçar que este extrato apresenta uma tonalidade rosa diferente do corante comercial (avermelhado), pelo que pode ser considerado como possível candidato corante de tonalidade rosa para a indústria alimentar. Estão em curso mais estudos de estabilidade, de forma a garantir as melhores condições de armazenamento e aplicação deste extrato.

Agradecimentos
Os autores agradecem à Fundação para a Ciência e Tecnologia (FCT, Portugal) e ao Fundo Europeu de Desenvolvimento Regional (FEDER), no âmbito do Programa PT2020, pelo apoio financeiro ao CIMO (UID/AGR/00690/2019); bolsa de doutoramento de C. L. Roriz (SFRH/BD/117995/2016), L. Barros e S. Heleno agradecem ao financiamento nacional pela FCT, I.P., no âmbito da celebração do contrato-programa de emprego científico institucional e individual, respetivamente. Este trabalho também foi financiado pelo FEDER, através do Programa Operacional Regional Norte 2020, no âmbito do projeto Mobilizador Norte-01-0247-FEDER-024479 (ValorNatural). M. Carocho agradece também ao ValorNatural pelo seu contrato. Os autores também agradecem ao programa FEDER-Interreg España-Portugal pelo apoio financeiro através do projeto TRANSCoLAB (0612_TRANS_CO_LAB_2_P).

Referencias

[1] N. Martins, C. L. Roriz, P. Morales, L. Barros, and I. C. F. R. Ferreira, *Food Funct.*, 8 (2017) 19.
[2] M. Carocho, P. Morales, and I. C. F. R. Ferreira, *Trends Food Sci. Technol.*, 45 (2015) 284.
[3] C. L. Roriz, J. C. M. Barreira, P. Morales, L. Barros, and I. C. F. R. Ferreira, *Lwt*, vol. 92 (2018) 101.

Caracterização fenólica e nutricional das infusões de cinco plantas aromáticas e suas propriedades bioativas

Cristina Caleja[1], Tiane C. Finimundy[1,2,*], Carla Pereira[1], Lillian Barros[1], Ricardo C. Calhelha[1], Marina Sokovic[3], Marija Ivanov[3], Ana Maria Carvalho[1], Eduardo Rosa[2], Isabel C.F.R. Ferreira[1]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
[2]CITAB - University of Trás-os-Montes and Alto Douro (UTAD), Department of Agronomy, Vila Real, Portugal.
[3]University of Belgrade, Department of Plant Physiology, Institute for Biological Research "Siniša Stanković", Bulevar Despota Stefana 142, 11000 Belgrade, Serbia.
**tiane@ipb.pt*

As infusões de plantas são aplicadas há séculos na medicina popular para fins medicinais e nutricionais [1]. Devido à sua importância económica e elevado consumo, tem-se verificado um crescente interesse não só pela sua composição química como também pelas suas diversas propriedades bioativas [2]. Neste estudo, foram selecionadas cinco espécies de plantas aromáticas: *Erica australis* L., *Genista tridentata* L., *Melissa officinalis*, L., *Mentha spicata* L. e *Prunella vulgaris* L. Foram preparadas infusões de cada planta e analisadas quanto à sua composição fenólica (HPLC/DAD-ESI/MS) e propriedades bioativas. Para a atividade antioxidante foram utilizados métodos que avaliam a inibição da pero xidação lipídica (TBARS) e da hemólise oxidativa (OxHLIA). A atividade antimicrobiana foi avaliada pelo método de microdiluição em placa utilizando bactérias Gram + (*Bacillus cereus* e *Listeria monocytogenes*) e Gram - (*Escherichia coli* e *Salmonela typhimurium*) e fungos (*Aspergillus niger*, *Aspergillus versicolor*, *Penicillium funiculosum* e *Penicillium verrucosum)*. A atividade citotóxica foi testada usando o método colorimétrico da sulforrodamina B em diferentes linhas celulares tumorais MCF-7 (adenocarcinoma da mama), NCI-H460 (carcinoma de pulmão), HeLa (carcinoma cervical), HepG2 (carcinoma hepatocelular) e numa cultura primária de células não tumorais (PLP2); para a atividade anti-inflamatória utilizou-se a linha de macrófagos RAW 246.7.

Foram identificados 52 compostos fenólicos, sendo que o composto maioritário nas infusões de *M. officinalis*, *M. spicata* e *P. vulgaris* foi o ácido rosmarínico, enquanto na de *E. australis* os mais abundantes foram os derivados de flavonoides identificados como quercetina e genisteína. As infusões de *P. vulgaris* e *M. officinalis* apresentaram os melhores resultados nos ensaios TBARS (IC_{50} de 4,2±0,04 µg/mL) e OxHLIA (IC_{50} de 24,8±0,3 µg/mL), respetivamente. Nenhuma das infusões mostrou hepatotoxicidade em células não-tumorais (GI_{50}>400 µg/mL). A infusão de *M. spicata* apresentou os melhores resultados de citotoxicidade contra a linha celular MCF-7 (GI_{50} de 283±10 µg/mL) e de atividade antimicrobiana, em especial contra a *Salmonela typhimurium* (MIC de 0,25 mg/mL) e os fungos *Aspergillus versicolor* (MIC de 0,25 mg/mL) e *Penicillium verrucosum* (MIC de 0,25 mg/mL), sendo a única planta a apresentar atividade anti-inflamatória (GI_{50} de 324±5 µg/mL). Este trabalho demonstrou o potencial das infusões destas plantas, ricas em compostos fenólicos com propriedades bioativas, para futura aplicação em diferentes sectores industriais.

Agradecimentos

Os autores agradecem à Fundação para a Ciência e a Tecnologia (FCT, Portugal) e ao FEDER no âmbito do programa PT2020 pelo apoio financeiro ao CIMO (UID/AGR/00690/2019); financiamento nacional da FCT, PI, através do contrato de programa institucional de emprego científico para o contrato de L. Barros e R.C. Calhelha; o contrato de C. Pereira através da celebração contrato de programa previso no nº 4, 5 e 6 do artigo 23º do Decreto-Lei nº 57/2016, de 29 de agosto, alterado pela Lei nº 57/2017, de 19 de julho; FEDER-Interreg España-Portugal pelo apoio financeiro através do projeto 0377_Iberphenol_6_E; FEDER através do Programa Operacional Regional Norte 2020, no âmbito do Projeto NORTE-01-0145-FEDER-023289: DeCodE; e à empresa Ervital (Castro Daire, Portugal) pela cedência das amostras.

Referências

[1] D. Twilley, S. Rademan, Medicinal Plants for Holistic Health and Well-Being (2015) 13.
[2] J. Merrills et al., Pharmacy Law and Practice (2013) 213.

Fatty acids profile in acorn gluten free bread

R. B. Martins[1,2*], M. C. Nunes[2], J. A. Peres[3], A. Raymundo[2], A I. R. N. A. Barros[1]
[1]CITAB - Centre for the Research and Technology of Agro-Environmental and Biological Sciences, Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5001-801 Vila Real, Portugal.
[2]LEAF – Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa. Tapada da Ajuda, 1349-017 Lisboa, Portugal.
[3]Centro de Química de Vila Real (CQVR), Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5001-801 Vila Real, Portugal.
**ritabeltraomartins@icloud.com*

Over time, celiac disease (CD) was discovered, and was understood that the only way to overcome this chronic disease is to promote to celiac patients a long life diet absent of gluten. Thus, is really important to find products to achieve these consumers' requirements. Although the market researchers highlight that the continuous improvement of Gluten Free (GF) bakery products, there is still much work to do in what is concerned about GF products nutritional and sensorial characteristics, specially when compared with their gluten containing counterparts [1, 2]

According to different authors, acorns used to be consumed ground in flour to bake bread, namely in scarcity years. Acorn flour is a naturally gluten free ingredient and presents an interesting nutritional profile. Acorn is rich in unsaturated fatty acids and has about 60% of oleic acid (ω9) and about 16% of linoleic acid (ω6) [3, 4]. These fatty acids can improve GF bread final nutritional profile with the objective of contribute to fulfil celiac patient's nutrient needs.

The aim of the present work is to characterize fatty acid profile in gluten free bread made with different levels of acorn flour incorporation. Breads were prepared from a previous developed GF recipe with buckwheat and rice flours, potato starch and Hydroxypropyl Methyl cellulose – HPMC as thickening agent [5]. Two levels of acorn flour (23% and 35%) were tested to compare fatty acid profile with control formulation.

Acknowledgments
The authors acknowledge the financial support provided by the FCT-Portuguese Foundation for Science and Technology PD/BD/135332/2017 under the Doctoral Programme "Agricultural Production Chains – from fork to farm", through the research unit UID/AGR/04033/2019 (CITAB) and UID/AGR/04129/2013 (LEAF).

Characterization of aroma compounds in barley and malt using a low-pressure assisted extraction procedure

Sebastian Reichel[1,2], Daniel O. Carvalho[2,*], João Rodrigo Santos[2], Petr Bednar[2], Luís F. Guido[2]

[1]Department of Analytical Chemistry, Faculty of Science, Palacky University Olomouc, Czech Republic
[2]REQUIMTE/LAQV – Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto
**daniel.carvalho@fc.up.pt*

Malt is produced from barley grains in a process known as malting and is used in beer production as a source of starch, largely contributing to beer's color and organoleptic characteristics. The malting process consists in the controlled germination of barley grains (green malt) and subsequent kilning and/or roasting of green malt (malt). According to its color, malt can be classified as a pale (lager) or a dark (specialty) malt, depending on kilning and roasting program temperatures [1]. The final heat treatment step is responsible for important changes in the chemical composition of malt and has a great impact on malt color and flavor due to the formation of aroma components such as characteristic aldehydes, ketones, alcohols, acids and furans [2].

Since the volatile flavor compounds from malt play an important role in the aroma composition of beer, this work aims at the characterization of volatile compounds present in barley and malt in order to understand flavor development during the malting process as well as to identify key aromatic compounds in specialty malts. Classical approaches for the analysis of flavor compounds usually involve solid-phase micro-extraction procedures combined with gas-chromatography. In this work, a simple, fast and reliable low-pressure assisted extraction method is presented: the sample and a container with a derivatizing solution (2,4-dinitrophenylhydrazine, 2,4-DNPH) are placed inside a closed vessel, under low pressure conditions to enhance volatile compounds extraction. During the extraction period, simultaneous derivatization of volatile carbonyl compounds from solid barley and malt samples occurs (Fig.1). At the end of this step, the solution containing the extracted compounds is analyzed by HPLC-DAD-ESI-MS for carbonyl compounds identification.

The current study demonstrates that the low-pressure assisted extraction procedure combined with HPLC-DAD-ESI-MS analysis is a valid procedure for the study of flavor volatiles from barley and malt. The proposed methodology allowed the identification of key volatile compounds in specialty malts and may be used as a valuable tool to understand the flavor development during the malting process and to improve malt flavor by manipulation of malting conditions.

Fig.1. Low-pressure extraction apparatus. A - vacuum gauge; B - cap; C - 100 mL flask; D - vacuum pump

tubing; E - valve; F - 2,4-DNPH solution container; G - sample.

Acknowledgments
The work was supported by UID/QUI/50006/2019 with funding from FCT/MCTES through national funds. D. Carvalho receives a research grant through the project UID/QUI/50006/2019. J.R. Santos thanks FCT (Fundação para a Ciência e Tecnologia) for funding through program DL 57/2016 – Norma transitória.

References

[1] D. Carvalho et al., Comprehensive Reviews in Food Science and Food Safety, 15 (2016) 927-943.
[2] L. Dong et al., Food Research International, 51 (2013) 783-789.

Irradiação UV-C de cogumelos para obtenção de vitamina D2

Rossana V. C. Cardoso[1,2], Ângela Fernandes[1], João C.M. Barreira[1], Ana M. Gonzaléz-Paramás[2], Lillian Barros[1], Isabel C.F.R. Ferreira[1,*]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2] Grupo de Investigación en Polifenoles (GIP), Unidad de Nutrición y Bromatología, Facultad de Farmacia, Universidad de Salamanca, Campus Miguel de Unamuno, E-37007 Salamanca, España

**iferreira@ipb.pt*

Inúmeras investigações descrevem o carater altamente nutritivo dos cogumelos, aliado às suas propriedades medicinais (e.g., antitumorais, antimicrobianas, hipocolesterolémicas, antioxidantes); propriedades estas atribuídas à presença de compostos bioativos nomeadamente o ergosterol (precursor da vitamina D2) e outros esteroides, os compostos fenólicos e as vitaminas. A vitamina D2, em particular, desempenha um papel importante na prevenção de diversas patologias e processos fisiopatológicos. Para além da suplementação e da dieta, as leveduras e os cogumelos são as únicas fontes de vitamina D2 (formada durante a exposição aos raios ultravioleta- UV) [1]. Uma vez que as fontes alimentares são escassas, a deficiência de vitamina D pode causar sérios problemas de saúde, tais como, raquitismo, osteoporose, esclerose múltipla, doenças cardiovasculares, entre outros [2].

Neste trabalho, avaliou-se o potencial da utilização de radiação UV-C no aumento do teor de vitamina D2 em amostras laminadas de *Agaricus bisporus* (J.E. Lange) Imbach e *Agaricus bisporus* Portobello. A irradiação foi realizada numa câmara UV com a intensidade de 0 (controlo), 200, 800 e 3200 mJ/cm^2 e tempo de exposição 0, 2, 6 e 10 min. A vitamina D2 foi determinada por cromatografia líquida de alta eficiência acoplada a um detetor de UV [2,3].

Verificou-se uma interação significativa (p <0,050) entre os fatores (tempo de exposição x intensidade UV-C). A aplicação da radiação UV-C promoveu um aumento na quantidade de vitamina D2, provavelmente devido à conversão de parte do conteúdo de ergosterol naturalmente presente nos cogumelos. No que diz respeito ao tempo de exposição, o período de 6 min resultou como sendo a escolha mais adequada (125 µg/g DW de vitamina D2), uma vez que não foram alcançados aumentos significativos com o tempo máximo testado (10 min). Por outro lado, a dose recomendada de radiação UV-C seria a de 200 mJ/cm, considerando que essa opção poderia representar uma vantagem económica, sem comprometer o aumento da vitamina D2.

Agradecimentos

Os autores agradecem à Fundação para a Ciência e Tecnologia (FCT, Portugal) e à FEDER, no âmbito do Programa PT2020, pelo apoio financeiro ao CIMO (UID / AGR / 00690/2019), Concessão da bolsa de doutoramento de R.V.C. Cardoso (SFRH /BD/137436/2018). L. Barros, J.C.M. Barreira e A. Fernandes também agradecem o financiamento nacional da FCT - Fundação para a Ciência e Tecnologia, PI, através do contrato de programa institucional de emprego científico para seus contratos. Este trabalho é financiado pelos Fundos Europeus Estruturais e de Investimento (FEEI) por meio do Programa Operacional Regional Norte 2020, no âmbito do Projeto Mobilizador ValorNatural®; e à FEEI através do Programa de Desenvolvimento Rural (PDR2020).

Referências

[1] H. Elangovan, S. Chahal, J. E. Gunton, Biochimica et Biophysica Acta, 1863 (2017) 907–916.

[2] O.Taofiq, Â. Fernandes, L. Barros, M. F. Barreiro, I. C. F. R. Ferreira, Trends in Food Science and Technology, 70 (2017) 82–94.T. Thongsook, T. Kongbangkerd, Food Science and Technology International, 17 (2011) 351–365.

[3] R.V.C. Cardoso, Â. Fernandes, J.C.M. Barreira, S.C. Verde, A. L. Antonio, A.M. Gonzaléz-Paramás, L. Barros, I.C.F.R. Food Chemistry, 278 (2019) 760-766.

Aplicação de frutos de *Lonicera caerulea* L. var. *Kamtschatica* no desenvolvimento de corantes alimentares com propriedades bioativas

Adriana K. Molina[1,*], Rúbia C.G. Corrêa[1], Carla Pereira[1], Maria Inês Dias[1], Sandrina A. Heleno[1], Paula Rodrigues[1], Marina Kostić[2], Marina Soković[2], João C.M. Barreira[1], Lillian Barros[1], Isabel C.F.R. Ferreira[1]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2]Department of Plant Physiology, Institute for Biological Research "Siniša Stanković", University of Belgrade, Bulevar Despota Stefana 142, 11000 Belgrade, Serbia

**iferreira@ipb.pt*

Os frutos de *Lonicera caerulea* L. (haskap) são muito apreciados pelo seu sabor comummente descrito como uma combinação entre o mirtilo e a framboesa. Por serem ricos em ácido ascórbico, antocianinas e outros compostos bioativos, são muitas vezes considerados "super frutos" [1,2]. Com o presente estudo, pretendeu estudar-se a variedade *Kamtschatica* destes frutos em termos de valor nutricional (métodos AOAC), composição em açucares (HPLC-RI), ácidos orgânicos (UFLC-PDA), tocoferóis (HPLC-fluorescência), ácidos gordos (GC-FID) e compostos fenólicos (HPLC-DAD/ESI-MS); bem como das suas propriedades bioativas (antioxidantes e antimicrobianas). Uma vez que apresentam elevadas concentrações de antocianinas, o objetivo foi também desenvolver formulações corantes líquidas e sólidas e avaliar a sua estabilidade ao longo de três meses de armazenamento, controlando as variações de cor, concentração de antocianinas, citotoxicidade e carga microbiana.

Os frutos de haskap apresentaram um valor nutricional equilibrado, apresentando como macronutrientes maioritários os hidratos de carbono. Os açucares livres encontrados em concentrações mais elevadas foram a frutose e a glucose; detetaram-se duas isoformas de tocoferol (α e γ) e cinco ácidos orgânicos, com predominância do ácido cítrico. Relativamente aos ácidos gordos, observou-se uma clara prevalência de ácidos gordos polinsaturados, principalmente ácido linoleico. No extrato de haskap foram detetados dois compostos fenólicos não antociânicos, sendo o maioritário o ácido-3-cafeoilquínico, e seis antocianinas, com prevalência da cianidina-3-*O*-hexósido. O extrato revelou ainda uma forte atividade antioxidante e antimicrobiana. Relativamente às formulações corantes, de um modo geral, todas demonstraram também atividade antioxidante e antimicrobiana. Das formulações preparadas (três líquidas e duas sólidas), as sólidas revelaram uma maior estabilidade ao longo dos 3 meses de armazenamento, com variações menos acentuadas de cor e concentração de antocianinas. Em termos de segurança alimentar, estas revelaram também uma menor contaminação microbiana, sendo que nenhuma das formulações revelou citotoxicidade. Assim, este estudo permitiu obter uma extensa caracterização nutricional e química dos frutos desta variedade de haskap, bem como o desenvolvimento de corantes naturais estáveis com elevado potencial de aplicação na indústria alimentar.

Agradecimentos

FCT e FEDER sob o Programa PT2020 pelo apoio financeiro ao CIMO (UID/AGR/00690/2019) e aos contratos de C. Pereira (no âmbito da celebração do contrato-programa previsto nos números 4, 5 e 6 do art. 23.º do D.L. n.º 57/2016, de 29 de agosto, alterado pela Lei n.º 57/2017, de 19 de julho), M.I. Dias e L. Barros (através de fundos nacionais da FCT, no âmbito da celebração do contrato-programa de emprego científico institucional), S.A. Heleno e J.C.M. Barreira (no âmbito da celebração do contrato-programa do emprego científico individual) FEDER-Interreg España-Portugal pelo financiamento ao projeto 0377_Iberphenol_6_E e TRANSCoLAB 0612_TRANS_CO_LAB_2_P; FEDER através do Programa Operacional Regional Norte 2020, no âmbito do Projeto NORTE-01-0145-FEDER-023289 (DeCodE) e projeto Mobilizador Norte-01-0247-FEDER-024479: ValorNatural®.

Referências

[1] G.B. Celli, A. Ghanem, M.S.L. Brooks, Food and Bioprocess Technology, 7 (2014) 1541.

[2] H.P.V. Rupasinghe et al., Journal of Functional Foods, 44 (2018) 24.

Prospeção da atividade antibacteriana de frutos e pedúnculos de *Lycium barbarum* L.

Tânia C.S.P. Pires[1,2], Maria Inês Dias[1], Lillian Barros[1], Maria José Alves[1], Celestino Santos-Buelga[2], Isabel C.F.R. Ferreira[1,*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]Grupo de Investigación en Polifenoles (GIP-USAL), Facultad de Farmacia, Universidad de Salamanca, Campus Miguel de Unamuno s/n, 37007 Salamanca, España.
iferreira@ipb.pt

O consumo de frutos de goji *(Lycium barbarum* L.) tem vindo a aumentar exponencialmente, não só devido às suas características nutricionais, mas também ao seu teor em compostos fenólicos, altamente correlacionados com os seus efeitos benéficos para a saúde. No entanto, com o crescente consumo deste fruto, surge a oportunidade de maximizar o potencial de utilização dos seus pedúnculos como um bio-resíduo com propriedades funcionais [1].

O objetivo do presente trabalho foi determinar o perfil fenólico e comparar a atividade antibacteriana de extratos hidrometanólicos obtidos a partir dos frutos de goji e dos seus pedúnculos, um subproduto com potencial para ser valorizado economicamente. O perfil fenólico foi determinado por cromatografia líquida de alta eficiência acoplada a um detetor de díodos e a um espetrómetro de massa (HPLC-DAD-ESI/MSn). A atividade antibacteriana foi testada utilizando um painel de cinco bactérias Gram-negativo e quatro bactérias Gram-positivo, obtidas a partir de isolados clínicos com perfis de resistência conhecidos. Foi calculada a concentração mínima inibitória (CMI) de cada um dos extratos, determinada por microdiluição com o método colorimétrico de cloreto de *p*-iodonitrotetrazólio (INT).

A concentração total de compostos fenólicos não revelou diferenças estatisticamente significativas entre frutos e pedúnculos, no entanto quando se compararam as famílias de compostos, os frutos apresentam maior quantidade de derivados de ácidos fenólicos (32,7 mg/g vs 17,2 mg/g nos pedúnculos) e os pedúnculos de flavonóis (48,5 mg/g vs 27,6 mg/g nos frutos). Ambas as amostras estudadas apresentaram melhores resultados (valores de CMI mais baixos) para as bactérias Gram-positivo testadas, com valores de CMI entre 2,5 e 10 mg/mL. Os valores mais baixos de CMI foram determinados em *E. faecalis* e *S. aureus* (2,5 mg/mL). Quanto às bactérias Gram-negativo, os pedúnculos revelaram os valores de CMI mais baixos para *A. baumannii* (20 mg/mL), *K. pneumonia* (10 mg/mL) e *P. aeruginosa* (10 mg/mL).

Os resultados obtidos permitem, por um lado, a obtenção de novos agentes antimicrobianos, para combater o uso indiscriminado de antibióticos de largo espetro e, consequentemente, o alto nível de tolerância dos microrganismos aos mesmos. Por outro lado, permite verificar a potencialidade do uso dos frutos e pedúnculos de *L. barbarum* como fontes de compostos bioativos, de interesse para a indústria alimentar e farmacêutica na substituição de compostos sintéticos tão amplamente utilizados.

Agradecimentos
FCT e FEDER sob o Programa PT2020 pelo apoio financeiro ao CIMO (UID/AGR/00690/2019), bolsa individual de doutoramento de T.C.S Pires (SFRH/BD/129551/2017) e aos contratos de M.I. Dias e L. Barros (através de fundos nacionais da FCT, no âmbito da celebração do contrato-programa de emprego científico institucional). Ao FEDER-Interreg España-Portugal pelo financiamento ao projeto 0377_Iberphenol_6_E e TRANSCoLAB 0612_TRANS_CO_LAB_2_P; FEDER através do Programa Operacional Regional Norte 2020, no âmbito do Projeto Mobilizador Norte-01-0247-FEDER-024479: ValorNatural®. Governo espanhol pelo apoio ao GIP-USAL (AGL2015-64522-C2-2-R).

Referencias

[1] Pires, T.C.S.P.; Dias, M.I.; Barros L.; Calhelha, R.C.; Alves, M.J.; Santos-Buelga, C.; Ferreira, I.C.F.R. Industrial Crops & Products, 122 (2018) 574–581

Efeito dos polifenóis da couve como modeladores da alergia alimentar

Telmo Francisco[1*], Carlos Guerreiro[1], Nuno Mateus[1], Victor de Freitas[1], Rosa Pérez-Gregorio[1]
[1]LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, 4169-007, Porto, Portugal;
**tel@fc.up.pt*

A alergia alimentar tem adquirido um papel cada vez mais relevante na sociedade atual dado que a sua prevalência tem aumentado enquanto epidemia ao longo das últimas décadas [1]. A inexistência de tratamentos e a severidade dos sintomas tornam necessário o estabelecimento de hábitos alimentares preventivos para o controlo desta doença. Uma dieta ocidental, caraterizada por um elevado consumo de comida processada e bebidas açucaradas, leva ao aumento do desenvolvimento de alergias alimentares. Estudos epidemiológicos relacionaram o consumo de frutas e vegetais com elevado conteúdo em componentes bioativos com uma menor incidência de alergias alimentares [2]. Os polifenóis são a família de componentes bioativos mais amplamente estudada tendo em conta as suas propriedades antialérgicas. Assim, estudos recentes demonstraram a capacidade dos polifenóis em perturbar algumas funções celulares tais como a inibição da formação de citosinas ou a inibição da proliferação de células T, ações fundamentais no desencadeamento da resposta imune. No entanto, a capacidade de interação dos polifenóis com as proteínas pode influenciar o mecanismo de modulação das alergias afetando a biodisponibilidade do polifenol e da proteína alergénica, assim como o conjunto de reações que levam à libertação de mediadores de histamina e aparecimento dos sintomas alérgicos [3,4].

Por conseguinte, o objetivo deste trabalho é avaliar a capacidade de ligação dos polifenóis presentes num dos vegetais mais amplamente consumidos em Portugal com as proteínas do ovo, a principal causa de alergia alimentar a nível mundial.

Os polifenóis da couve foram extraídos com uma solução hidroalcoólica. Posteriormente foram identificados por LC-MS/MS e quantificados pelo método de Folin-Ciocalteu. A reatividade dos polifenóis foi testada por HPLC e a reatividade das proteínas por SDS-PAGE. Uma vez comprovada a capacidade de interação dos polifenóis da couve com as proteínas do ovo, foi verificado que esta reatividade é influenciada pelo rácio molar aplicado. Foi ainda possível observar um efeito matriz dadas as diferenças observadas entre os ensaios realizados com a ovalbumina (proteína maioritária da clara de ovo) isolada ou com o conjunto de proteínas da clara de ovo.

Em resumo, o estudo dos mecanismos de interação dos polifenóis com os alergénios alimentares através da utilização de técnicas analíticas minuciosas permite uma melhor compreensão sob o ponto de vista molecular de que modo ocorrem estas interações, fazendo com que este tipo de estudos contribua como ferramenta essencial para o combate a um problema de saúde mundial que é a alergia alimentar.

Agradecimientos
Projeto PTDC/SAU-NUT/30448/2017 e LAQV (UID/QUI/50006/2013POCI/01/0145/FEDER/007265) da FCT/MEC financiado através de fundos nacionais e cofinanciado pelo FEDER, nos termos do acordo de parceria PT2020.

Referencias

[1] S. Prescott, K.J.. Allen, Pediatric allergy and immunology, 22(2) (2011) 155-160.
[2] U. Nurmatov, G. Devereux, A. Sheikh, Journal of Allergy and Clinical Immunology, 127(3) (2011) 724-733 e30.
[3] P. Lorenz, M. Heinrich, M. Garcia-Käufer, F. Grunewald, S. Messerschmidt, A. Herrick, K. Gruber, C. Beckmann, M. Knoedler, R. Huber, C. Steinborn, F.C. Stintzing, C. Gründemann, Journal of Ethnopharmacology, 194 (2016) 642-650.
[4] F. Shen, F. Niu, J. Li, Y. Su, Y. Liu, Y. Yang, Food Research International, 59 (2014) 100-107.

The use of seaweed in daily diets as a source of nutrients

Paula García-Oliveira[1,2], Anxo Carrerira-Casais[2,3], Eliana Pereira[2,*], Cristina Caleja[2], Catarina Lourenço-Lopes[1], Lillian Barros[2], Jorge Pérez-Juste[3], Miguel A. Prieto[1], Jesus Simal[1], Isabel C.F.R. Ferreira[2]

[1] Nutrition and Bromatology Group, School of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain; Food Quality Center, INIA, C/Universidad s/n, 42004 Soria, Spain

[2]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;

[3]Department of Physical Chemistry, University of Vigo Biomedical Research Center of Galicia (CINBIO), E36310, Vigo, Spain;

**eliana@ipb.pt*

Seaweed plays an important role in the biosphere being responsible for most of the production in aquatic ecosystems [1]. Although commonly consumed since ancient times in Asia, their consumption has been increasing in Europe and North America [2]. These species are known for their excellent nutritional value, especially as a protein sources and low lipid and caloric content. In addition, they are rich in several bioactive compounds, such as vitamins, essential fatty acids and phenolic compounds, providing important health benefits to consumers [3].
This work aims to determine ash, proteins, fat, carbohydrates and energy contents, as also the composition in free sugars, organic acids and fatty acids of some seaweeds species, namely *Himanthalia elongate* L., S.F. Gray; *Laminaria ochroleuca* Bach.Pyl.; *Saccharina latissima* L.; *Porphyra* sp. C.Agardh; *Palmaria palmata* (L.) Kuntze, and *Undaria pinnatifida* (Harvey) Suringar.

The nutritional aspects were determined using official methodologies for food analysis, while free sugars were identified by HPLC-RI, organic acids by UPFLC-PDA and fatty acids by GC-FID.

Proteins stood out as the main macronutrients present, with values that oscillated between 6 and 30 g/100 g of dry weight (dw) for *S. latissima* and *Porphyra* sp., respectively. On the other hand, a low lipid content was evident in all the studied seaweed species with values below 1 g/100 g dw, as well as low carbohydrates' content. The energy values ranged from 218 and 370 kcal/100 g dw for *L. ochrouleuca* and *Porphyra* sp, respectively.
Furthermore, several compounds of interest were identified, namely free sugars and organic acids, in this case being oxalic acid the only molecule present in all species. Saturated, unsaturated and polyunsaturated fatty acids were also determined, showing a clear heterogeneity of concentrations depending on the species.

The present study demonstrates the high potential of these seaweed species as an alternative source of non-animal protein, as well as some molecules with bioactive properties. Thus, the incorporation of this food into the daily diet will contribute for the improvement of a number of functionalities.

Agradecimientos
The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) and FEDER under Programme PT2020 for financial support to CIMO (UID/AGR/00690/2019). L. Barros thanks FCT, P.I., through the institutional scientific employment program-contract for her contract; research contract of C. Caleja (Project AllNatt, POCI- 01-0145-FEDER-030463). The authors are also grateful to Ministerio de Ciencia, Innovación y Universidades for Anxo Carreira-Casais FPU grant; and to Xunta de Galicia for Paula García-Oliveira predoctoral grant.

Referencias

[1] L Hasselström, W Visch, F Gröndahl, GM Nylund, H Pavia. Marine Pollution Bulletin, 113 (2018) 53-64.
[2] E-K, Kim, S-Y Ju. Nutrients, 11, (2019) 2187.
[3] Fernández-Segovia, MJ Lerma-García, A Fuentes, JM Barat. Food Res. Int.111, (2018) 212–219

Análise comparativa dos frutos da *Opuntia ficus-indica* e *O. robusta*

A. Gomes[1], L. Espírito Santo[1], A.S.G. Costa[1], M. A. Nunes[1], Ana F. Vinha[1,2], M.B.P.P. Oliveira[1*]
[1]REQUIMTE / LAQV, Dep. Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal.
[2]FP-ENAS (Unidade de Investigação UFP em Energia, Ambiente e Saúde), CEBIMED (Centro de Estudos em Biomedicina), Fundação Fernando Pessoa, Porto, Portugal.
* beatoliv@ff.up.pt

As espécies de Opuntia, popularmente conhecidas como figueira da índia, são hoje parte do ambiente natural e dos sistemas agrícolas de muitas regiões do Mundo. Em muitos países *Opuntia* spp. servem para várias finalidades, sendo difícil encontrar uma planta tão distribuída e explorada, sobretudo em zonas áridas e semi-áridas com uma economia de subsistência. A falta de recursos naturais e produtivos nessas regiões forçam os agricultores a dar atenção a estas espécies. As opuntias são uma fonte inesgotável de produtos e funções, inicialmente como uma planta selvagem e posteriormente como uma planta cultivada [1]. A *Opuntia ficus-indica* é a espécie com maior interesse agronómico.

Procedeu-se à caracterização nutricional e antioxidante dos frutos de duas espécies de *Opuntia, Opuntia ficus-indica e Opuntia robusta, p*roduzidas e cedidas por um produtor de Torres Novas, (Portugal).

O perfil nutricional dos frutos foi determinado por métodos AOAC [2] e a composição em açúcares foi determinada por HPLC-ELSD [3]. A extração dos compostos antioxidantes utilizou diferentes solventes: (a) 100% de água, (b) água/etanol (1:1) e (c) 100% de etanol. O teor total de fenólicos e flavonoides, a inibição do radical DPPH e o poder antioxidante do ião férrico (FRAP) dos extratos das amostras foram avaliados por métodos espetrofotométricos [4].

O perfil nutricional dos frutos é semelhante. Em geral, os frutos apresentam um teor baixo em gordura e revelam-se uma fonte interessante de proteína. A *Opuntia ficus-indica* apresenta um teor ligeiramente superior de fibra total. Por sua vez, a *Opuntia robusta* contém níveis mais elevados de minerais. Os frutos de ambas as espécies apresentam teores semelhantes de açúcares. Em relação à atividade antioxidante, a mistura água/etanol (1:1) permitiu uma extração mais eficiente. Os frutos da *Opuntia robusta* apresentam maior atividade antioxidante.

Dadas as semelhanças químicas entre os frutos das duas espécies, justifica-se o aumento da produção da *O. robusta*, e a sua inclusão na dieta alimentar e no processamento industrial. Como tal, o seu cultivo deve ser promovido, tendo em conta que ambas as espécie permitem uma produção agrícola sustentável, não tendo como fator limitante a água e a qualidade do solo.

Agradecimentos:
Os autores agradecem o financiamento do projeto UID/QUI/50006/2019, através de fundos nacionais da FCT/MCTES (Portugal). Os autores agradecem também ao produtor Paulo Costa (Torres Novas), por gentilmente fornecer as amostras.

Referencias:
[1] Barbera O. e P. Inglese, 1993. La coltura del ficodindia. Calderini Edagricole. Bologna, Italy. 189.
[2] AOAC, Métodos oficiais de análise da Association of Analytical Chemistry, 19ª ed., Maryland, EUA, AOAC International, 2012.
[3] Chunmei Ma, Zhen Sun, Changbao Chen, Lili Zhang, Shuhua Zhu. Food Chemistry,145 (2014) 784-788.
[4] Costa, A.S.G., Alves, R.C., Vinha, A.F., Barreira, S., Nunes, M.A., Cunha, L., Oliveira, M.B.P.P., Ind. Crops and Prod, 53 (2014) 350-357.

Carboximetilación del almidón de yuca ecuatoriano (*Manihot esculenta Crantz*) por modificación química Carboximetilación del almidón de yuca ecuatoriano

Silva Samanta[1], Muñoz Nelly[2], Chango Iván[3], Maldonado Alvarado Pedro[4]

[1,2,3,4]Escuela Politécnica Nacional, Ladrón de Guevara E11-253, Quito, Ecuador
pedro.maldonado@epn.edu.ec
samanta.silva@epn.edu.ec

Las provincias de mayor producción de yuca en el Ecuador son Manabí, Esmeraldas. La extracción de almidón de yuca se ha convertido en una importante fuente de ingresos para los pequeños productores de esas zonas. La modificación de almidón mejora las características fisicoquímicas del almidón nativo, pudiendo ser utilizado como ingrediente en la industria alimenticia, farmacéutica y cartonera, proveyendo un nuevo valor agregado a este producto. Un método para la modificación a nivel estructural es la carboximetilación mediante una modificación química. [1], [2]

El objetivo de este trabajo fue estudiar modificaciones químicas por carboximetilación de dos variedades de almidón de yuca ecuatoriano (INIAP 650 e INIAP 651).

La modificación del almidón se realizó en tres medios diferentes de reacción: agua, alcohol isopropílico (IP) y dimetilsulfoxido (DMSO), como agente catalizante se usó hidróxido de potasio (KOH) e hidróxido de sodio (NaOH) y como agentes modificantes ácido cloroacético (AMCA) y cloroacetato de sodio (SMCA). En el proceso de modificación química se consideró, el tiempo de activación 1 h y tiempo de reacción 2,5 h, ambos a 65 °C para todas las experimentaciones En los productos carboximetilados, se analizó el grado de sustitución del almidón por espectrofotometría de infrarrojo con transformada de Fourier (FTIR), la formación de grupos carboxilo mediante titulación ácido-básica y propiedades reológicas con el uso de un reómetro.[3]–[5]

Los resultados de FTIR mostraron la presencia de bandas elásticas C = O de los nuevos grupos ácidos unidos al almidón en forma de carboxilato en comparación con la estructura original del almidón. En las bandas aproximadas de 1 600, 1 400 y 1 300 cm-1, la absorbancia en el almidón modificado en medio acuoso, IP y DMSO con el agente modificante SMCA fue de 1.478; 3.043 y 2.619, respectivamente. Los resultados del contenido de grupos carboxilo fueron 2,40% en medio acuoso, 3,39% en medio IP y 5,59% en DMSO. En las propiedades reológicas se encontró una viscosidad final de 0.2067 Pa.s para el medio acuoso, 0.03801Pa.s para el medio IP y 0.03874 Pa.s en DMSO respectivamente, en comparación con la viscosidad del almidón no modificado que fue 0.06258 Pa. s.

Se obtuvo mejores resultados al utilizar SMCA como agente modificante en comparación con el AMCA. El medio IP proporciona mayor grado de sustitución y mejor solubilidad en agua fría en comparación con los otros medios.

Agradecimientos

Un agradecimiento especial al Departamento de Ciencias de Alimentos y Biotecnología de la Escuela Politécnica Nacional del Ecuador y al Proyecto PREDU 2016 015 a cargo del PhD Pedro Maldonado Alvarado por su invaluable colaboración y asesoría en el desarrollo del presente trabajo.

Referencias

[1] J. N. BeMiller, *Starch: Modification*, 2nd ed., vol. 3–4. Elsevier Ltd., 2015.
[2] A. Bertolini, *Starches Characterization, Properties and Applications*, 1st ed. New York: Taylor and Francis Group, LLC, 2010.
[3] S. E. Barrios, J. M. Contreras, F. López-Carrasquero, and A. J. Müller, “Chemical modification of cassava starch by Carboxymethylation reactions using sodium Monochloro acetate as modifying agent,” *Rev. la Fac. Ing.*, vol. 27, no. 2, pp. 97–105, 2012.
[4] R. A. Flores Geant, “Desarrollo De Almidones Funcionalizados Y Evaluación de las Propiedades Reológicas,” 2006.
[5] Ž. Stojanović, K. Jeremić, S. Jovanović, and M. D. Lechner, “A comparison of some methods for the determination of the degree of substitution of carboxymethyl starch,” *Starch/Staerke*, vol. 57, no. 2, pp. 79–83, 2005.

Development of a natural ingredient from kiwi epicarp with potential application in the food industry

C. Caleja[1], M. Dias[1,2], C. Pereira[1], R.C. Calhelha[1], M. Kostic[3], M. Sokovic[3], Débora Tavares[4], I.J. Baraldi[2], L. Barros[1], I.C.F.R. Ferreira[1*]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
[2] Departamento Acadêmico de Alimentos (DAALM), Universidade Tecnológica Federal do Paraná, Campus Medianeira, 85884-000, Paraná, Brasil
[3]University of Belgrade, Department of Plant Physiology, Institute for Biological Research "Siniša Stanković", Bulevar Despota Stefana 142, 11000 Belgrade, Serbia
[4]KiwiCoop, Rua Kiwicoop, nº 37 – Vila Verde 3770-305 Oliveira do Bairro, Portugal
**iferreira@ipb.pt*

Kiwifruit is a recognized source of bioactive compounds with beneficial properties for consumers' health [1]. Although only pulp is normally consumed, there are several studies in literature that have been exploring the fruits epicarp, which is characterized as an excellent source of bioactive compounds. Thus, since the food industry produces annually tons of this normally discarded and unused residue [2], this work aimed to characterize two varieties of kiwi (*Actinidia delicious* cv. "Hayward" - green pulp kiwi variety and *Actinidia* spp. - red pulp kiwi variety), comparing the two pulps and epicarps. This study will valorize these bio-residues.

The proximal composition (protein, fat, carbohydrates and ash contents, and energy) of the pulp of these varieties, as well as the composition in free sugars, fatty acids, organic acids and tocopherols, and the study of the bioactivities (antioxidant, anti-inflammatory, cytotoxic and antimicrobial activities) of the pulp and epicarp were evaluated. A hydroethanolic extraction was used to obtain compounds subsequently identified and quantified by HPLC-DAD-ESI/MS.

The results revealed that pulps have a high water content and low amount of other macronutrients. Both epicarp varieties presented a higher concentration of phenolic compounds than the corresponding pulp. Additionally, only *Actinidia* spp. (red pulp kiwi variety) presented an anthocyanin, cyanidin-*O*-pentosylhexoside. α-tocopherol was the most abundant vitamer in all the analyzed parts. Four organic acids (quinic, malic, citric and ascorbic acids) were identified in all the studied samples. The best antioxidant activity was shown by the epicarps, highlighting the green pulp kiwi as the best variety. Similarly, only the epicarp of the green pulpkiwi variety presented positive results for all the tested cell lines, being able to inhibit the cell growth in a moderate way. Additionally, none of the extracts showed toxicity in a porcine liver cell line at the highest tested concentration (GI_{50}> 400 µg/mL). Both kiwi varieties also demonstrated an excellent antimicrobial activity against some pathogenic bacteria.

These results confirm the potential application of kiwi epicarp in the food industry as a source of functional compounds with bioactive properties, contributing in the valorization of these bio-residues.

Acknowledgements
The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) and FEDER under Programme PT2020 for financial support to CIMO (UID/AGR/00690/2019); national funding by FCT, P.I., through the institutional scientific employment program-contract for L. Barros and R. Calhelha's contract, and Carla Pereira's contract though the celebration of program-contract foreseen in No. 4, 5 and 6 of article 23º of Decree-Law No. 57/2016, of 29th August, amended by Law No. 57/2017, of 19th July; research contract of C. Caleja (Project AllNatt, POCI- 01-0145-FEDER-030463); to FEDER-Interreg España-Portugal programme for financial support through the project 0377_Iberphenol_6_E. The authors are grateful for financial support to the Ministry of Education. Science and Technological Development of Republic of Serbia, grant number 173032. The authors also thank the company KiwiCoop (Oliveira do Bairro, Portugal) for providing the kiwi samples.

References

[1] C.H. Zhu et al., Storage and Process, 13 (2013), 57-62.
[2] P.A. Folletta et al., Crop Protection, 115 (2019), 113-121.

Punica granatum L. bioresidues as a source of compounds with bioactive properties

C. Caleja[1], F. Veloso[1,2], T.C.S.P. Pires[1], J. Pinela[1], R.C. Calhelha[1], L. Barros[1], A. Genena[2], J.C.M. Barreira[1], I.C.F.R. Ferreira[1*]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
[2] Departamento Acadêmico de Alimentos (DAALM), Universidade Tecnológica Federal do Paraná, Campus Medianeira, 85884-000, Paraná, Brasil
**iferreira@ipb.pt*

Punica granatum L. (pomegranate), is a fruit that has been widely studied due to its composition in specific phenolic compounds, having also been described as displaying excellent bioactive properties (antioxidant, antimicrobial, and anti-inflammatory activity), with preventive action against some diseases [1,2]. Given that the inedible part of this fruit can represent up to about 50% of the total weight, this bio-waste has high potential as a source of bioactive compounds of interest [3].

Thus, this study compared different types of solvents in the extraction of phenolic compounds from the exocarp, mesocarp and pericarp of two pomegranate varieties: Mollar de Elche (yellow pomegranate) and Purple Queen (red pomegranate).

Chemical characterization was performed by HPLC-DAD-ESI/MS and revealed the presence of fourteen phenolic compounds in the Mollar de Elche, highlighting punicalagin and galloyl-HHDP-glucose as the major compounds. The extracts of pomegranate Purple Queen showed the same 14 phenolic compounds, despite being present in lower amounts, but this cultivar revealed also three anthocyanins, which may justify the characteristic reddish color of its bark.

Additionally, the antioxidant activity (inhibition of thiobarbituric acid reactive species formation in brain homogenates and inhibition of oxidative hemolysis, OxHLIA), antibacterial (against a panel of 5 Gram-positive bacteria and 3 Gram-negative bacteria, using the microdilution method), anti-inflammatory activity (rat macrophage cells), and cytotoxic potential (in human tumor cell lines by the sulforhodamine B method). Mollar de Elche stood out for its higher antioxidant and antibacterial activity, and cytotoxicity.

In general, the different extracts obtained from the by-products of both pomegranate varieties represent a source of phenolic compounds that allow it to exhibit excellent bioactive properties with potential application in the food industry as a natural ingredient, which will allow valuing these bio-residues.

Acknowledgements
The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) and FEDER under Programme PT2020 for financial support to CIMO (UID/AGR/00690/2019); national funding by FCT, P.I., through the institutional scientific employment program-contract for L. Barros and R. Calhelha's contract, though the celebration of program-contract foreseen in No. 4, 5 and 6 of article 23º of Decree-Law No. 57/2016, of 29th August, amended by Law No. 57/2017, of 19th July; research contract of C. Caleja (Project AllNatt, POCI- 01-0145-FEDER-030463); to FEDER-Interreg España-Portugal programme for financial support through the project 0377_Iberphenol_6_E. This work is funded by the European Regional Development Fund (ERDF) through the Regional Operational Program North 2020, within the scope of Project NORTE-01-0145-FEDER-023289: DeCodE and project Mobilizador Norte-01-0247-FEDER-024479: ValorNatural®.

References

[1] E.P. Lansky & R.A. Newman, Journal of Ethnopharmacology, 109 (2007),177-206.
[2] N. Braidy et al., Journal of Traditional and Complementary Medicine, 4 (2014), 232–238.
[3] X. Yang, et al., Food Hydrocolloids, 85 (2018), 30–38.

Modelling and optimization of the extraction process of pigments from seaweed from the Galician coast

C. Jiménez-López[1,2], C. Lourenço-Lopes[1], P. García-Oliveira[1], A.G. Pereira [1,2], M.A. Prieto[1], L. Barros[2], I.C.F.R. Ferreira [2], J. Simal-Gandara[1]*

1 Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain.

2 Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.

**jsimal@uvigo.es*

Today, people demand natural products and reject chemical additives due to the association of collateral effects to those synthetic products, such as hyperactivity or allergies. That is why finding new natural pigments that have no adverse effects is important. This is one of the reasons why large-scale cultivation of algae has been promoted. The algae present a wide variety of pigments among which it is worth highlighting carotenoids, chlorophyll and phycobilins (1,2).

In this work, high hydrostatic pressure (HHP) was applied to the extraction of pigments from eight edible algae species (*Laminaria spp., Saccharina latissimi, Himanthalia elongate, Undaria pinnatifida, Porphyra spp., Palmaria palmate, Codium spp.* and *Ulva spp*.).

The process was optimized by response surface methodology using a five-level central composite design combining the independent variables of processing time (*t*, 5-90 min), pressure (*P*, 10-600 MPa) and solvent (*S*, 0-100 % of ethanol, v/v). As a result, it was observed that each class of pigments will be extracted better under different conditions due, among other things, to the different polarity of the different kinds of pigments. Achieving the optimal conditions and maximizing the responses is an important step to guide the choice of a suitable and sustainable process, achieving in this way a profitable process at industrial level.

In conclusion, the present study contributes to the valorisation of edible algae species which are common in the North-West region of Spain, by the obtaining colorants as an alternative as an alternative to the most commonly used, which are known for their adverse effects. In addition, this type of pigments have another series of advantages such as that they come from natural resources and do not require large extensions for their cultivation (3).

The analysis presented provides important data that allows the comparison between different extraction conditions, in terms of efficiency, and consequent related decision making. In an industrial level, these methodologies reduce costs related to energy, solvent consumption, equipment investment, etc. Achieving the optimal conditions and maximizing the responses is an important step to guide the choice of a suitable and sustainable process.

Acknowledgment

To AlgaMar for the algae material provided (www.algamar.com). To MICINN for the financial support for the Ramón&Cajal researcher of M.A. Prieto. To University of Vigo for the financial support for the pre-doctoral researchers of A.G. Pereira and C. Jiménez López. The authors are also grateful to the Interreg España-Portugal for financial support through the project 0377_Iberphenol_6_E

References

1. Anyanwu RC, Rodriguez C, Durrant A, Olabi AG. Micro-Macroalgae Properties and Applications. Ref Modul Mater Sci Mater Eng. 2018;1–28.
2. Balina K, Romagnoli F, Blumberga D. Seaweed biorefinery concept for sustainable use of marine resources. Energy Procedia [Internet]. 2017;128:504–11.
3. Wang HMD, Li XC, Lee DJ, Chang JS. Potential biomedical applications of marine algae. Bioresour Technol [Internet]. 2017;244(May):1407–15.

Optimización de la extracción de compuestos fenólicos a partir de 8 especies de algas comestibles de las costas de Galicia utilizando la metodología de superficie respuesta

C. Jiménez-López[1,2], C. Lourenço-Lopes[1], P. García-Oliveira[1], A.G. Pereira [1,2], M.A. Prieto[1], L. Barros[2], I.C.F.R. Ferreira [2], J. Simal-Gandara[1]*

1 Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain.

2 Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.

**jsimal@uvigo.es*

Aproximadamente tres tercios de la superficie del planeta están cubiertos por océanos. Es, por lo tanto, lógico que casi el 90% de la biomasa existente en la Tierra se encuentra contenida en ellos, lo que los convierte en una fuente muy interesante de compuestos con posibles funcionalidades biológicas. Los ecosistemas acuáticos incluyen las macroalgas, plantas acuáticas y fotosintéticas que presentan características muy heterogéneas, ya que suponen un grupo muy amplio y variado. Las algas no solo generan impactos ecológicos y medioambientales, sino que también tienen un alto interés económico. Muchas de esas algas contienen compuestos con capacidades bioactivas, por lo que son de alta importancia para la industria alimentaria y farmacéutica. Como se cita en numerosas referencias bibliográficas, los compuestos contenidos en estas matrices vegetales son capaces de producir bioactividades como antioxidantes, antimicrobianas, antiinflamatorias, antifúngicas, antihelmínticas, antivirales, antiproliferativas, citotóxicas, anticoagulantes, radioprotectoras, etc. (1).

En el presente estudio, se utilizó la extracción asistida por altas presiones hidrostáticas como técnica para obtener extractos ricos en compuestos fenólicos, conocidos por sus altos potenciales como moléculas bioactivas (2,3), a partir de 8 especies de algas comestibles (Tabla 1). El proceso de extracción fue optimizado gracias a una metodología de superficie de respuesta que utiliza un diseño circunscrito compuesto central basado en 5 niveles y 3 variables independientes: tiempo (*t*, 5-90 min), presión *P*, 10-600 MPa) y porcentaje de etanol en el solvente (*S*, 0-100 % etanol, v/v).

Los resultados permiten concluir que las altas presiones es una técnica emergente efectiva en la extracción de este tipo de compuestos, con la ventaja de que pueden utilizarse solventes verdes y tiempos bajos de extracción.

Tabla 1. Algas comestibles utilizadas en el estudio.

Nombre común local	Nombre científico
Kombu	*Laminaria spp.*
Kombu real	*Saccharina latissima*
Espagueti de mar	*Himanthalia elongata*
Wakame	*Undaria pinnatifida*
Nori	*Porphyra spp.*
Dulse	*Palmaria palmata*
Alga percebe	*Codium spp.*
Lechuga de mar	*Ulva spp.*

Agradecimientos

A AlgaMar por la donación del material, en este caso, algas (www.algamar.com). Al MICINN por el soporte financiero mediante una Ramón&Cajal del Investigador M.A. Prieto. A la Universidad de Vigo por el financiamiento de las investigadoras pre-doctorales A.G. Pereira y C. Jiménez López. Los autores también están agradecidos a Interreg España-Portugal a por el apoyo financiero del Proyecto0377_Iberphenol_6_E.

Referencias

1. Nwosu F, Morris J, Lund VA, Stewart D, Ross HA, McDougall GJ. Anti-proliferative and potential anti-diabetic effects of phenolic-rich extracts from edible marine algae. Food Chem. 2011;126(3):1006–12.
2. Onofrejová L, Vašíčková J, Klejdus B, Stratil P, Mišurcová L, Kráčmar S, et al. Bioactive phenols in algae: The application of pressurized-liquid and solid-phase extraction techniques. J Pharm Biomed Anal. 2010;51(2):464–70.
3. Klejdus B, Plaza M, Snóblová M, Lojková L. Development of new efficient method for isolation of phenolics from sea algae prior to their rapid resolution liquid chromatographic – tandem mass spectrometric determination. J Pharm Biomed Anal. 2017;135:87–96.

Thymus carnosus extracts as a source of phytochemicals for neuroprotection and anti-aging products

Carlos Martins-Gomes[1,2,*], Fernando M. Nunes[3,4], Amélia M. Silva[1,2]

[1]Department of Biology and Environment (DeBA-ECVA), University of Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5000-801 Vila Real, Portugal
[2]Centre for Research and Technology of Agro-Environmental and Biological Sciences (CITAB-UTAD), Quinta de Prados, 5000-801 Vila Real, Portugal
[3]Department of Chemistry (DQ-ECVA), UTAD, Quinta de Prados, 5000-801 Vila Real, Portugal
[4]Chemistry Research Center – Vila Real (CQ-VR), Food and Wine Chemistry Lab, UTAD, Quinta de Prados, 5000-801 Vila Real, Portugal
**camgomes@utad.pt*

Nowadays, the study of medicinal and aromatic plants (MAPs) aiming the application in pharmaceutical and cosmetic industry is one of the main topics of interest. MAPs have several natural characteristics that promote and favour their use, such as: i) the large variety of species available for study; ii) the great intra- and inter-species variability is reflected in their phytochemicals profiles; iii) their use in traditional medicine provides a base for the study of the medicinal properties; and others. Although, in most cases there is a lack of scientific evidence supporting traditional medicine uses and also reduced or non-existing knowledge regarding the phytochemical composition of most MAPs. There are exceptions, and several MAPs have been studied for industry application, as is the case of *Thymus* genus, in which it is possible to find some species with great value. For example, *Thymus pulegioides*, a species with extracts rich in rosmarinic acid, that has been described to have anti-proliferative, neuroprotective, anti-aging and anti-diabetic properties [1].

Thymus carnosus, an endemic species from the Iberian Peninsula, is also rich in rosmarinic acid and salvianolic acids, and has recently been studied to evaluate and characterize the potential bioactivities and uses. In addition to a high content in phenolic acids, HPLC-DAD-ESI-MS^n analysis revealed that *T. carnosus* hydroethanolic extract was also very rich in the pentacyclic triterpenoids ursolic and oleanolic acid, which makes it stand from other species in the same genus [2].

T. carnosus aqueous decoction and hydroethanolic extracts were evaluated regarding their potential as neuroprotective and anti-aging agents, by studying their capacity to inhibit three enzymes: acetylcholinesterase, tyrosinase and elastase. The main extract components, rosmarinic, ursolic and oleanolic acids (as standards) were also tested, to compare and relate the phytochemical composition with its bioactivities.

Our results show that both extracts are a valuable source of phytochemicals with neuroprotective activity, as both inhibited acetylcholinesterase activity. A selective inhibition of elastease and tyrosinase was observed, as aqueous decoction only inhibit tyrosinase and hydroehtanolic extract only inhibited elastase. The inhibitory effect of individual standards supports theses findings, as all of them selectively inhibit elastase but not tyrosinase, demonstrating an extract composition-depent inhibition.

These findings highlight the potential application of *Thymus carnosus* in various industries, such as pharmaceutical and cosmetic.

Acknowledgments
This research was funded by the Portuguese Foundation for Science and Technology (Fundação para a Ciência e Tecnologia (FCT), Portugal) through its funding to CITAB (UID/AGR/04033/2019), to CQ-VR (PEst-OE/QUI/UI0616/2014) and to CMG (SFRH/BD/145855/2019).

References
[1] Taghouti, M., Martins-Gomes, C., Schäfer, J., Félix, L.M., Santos J.A., Bunzel M., Nunes, F.M., Silva, A.M., Food&Function, 9 (2018) 3617–3629.
[2] Martins-Gomes, C., Taghouti, M., Schäfer, J., Bunzel, M., Silva, A.M., Nunes, F.M., Journal of Functional Foods, 43 (2018) 154-164.

Conteúdo Fenólico dos Azeites Virgem Extra Monovarietais Portugueses

Alfredo Esteves[1*], Marlene Costa[1], Fátima Paiva-Martins[1]

[1]REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, Porto, Portugal

**up201305498@fc.up.pt*

O azeite é obtido a partir do fruto de várias variedades de *Olea europaea* L., que apresentam características bioquímicas específicas, fornecendo azeites com diferentes composições. A composição fina do azeite, no entanto, também é influenciada por outros fatores, como condições climáticas. Assim, é necessário estudar o azeite obtido pelo mesmo processo da mesma variedade em várias colheitas a fim de entender o impacto de variedade na composição fenólica do azeite. Outro fator importante é o grau de maturação das azeitonas utilizadas na sua produção, pois durante a maturação ocorrem variações no perfil de alguns compostos como polifenóis e tocoferóis. Essas alterações químicas são refletidas nas características sensoriais, estabilidade oxidativa e/ou valor nutricional do azeite virgem extra.

Este trabalho teve como objetivo avaliar a composição em tocoferóis e polifenóis de alguns azeites virgens extra monovarietais portugueses (AVEM) (Cvs. Galega, Cordovil, Verdeal, Madural e Cobrançosa, que são variedades permitidas na produção de azeite virgem extra DOP). As amostras foram obtidas em plantações industriais, embaladas e prontas para entrega comercial, durante a safra 2018/2019. Todos os AVEM obtidos apresentaram valores de acidez e de índices de peróxido inferiores a 0,3% e 7 meq / kg, respetivamente, de acordo com a alta qualidade desses azeites monovarietais. O teor total de polifenóis foi superior a 400 ppm para todos os azeites monovarietais, sendo o maior teor observado para o AVEM de Verdeal, com mais de 672 ppm. O conteúdo de α-tocoferol foi variou entre 265 e os 432 ppm. O AVEM de Cobrançosa de diferentes locais não apresentou diferença significativa no conteúdo, tanto em polifenóis quanto em tocoferóis. O polifenol mais abundante encontrado em todas as variedades foi a oleuropeína aglicona, seguida pela oleoceína e pelo oleocantal.

Agradecimentos:

O trabalho foi apoiado por UID/QUI/50006/2019 com financiamento da FCT/MCTES através de fundos nacionais e pela PTDC/OCE-ETA/32492/2017 – POCI-01-0145-FEDER-032492 - PHENOLIVA.

Influência do tamanho de gota e razão O/A na atividade antioxidante de galatos em sistemas emulsionados

Marlene Costa[1], Fátima Paiva-Martins[1], Sónia Losada-Barreiro[1,2], Carlos Bravo-Díaz[2], António Vicente[3], Luís S. Monteiro[3]

[1]REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, Porto, Portugal

[2]Universidade de Vigo, Faculdade de Química, Departamento de Química Física, Vigo, Espanha

[3]Centro de Química, Universidade do Minho, Braga, Portugal

A eficiência dos antioxidantes (AOs) em sistemas emulsionados alimentares depende tanto da sua reatividade quanto da sua concentração na região interfacial, onde se acredita que a oxidação tenha início. Neste trabalho determinou-se a distribuição de uma série homóloga de derivados do ácido gálico (AG) de lipofilicidade crescente em emulsões e nanoemulsões de óleo de peixe em água pelo modelo cinético da pseudofase[1]. Uma das hipóteses em que se baseia a aplicação do modelo cinético da pseudofase para a determinação da distribuição de antioxidantes é que a sua aplicação é independente do tamanho da gota do sistema emulsionado. Observou-se que o menor tamanho de gota encontrado nas nanoemulsões não afetou as constantes de partição do ácido gálico e seus ésteres, de acordo com nossa hipótese. Os resultados mostram que a concentração na região interfacial $(AO)_I$, dependendo da cadeia alquílica lateral dos Aos, foi muito maior (~ 119 - 190 vezes para a fração de emulsionante $\Phi_I = 0,005$ e ~ 55-95 vezes para a fração de emulsionante $\Phi_I = 0,01$) do que a concentração estequiométrica dos AOs no sistema emulsionado. Como a eficiência antioxidante dos compostos nos sistemas emulsionados utilizados correlacionou sempre positivamente com a sua concentração na região interfacial, o volume de emulsionante empregue para estabilizar cineticamente os sistemas emulsionados deve ser o menor possível. Além do tamanho da gota ser menor, a estabilidade oxidativa das nanoemulsões foi superior à estabilidade oxidativa da emulsão usada na sua preparação, indicando que a velocidade das reações químicas durante a oxidação não depende da área de superfície da reação. O aumento da razão óleo / água aumentou em geral a estabilidade oxidativa dos sistemas emulsionados, mas diminuiu a eficiência antioxidante dos derivados mais lipofílicos quando comparados com os mais hidrofílicos, porque o aumento do volume da região oleosa diminuiu a concentração interfacial dos antioxidantes mais lipofílicos.

Agradecimentos:

FEDER (COMPETE) e FCT – UID/QUI/50006/2013 – POCI-01-0145-FEDER-007265) e Marlene Costa agradece à FCT pela bolsa de doutoramento (SFRH/BD/100889/2014).

Referencias:

[1] Losada-Barreiro, S., Sánchez Paz, V., Bravo Díaz, C., Paiva Martins, F., Romsted, L. S. J. Colloid. Interface Sci., 2012, 370, 73-79

ALM20

Ingredientes naturais como agentes conservantes: aplicação em formulações nutracêuticas

Filipa A. Fernandes[1,2], Márcio Carocho[1], Sandrina A. Heleno[1], Paula Rodrigues[1], Maria Inês Dias[1], José Pinela[1], Lillian Barros[1], Jesus Simal-Gandara[2], Miguel A. Prieto[1,2], e Isabel C. F. R. Ferreira[1,*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;

[2]Grupo de Nutrición y Bromatología, Departamento de Química Analítica y Alimentaria, Facultad de Ciencias de Ourense, Universidad de Vigo-Ourense Campus, E-32004 Ourense, Spain.

*iferreira@ipb.pt

A crescente preocupação dos consumidores pela segurança dos produtos alimentares, leva a uma preferência por produtos sem aditivos artificiais [1], aumentando a procura de aditivos naturais por parte da indústria. Assim, o objetivo principal deste trabalho consistiu no estudo de ingredientes naturais de reconhecida bioatividade (ácido cítrico e flor de castanheiro) como conservantes de uma formulação nutracêutica comercial à base de *Aloe arborescens* Mill., em substituição do conservante artificial já utilizado (benzoato de sódio). Estas formulações foram posteriormente caracterizadas relativamente ao seu valor nutricional [2] (teor em minerais, humidade, cinzas, proteínas, gordura total, hidratos de carbono e energia), perfil individual em açúcares livres (HPLC-RI), ácidos orgânicos (UFLC-PDA), ácidos gordos (GC-FID) e compostos fenólicos (HPLC-DAD-ESI/MS); e ainda em termos de atividade antioxidante através da inibição da peroxidação lipídica em tecidos cerebrais de porco (TBARS) e da inibição da hemólise oxidativa (OxHLIA). Foram preparadas formulações diferentes com o objetivo de avaliar a capacidade dos ingredientes naturais na inibição do crescimento microbiano, tendo sido contaminadas com diferentes microrganismos (*Escherichia coli*, *Bacillus cereus*, *Aspergillus parasiticus* e *Zygosaccharomyces rouxii*) e, posteriormente, analisadas quanto à quantidade destes microrganismos ao longo de 45 dias. Todos os resultados foram comparados com os obtidos nas formulações com o conservante artificial (benzoato de sódio) e sem conservante. Não se verificaram diferenças significativas entre as formulações. Os hidratos de carbono foram encontrados em maior quantidade (99 g/100 g de massa fresca (mf)), seguidos do teor em proteínas (0,39 g/100 g mf), enquanto que a gordura total apresenta o menor conteúdo (0,05 g/100 g mf); o valor médio de energia foi de 397 kcal/100 g mf. Foram encontrados diferentes minerais (potássio, sódio, cálcio, magnésio, manganês, zinco, ferro e cobre), sendo o cálcio o maioritário com um valor médio de 105 mg/100 g mf. Foram também identificados os açúcares, frutose, glucose e trealose, e dois ácidos orgânicos, destacando-se a frutose (13 g/100 g mf) e o ácido málico (0,40 g/100 g mf), respetivamente. Foram quantificados dezassete ácidos gordos com maior abundância dos ácidos palmítico (C16:0, 37%) e esteárico (C18:0, 14%). Relativamente aos compostos fenólicos foi evidente a presença de 10 compostos fenólicos (2 ácidos fenólicos, 3 flavonoides, 2 aloínas e 3 outas antraquinonas), destacando-se a aloenina (flavonoide) como composto maioritário (0,14 µg/100 g mf). No que concerne à bioatividade verificou-se uma maior atividade nas formulações incorporadas com flor de castanheiro com valores de EC_{50} de 0,11 µg/mL (TBARS) e de IC_{50} 128 µg/mL (OxHLIA - Δt = 60 min). Quanto à estabilidade das formulações desenvolvidas, ambas se mostraram eficazes na inibição do crescimento dos microrganismos, verificando-se uma redução do número de colónias superior à formulação incorporada com benzoato de sódio. Os resultados obtidos neste estudo permitem concluir que os conservantes naturais utilizados não têm influência na composição nutricional e química do nutracêutico estudado e demonstraram ser uma boa alternativa ao benzoato de sódio na conservação deste nutracêutico.

Agradecimentos

FCT E FEDER sob o programa PT2020 pelo apoio financeiro ao CIMO (UID/AGR/00690/2019), bolsa individual de doutoramento de Filipa Fernandes (SFRH/BD/145467/2019), fundos nacionais através da FCT- Fundação para a Ciência e Tecnologia, I.P., no âmbito da Celebração do contrato-programa de emprego científico individual de Sandrina Heleno e Institucional de Maria Inês Dias, José Pinela e Lillian Barros. Ao FEDER-Interreg España-Portugal pelo financiamento ao projeto 0377_Iberphenol_6_E e TRANSCoLAB 0612_TRANS_CO_LAB_2_P., Projeto *Mobilizador* Norte-01-0247-FEDER-024479: ValorNatural® pelo contrato de Márcio Carocho. Ao MICINN pelo apoio financeiro Ramón & Cajal dado ao investigador M.A. Prieto; à Junta da Galiza pelo apoio financeiro de Axudas Conecta Peme ao projeto IN852A 2018/58 NeuroFood. Á Kontaktotal - Consultores Associados, Lda. - Dep. CuraNatura pela colaboração neste projeto.

Referências

[1] M. Carocho, P. Morales, I. C. F. R. Ferreira, Trends in Food Science & Technology, 45 (2015) 284-295.

[2] AOAC. AOAC Official Methods of Analysis, 20th edition AOAC International (2016).

ALM21

Perfil fenólico e propriedades bioativas do epicarpo de jabuticaba

Bianca R. Albuquerque[1,2], Ricardo C. Calhelha[1], Carla Pereira[1], Tânia C.S.P. Pires[1], Lillian Barros[1], M. Beatriz P.P. Oliveira[2], Isabel C.F.R. Ferreira[1]*

[1]Centro de Investigação de Montanha (CIMO), ESA, Instituto Politécnico de Bragança, Santa Apolónia, 1172, 5300-253, Bragança, Portugal

[2] REQUIMTE, Faculdade de Farmácia, Universidade do Porto, Portugal

**iferreira@ipb.pt*

A jabuticabeira é uma árvore frutífera nativa do Brasil, sendo encontrada principalmente na Mata Atlântica. Os seus frutos, denominados por jabuticabas, são pequenas bagas de aproximadamente 2 – 3,5 cm que possuem uma coloração preta a roxa, quando maduros. São muito apreciados para consumo *in natura* devido ao agradável sabor da sua polpa; no entanto, o epicarpo, que é rígido e possui um sabor adstringente, não é comumente consumido, sendo responsável por grande parte do resíduo gerado no processamento de produtos derivados de jabuticaba [1]. A intensa coloração desta parte dos frutos é devida à concentração de pigmentos presentes na sua composição, nomeadamente antocianinas, que são compostos de grande interesse devido à sua coloração atrativa e às suas propriedades benéficas para a saúde [2]. Além disso, a presença de outros compostos fenólicos também tem sido relatada no epicarpo de jabuticaba [1,3]. Com o objetivo de valorizar este biorresíduo, o presente estudo teve como foco a determinação do seu perfil fenólico e a avaliação das suas propriedades bioativas, nomeadamente a atividade antioxidante, antimicrobiana e antiproliferativa. Os compostos fenólicos presentes no extrato do epicarpo de jabuticaba (EEJ) foram detetados por HPLC-DAD-ESI/MS. Os ensaios de bioatividade foram realizados por métodos *in vitro:* a atividade antioxidante foi determinada através da inibição da formação de substâncias reativas do ácido tiobarbitúrico (TBARS) e da inibição da hemólise oxidativa (OxLHIA); a atividade antimicrobiana foi avaliada pelo método da microdiluição contra oito bactérias patogénicas; e a citotoxicidade foi analisada pelo ensaio da sulforrodamina B com quatro linhas celulares tumorais e uma cultura primária de células não-tumorais.

O epicarpo de jabuticaba apresentou um perfil fenólico constituído por catorze compostos fenólicos não antociânicos e dois antociânicos, sendo a cianidina-3-*O*-glucósido o composto mais abundante. Em relação às propriedades bioativas, o EEJ apresentou uma elevada atividade antioxidante, atividade antiproliferativa contra três linhas celulares tumorais e atividade antimicrobiana contra todas as bactérias avaliadas. Não foi observada hepatotoxicidade em células não-tumorais na maior concentração de extrato avaliada. Conclui-se, assim, que o EEJ apresenta uma composição rica em compostos fenólicos, principalmente em antocianinas, e que possui consideráveis propriedades bioativas, o que potencia o interesse da exploração deste biorresíduo para a obtenção de compostos de interesse para a indústria alimentar e farmacêutica.

Agradecimentos

Os autores agradecem à Fundação para a Ciência e a Tecnologia (FCT, Portugal) e ao FEDER no âmbito do programa PT2020 pelo apoio financeiro ao CIMO (UID/AGR/00690/2019); financiamento nacional da FCT, PI, através do contrato de programa institucional de emprego científico para o contrato de L. Barros e R.C. Calhelha; o contrato de C. Pereira através da celebração contrato de programa previso no nº 4, 5 e 6 do artigo 23º do Decreto-Lei nº 57/2016, de 29 de agosto, alterado pela Lei nº 57/2017, de 19 de julho; e bolsas de doutoramento de B. Albuquerque (SFRH/BD/136370/2018) e T.C.S.P. Pires (SFRH/BD/129551/2017); FEDER através do Programa Operacional Regional Norte 2020, no âmbito do Projeto NORTE-01-0145-FEDER-023289 (DeCodE) e projeto *Mobilizador* Norte-01-0247-FEDER-024479: ValorNatural®; FEDER-Interreg España-Portugal pelo apoio financeiro através do projeto 0377_Iberphenol_6_E e TRANSCoLAB 0612_TRANS_CO_LAB_2_P.

Referencias

[1] P. Morales, L. Barros, M.I. Dias, C. Santos-Buelga, I.C.F.R. Ferreira, E.R. Asquieri, J.J. Berrios, Food Chemistry, 208 (2016) 220.

[2] D. Li, P. Wang, Y. Luo, M. Zhao, F. Chen, Critical Reviews in Food Science and Nutrition, 57 (2017) 1729.

[3] M. Plaza, A.G. Batista, C.B.M. Cazarin, M. Sandahl, C. Turner, E. Östman, M.R.M. Júnior, Food Chemistry, 211 (2016) 185.

Carboximetilación del almidón de yuca ecuatoriano (*Manihot esculenta Crantz*) por modificación química Carboximetilación del almidón de yuca ecuatoriano

Silva Samanta[1], Muñoz Nelly[2], Chango Iván[3], Maldonado Alvarado Pedro[4]
[1,2,3,4]Escuela Politécnica Nacional, Ladrón de Guevara E11-253, Quito, Ecuador
pedro.maldonado@epn.edu.ec
samanta.silva@epn.edu.ec

Las provincias de mayor producción de yuca en el Ecuador son Manabí, Esmeraldas. La extracción de almidón de yuca se ha convertido en una importante fuente de ingresos para los pequeños productores de esas zonas. La modificación de almidón mejora las características fisicoquímicas del almidón nativo, pudiendo ser utilizado como ingrediente en la industria alimenticia, farmacéutica y cartonera, proveyendo un nuevo valor agregado a este producto. Un método para la modificación a nivel estructural es la carboximetilación mediante una modificación química. [1], [2]
El objetivo de este trabajo fue estudiar modificaciones químicas por carboximetilación de dos variedades de almidón de yuca ecuatoriano (INIAP 650 e INIAP 651).
La modificación del almidón se realizó en tres medios diferentes de reacción: agua, alcohol isopropílico (IP) y dimetilsulfoxido (DMSO), como agente catalizante se usó hidróxido de potasio (KOH) e hidróxido de sodio (NaOH) y como agentes modificantes ácido cloroacético (AMCA) y cloroacetato de sodio (SMCA). En el proceso de modificación química se consideró, el tiempo de activación 1 h y tiempo de reacción 2,5 h, ambos a 65 °C para todas las experimentaciones En los productos carboximetilados, se analizó el grado de sustitución del almidón por espectrofotometría de infrarrojo con transformada de Fourier (FTIR), la formación de grupos carboxilo mediante titulación ácido-básica y propiedades reológicas con el uso de un reómetro.[3]–[5]
Los resultados de FTIR mostraron la presencia de bandas elásticas C = O de los nuevos grupos ácidos unidos al almidón en forma de carboxilato en comparación con la estructura original del almidón. En las bandas aproximadas de 1 600, 1 400 y 1 300 cm-1, la absorbancia en el almidón modificado en medio acuoso, IP y DMSO con el agente modificante SMCA fue de 1.478; 3.043 y 2.619, respectivamente. Los resultados del contenido de grupos carboxilo fueron 2,40% en medio acuoso, 3,39% en medio IP y 5,59% en DMSO. En las propiedades reológicas se encontró una viscosidad final de 0.2067 Pa.s para el medio acuoso, 0.03801Pa.s para el medio IP y 0.03874 Pa.s en DMSO respectivamente, en comparación con la viscosidad del almidón no modificado que fue 0.06258 Pa. s.
Se obtuvo mejores resultados al utilizar SMCA como agente modificante en comparación con el AMCA. El medio IP proporciona mayor grado de sustitución y mejor solubilidad en agua fría en comparación con los otros medios.

Agradecimientos
Un agradecimiento especial al Departamento de Ciencias de Alimentos y Biotecnología de la Escuela Politécnica Nacional del Ecuador y al Proyecto PREDU 2016 015 a cargo del PhD Pedro Maldonado Alvarado por su invaluable colaboración y asesoría en el desarrollo del presente trabajo.

Referencias

[1] J. N. BeMiller, *Starch: Modification*, 2nd ed., vol. 3–4. Elsevier Ltd., 2015.
[2] A. Bertolini, *Starches Characterization, Properties and Applications*, 1st ed. New York: Taylor and Francis Group, LLC, 2010.
[3] S. E. Barrios, J. M. Contreras, F. López-Carrasquero, and A. J. Müller, “Chemical modification of cassava starch by Carboxymethylation reactions using sodium Monochloro acetate as modifying agent,” *Rev. la Fac. Ing.*, vol. 27, no. 2, pp. 97–105, 2012.
[4] R. A. Flores Geant, “Desarrollo De Almidones Funcionalizados Y Evaluación de las Propiedades Reológicas,” 2006.
[5] Ž. Stojanović, K. Jeremić, S. Jovanović, and M. D. Lechner, “A comparison of some methods for the determination of the degree of substitution of carboxymethyl starch,” *Starch/Staerke*, vol. 57, no. 2, pp. 79–83, 2005.

Complexation of resveratrol with γ-cyclodextrin for lemon juices enrichment: effects on stability and antioxidant activity

Andreia F. R. Silva,[1] Mariana Monteiro,[1] Daniela Resende,[1] Susana S. Braga,[1] Manuel A. Coimbra,[1] Artur M. S. Silva,[1] Susana M. Cardoso[1*]

[1]QOPNA & LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
**susanacardoso@ua.pt*

Diet is currently considered as one of the most important strategies to fight cardiovascular diseases. Resveratrol (RSV) is a natural compound occurring in grapes that assumes particular relevance due to its pleiotropic health benefits. Its application as a functional food ingredient still poses several challenges, including stability, solubility and bioavailability issues. On the other hand, cyclodextrins (CD) have been used extensively as carriers to increase the solubility of poorly water-soluble compounds by the formation of inclusion complexes [1], and γCD is considered the most suitable for food applications due to its inferior toxicity and higher digestibility [2].

This work intended to elucidate the impact of γCD complexes on the stability, retention and protection of antioxidant activity of *trans*-RSV in lemon juices. The γCD complexes, obtained by mixing an aqueous solution of γCD with an ethanolic solution of *trans*-RSV, were characterized in the solid state by Fourier Transform Infrared Spectroscopy (FTIR) and powder X-ray diffraction (PXRD). Lemon juices were supplemented with 0.625 mg/mL of *trans*-RSV in its free form (RSV-juice) or complexed with γCD (γCD·RSV-juice), while citric acid (0.18 M), also supplemented with *trans*-RSV (RSV-CA) or γCD·RSV (γCD·RSV-CA), were used as controls. All samples were storage at both 4ºC and at room temperature in dark, for a period of 1 month. The quantification of RSV in the fortified samples was determined by Ultra high-pressure liquid chromatography at 306 nm, while the antioxidant activity was determined by the $ABTS^{\bullet+}$ scavenging assay. Analyses were performed at 5 distinct points along the storage period, namely just after juice preparation (t0) and at days 7, 14, 24 and 30 (t30).

FTIR and PXRD analysis confirmed the formation of an inclusion complex, by observation of a new solid phase for the γCD·RSV powder. Furthermore, this phase was isostructural with model complexes featuring γCD packed in infinite channels where the guest molecules are lodged. Regarding the application in juices, at t0, the *trans*-RSV dissolved in γCD·RSV-juice, RSV-juice, γCD·RSV-CA and RSV-CA corresponded to 45.9%, 4.3%, 9.1% and 4.1% of the supplemented amount, respectively, suggesting that γCD effectively promoted the solubility of *trans*-RSV in the aqueous solution, mainly in the lemon juice matrix. The amount of RSV found dissolved in the juice was decreased over time, reaching 105-110 μg/mL and 2-14 μg/mL in γCD·RSV-juice and RSV-juice after 1 month, respectively. Consistent with its richness in RSV, γCD·RSV-juice exhibited a superior antioxidant ability when compared to the remaining samples. The overall study allowed to conclude that γCD can serve as an efficient carrier to promote solubility of RSV in lemon juices, also improving their antioxidant potential for at least 30 days.

Acknowledgments
Thanks to the project NETDIAMOND (POCI-01-0145-FEDER-016385). Thanks are also due to the University of Aveiro, FCT/MEC for financial supporting QOPNA research Unit (FCT UID/QUI/00062/2019), through national funds and co-financed by the FEDER, within the PT2020 Partnership Agreement. Andreia Silva acknowledges FCT for the Ph.D. grant SFRH/BD/142100/2018. Susana Cardoso thanks the research contract under the project AgroForWealth (CENTRO-01-0145-FEDER-000001), funded by Centro2020.

References
[1] Venuti, V.; Cannavà, C.; Cristiano, M.C.; Fresta, M.; Majolino, D.; Paolino, D.; Stancanelli, R.; Tommasini, S.; Ventura, C.A. Colloids Surfaces B Biointerfaces, 115 (2014), 22–28.
[2] Saokham, P.; Loftsson, T. International Journal of Pharmacy, 516 (2017), 278–292.

Validation of a GC-MS method to quantify acrylamide in biscuits and the use of asparaginase for its mitigation

João Siopa[1*], Fernanda Cosme[1,2], Fernando M. Nunes[1,3]

[1] Centro de Química de Vila Real (CQ-VR) – Food and Wine Chemistry Lab, Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5001-801, Vila Real, Portugal
[2] Departamento de Biologia e do Ambiente, Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5001-801, Vila Real, Portugal
[3] Departamento de Química, Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5001-801, Vila Real, Portugal
**siopa@utad.pt*

Acrylamide (2-propenamide) is a product of Maillard reaction (MRP) and it is mainly generated through the reaction of the carbonyl group of reducing sugars and the amine group of asparagine [1]. Acrylamide was first detected in heat-processed foodstuffs in 2002 and since then many studies have been made to understand more about this MRP [2]. It is present in a variety of widely consumed products, such as fries and potato chips, breakfast cereal, biscuits, bread, coffee, etc., and it's considered to be potentially carcinogenic and neurotoxic [3]. Therefore, it is necessary to study strategies to mitigate the formation of acrylamide in those foods, without negatively affecting the sensory characteristics. In 2017 the EU has set maximum levels of acrylamide in a range of food products, including biscuits [4]. Thus, the determination of acrylamide nowadays is of the utmost importance for the food industries.

In this work, a method was developed and optimized for its application in biscuits and cookies by GC-SIM-MS by the combination of various methods previously described in the literature. This new method aimed to be simpler without losing precision and accuracy. Therefore the use of an isotopically labelled internal standard, the use of bromination for obtaining 2,3-dibromopropionamide (2,3-DBP) followed by in-situ debromination by co-injection of trimethylamine was used. The method developed presented good precision and accuracy.

The effectiveness of asparaginase as an acrylamide mitigating agent was also tested. Samples were previously prepared with L-asparaginase, in different concentrations, and acrylamide was quantified. The biscuits colour was also evaluated, using the CIELab method, in order to understand the effects of the treatment on the final product. Asparaginase treatment showed to be effective in reducing the acrylamide content to substantially lower levels, as the final product were slightly lighter.

Acknowledgements
We would like to thank the financial support provided by MobFood – «Mobilização de conhecimento científico e tecnológico em resposta aos desafios do mercado Agroalimentar» (POCI-01-0247-FEDER-024524), under the framework of the project reference BIM/UTAD/42/2018, pelo Consórcio «MobFood» (AI 0046), funded by FEDER, through Incentives System for Research and Technological Development under the Operational Program for Competitiveness and Internationalization of Portugal2020. We also want to thank the funds from the Portuguese Foundation for Science and Technology (FCT) to CQ-VR (PEst-OE/QUI/UI0616/2014). Additional thanks to Cerealis company.

References

[1] J. J. Knol, J. P. H. Linssen, M. A. J. S. van Boekel, Food Chem., 120(2010) 1047-1057.
[2] X. Xu, X. An, Food Res Int., 84 (2016), 9-17.
[3] M. Friedman, J. Agric. Food Chem., 51 (2003), 4504-4526.
[4] C/2017/7658, OJ L304 (21.11.2017) 24-44, available at http://data.europa.eu/eli/reg/2017/2158/oj (Accessed 30 September 2019).

QUÍMICA Y MEDIOAMBIENTE

Modeling circular economy on combined treatment of chemical adsorption by bentonite and sulfate radical thermal activation-catalyzed sodium percarbonate of red winery wastewater

Nuno Jorge[1]; André Cunha[2]; Ana R. Teixeira[2]; Marco S. Lucas[2]; José A. Peres[2]

[1] *Campus da Auga, Campus Universitário de Ourense, Universidad de Vigo, As Lagoas, 32004, Ourense, España*

[2] *Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5001-801, Vila Real, Portugal*

**e-mail: njorge@uvigo.es*

Red winery wastewater (WW) is an effluent rich in alcohols (methanol, ethanol and glycerol), sugars, organic acids (acetic, tartaric, propionic), aldehydes, phenolic compounds, fermentation products, soaps and detergents resulting from cleaning operations [1,2] with high levels of TOC, COD, total polyphenols and low biodegradability as observed on Table 1.

A 4R circular economy model (recover, reduction, reuse and recycle) can be adapted from Kirchherr et al. [3], to reuse the wastewater for irrigation of crops by recovering bentonite for adsorption purposes. The addition of activated sodium bentonite at conditions 5.0 g/L, pH 3, agitation 350 rpm/24h, temperature 298.15 K, decreased 69.1, 68.4 and 99.4% TOC, COD and total polyphenols. Sulfate radical (SR) thermal activation catalyzed by sodium percarbonate (SPC) demonstrated the best efficiency at 70ºC, pH 7 with 37.2 and 32.8% TOC and COD removal. The combined treatment of bentonite adsorption/SR-thermal activation catalyzed by SPC achieved 76.6, 75.2, 92.6, 98.1 and >99% TOC, COD, turbidity, TSS and total polyphenols removal (Table 1), respectively. After a chromatic characteristics analysis, the combined treatment removed the wastewater color (L* = 95.51%, a* = 1.02, b* = 8.34) which corresponded to the lowest concentration of phenolics (149 mg gallic acid/L total phenols, 3 mg/L total anthocyanins, 1.01 mg/L total pigments and <0.1 mg/L total tannins). The final treatment made possible the wastewater reuse at low cost (0.77 €/m^3) due to the low phytotoxicity observed on seed germination (GI ≥ 80%). In conclusion, the combined treatment of bentonite with SR-thermal activation catalyzed by SPC is a promising technology for wastewater reuse.

Table 1. Characterization of RWW after bentonite adsorption/SR-thermal activation treatment

Process	Time	COD		BOD_5	Turbidity		TSS		Total polyphenols	
	Hours	mg O_2/L	Removal (%)	mg O_2/L	NTU	Removal (%)	mg/L	Removal (%)	mg/L	Removal (%)
Blanc	0	9869		1249	1205.0		3910	0.0	87	
Adsorption	24	3119	68.4	741	224.0	81.4	222	94.3	1	99.4
SR Thermal activation	26	2444	75.2	228	88.7	92.6	75	98.1	<0.1	>99

Acknowledgements

The authors are grateful for the financial aid of the project I&D Interact – Integrative Research in Environment, Agro-Chain and Technology, action number NORTE-01-0145-FEDER-000017. Marco S. Lucas acknowledges also the Investigador FCT project (IF/00802/2015).

References

[1] R.R. Solís, F.J. Rivas, L.C. Ferreira, A. Pirra, J.A. Peres, Journal of Environmental Science and Health, Part A, 53 (2010) 124 – 131.

[2] M.S. Lucas, R. Mosteo, M.I. Maldonado, S. Malato, J.A. Peres, Journal of Agricultural and Food Chemistry, 57 (2009) 11242 – 11248.

[3] J. Kirchherr, D. Reike, M. Hekkert, Resources, Conservation & Recycling, 127 (2017) 221 – 232.

AMB02

Procesos avanzados de oxidación para la degradación del plaguicida metomilo en aguas de drenes del sector de Uraca, región Arequipa, Perú.

Bernal Miriam[1,*], Roxana Urday[1], Fernández Luz[1], Rodriguez Uro VH[1], Medina Cynthia[1], Quispe Grecia[1], Villasante Andrea[1], Rengifo Herrera JA[2]

(1)Universidad Nacional de San Agustín, Calle Santa catalina N°117, Arequipa, Perú.

(2) Centro de Investigación y Desarrollo en Ciencias Aplicadas, Universidad Nacional de la Plata., La Plata, Argentina.

**mbernalt@unsa.edu.pe*

El metomilo es uno de los plaguicidas más usados en la agricultura peruana, según Van et al., (2013) lo categorizan como un agente altamente toxico y peligroso para el medioambiente, su alta solubilidad en el agua causa fácilmente su dispersión y contaminación en aguas. Los procesos avanzados de oxidación, se basan en procesos fisicoquímicos capaz de producir cambios profundos en la estructura química de los contaminantes, plantean una alternativa de solución para la rápida y efectiva degradación de este plaguicida. Este trabajo de investigación tuvo como objetivo la degradación del plaguicida metomilo, mediante los procesos avanzados de oxidación (Foto Fenton, H2O2/UV y Ozono), en agua destilada, agua simulada y agua real de los drenes del sector de uraca, región Arequipa, Perú. Para el trabajo de investigación se montaron sistemas de experimentación para cada método, los métodos utilizados fueron Foto Fenton, H2O2/UV y Ozono en medio alcalino. La experimentación de dividió en tres etapas, la primera fase se realizó experimentación para obtener las condiciones óptimas para la degradación de metomilo en agua destilada, la segunda fase se utilizó como sustrato aguas simuladas con posibles interferentes(aniones), y la tercera fase se realizó la degradación de metomilo en aguas reales provenientes de los drenes del sector de uraca, región Arequipa, Perú. Los resultados de la investigación revelan que en condiciones óptimas de cada tratamiento (Foto Fenton, H2O2/UV y Ozono), se logra la degradación de metomilo en 99%, 99% y 96% respectivamente, en aguas simuladas, 23%, 99% y 0% y en agua real 94%, 99% y 40%. De los resultados se puede observar que a condiciones óptimas se logran alta degradación del plaguicida metomilo en los tres métodos, sin embargo, el efecto de los aniones en aguas simuladas, reduce la degradación afectando más al proceso de ozono y foto fenton. En agua real se puede observar que también se degrado el plaguicida metomilo, se puede observar que el método H2O2/UV y Foto Fenton tuvieron la mayor degradación. Podemos concluir que los procesos avanzados de oxidación son metodologías que son efectivas para la degradación de metomilo en aguas reales en condiciones de laboratorio. Los procesos avanzados de oxidación homogéneos como los experimentados en este trabajo de investigacion podrían aplicarse en ambientes acuáticos, que presenten problemas de presencia de plaguicidas, en pro de mantener el ambiente y de proteger la salud de las personas.

Agradecimientos

A la Universidad Nacional de San Agustín de Arequipa Perú, Promotora del Proyecto de Investigación “Procesos avanzados de oxidación fotoquímicos para la destrucción de plaguicidas presentes en el rio Majes en el sector de Uraca, Arequipa” Con Nº de Contrato IBA-038-2017.

Referencias

[1] Conte, L.O.,. Schenone,A.V., Giménez, B.N. y. Alfano, O.M. Photo-Fenton degradation of a herbicide (2,4-D) in groundwater for conditions of natural pH and presence of inorganic anions. Journal of Hazardous Materials. 372, (2019). 113-120.

[2] Chang, Trinh, Chiu, Chang,Chiang,Ji, Tseng, Chang,Chen. UV- C irradiation enhanced ozonation for the treatment of hazardous insecticide methomyl. Journal of the Taiwan Institute of Chemical Engineers. (2015) 100-104

[3] Chelme-Ayala P, El Din M.G., W. Smith D. Degradation of bromoxynil and trifluralin in natural water by direct photolysis and UV plus H2O2 advanced oxidation process. Wáter research. (2010). 2221-2228

[4] Van, Yue, Deng, Tjeerdema Environmental fate and toxicology of methomyl. Reviews of Environmental Contamination and Toxicology (2013). 93-109

Contaminación y Acumulación de metales tóxicos (As, Al, Pb, Fe) en agua, vegetales y plantas medicinales de mayor consumo en la ciudad de Arequipa, Perú

J. Esther Chavez[1*], Betty Paredes[2] Karina Moran M[1], Apucusi V. Christian[3],- Greg Carling[4]
Universidad Nacional de San Agustín, (1) Departamento Académico de ingeniería Química, (2) Departamento Académico de Química, (3) Departamento Académico de Metalurgia y Ambiental, Avenida Independencia s/n Arequipa, Perú
(4) Brigham Young University, Provo, Utah, EE. UU.
**jchavez9@unsa.edu.pe*

Los metales pesados son conocidos por su gran impacto en la salud humana desde el punto de vista toxicológico, con los siguientes efectos sobre los seres humanos al sistema inmunológico y a la integridad del ADN de las células, a través de la ingesta directa por productos como vegetales, hortalizas y plantas medicinales [1], debido a la contaminación del agua y suelo, por fuentes antropogénicas (agricultura, minería e industrias) y fuentes naturales (lluvias ácidas, erosión del suelo, erupciones volcánicas) incrementado por los efectos del cambio climático.[2]

Las plantas son comercializadas en los diversos mercados de la ciudad de Arequipa, Perú, e ingeridas en la preparación de las comidas (poro, cilandro, ajo), también por medio de infusiones medicinales (hierbabuena y alfalfa), ingresando directamente al organismo y causar efectos negativos (bioacumulación) sobre la salud de la población, de menor recursos económicos.

El área de estudio se encuentra ubicado en el centro poblado Los Tunales del distrito de Tiabaya en la provincia de Arequipa (microcuenca del río Chili), se realizó en junio de 2018 el monitoreo de las aguas superficiales del río Chili, utilizando la técnica de espectrometría masas por plasma acoplado inductivamente (ICPMS), los resultados de las concentraciones son: As 0.01564 mg/l, Al 1.26 mg/l, Fe 1.38 mg/l, encontrándose por encima de lo establecido por normativa internacional (unión europea), Pb 0.00241 mg/l, para muestras sin filtrar; dichas aguas son utilizadas para el riego de vegetales y plantas.
Estos estudios llevaran a planes de acción conducentes a tareas de mitigación y remediación.

Las concentraciones promedio en las plantas (verduras y plantas medicinales) son la tabla 1. :

Tabla 1: Concentración de metales en plantas

Plantas	Codex Alimentario	Aluminio	Arsénico	Hierro	Plomo
	Pb (mg/kg)	mg/kg			
Poro	0.1	9,34	0,16	27,82	0,06
Cilandro	0.1	71,56	0,34	139,4	0,34
Ajo	0.1	2,23	0,03	19,98	0,02
Hierbabuena	0.1	72,6	0,46	120,62	0,04
Alfalfa	0.1	74,55	0,55	137,5	0,35

Fuente: Elaboración propia.

Agradecimientos

A la Universidad Nacional de San Agustín de Arequipa Perú, Promotora del Proyecto de Investigación "Estudio de la Acumulación de Hg, Cr, Pb, Cd y As en vegetales y plantas medicinales de mayor consumo en la localidad de Arequipa Perú y su relación con las concentraciones en sangre y plasma como indicadores biológicos de contaminación" Con Nº de Contrato IBA-034-2016.

Referencias

[1] V. Angelova, R. Ivanova, V. Delibaltova, K. Ivanov, Industrial Crops and Products 19 (2004) 197-205
[2] B. Paredes, J. Zegarra, J. Zanabria, F. Cuadros, J. Chávez, P. Huanca, Avances en Ciencias e Ingeniería (2018) 13-22
[3] ANA-Autoridad Nacional del Agua, Metodología para la determinación del índice de calidad de agua ICA-PE, aplicado a los cuerpos de agua continentals superficiales, ANA (Eds. 1), Lima, 2018.

Superparamagnetic hybrid nanostructured materials for environmental decontamination

L. Alves[1,*], S. Yáñez Vilar[1] , Y. Piñeiro[1], J. Rivas[1]

[1] Departamento de Física Aplicada, Universidade de Santiago de Compostela, Faculdade de Física, 15782, Santiago de Compostela, Espanha
*lisandracristina.decastro@usc.es

Currently, human activity is not the only cause of pollution worldwide, seasonal biogenic toxicity is also found to be widespread in water resources, soils and ultimately in the food chain, causing disease in animals and humans, thus producing numerous economic losses.

A wide variety of contaminants with a broad chemical profile (nanoparticles, toxins, polycyclic aromatic hydrocarbons (PAHs), dyes, drugs, endocrine disruptors, heavy metals, etc.) can be found highly dissolved in water due to the low efficiency of conventional wastewater treatment processes. Therefore, alternative innovative measurements should be implemented to avoid the biotransformation and accumulation of these contaminants, within the food matrix thus affecting, human and animal health.

Many treatment technologies were introduced so far including activated carbon adsorption, biodegradation, ozonation, photo-Fenton, photo-oxidation, electrochemical oxidation, and photo-electrolysis [1,2]. However, the low efficiency, incomplete degradation, and high energy consumption limit the wide application of these technologies.

Hybrid nanostructured magnetic materials with specific catalytic properties and chemical affinities with remediation capabilities provide a new generation of contaminant cleaners and are easily separated from the matrix material by magnetic extraction. Allowing, a facile and economically cost-effective handle and industrial scale production. In this work, we presented a set of nanostructured magnetic materials with different coatings for magnetic extraction of contaminants (Fig.1.), which can be used in water, beverages or food matrices.

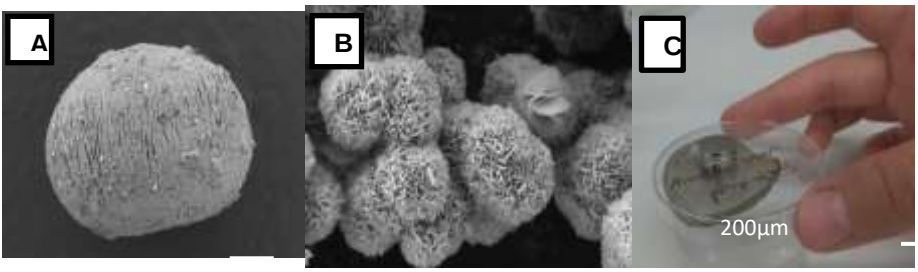


Fig.1. SEM microgram of a magnetic bead (A), magnetic flower-like BiO nanoparticles (B) and cellulose magnetic filter (C).

Acknowledgments

This work was supported by EP-INTERREG V A (POCTEP) Funds (project NANOEATERS/1378), the Program for Consolidation of Reasearch Units of Competitive Reference GRC2017 of Xunta de Galicia ((Grant N. ED431C 2017/22) and the Consellería de Educación Program for the Development of Strategic Grouping in Materials (AEMAT) at the University of Santiago de Compostela (Grant N. ED431E2018/08).

References

[1] X. Author, Y. Author, Z. Author, Journal name, 20 (2001) 537. Lin, A. Y. C., Lin, C. A., Tung, H. H., & Chary, N. S. (2010). Journal of Hazardous Materials, 183(1-3), 242-250

[2] Yu, J. G., Zhao, X. H., Yang, H., Chen, X. H., Yang, Q., Yu, L. Y., Chen, X. Q. (2014). Science of the Total Environment, 482, 241-251

Efecto de la concentración de metales en la actividad de un biorreactor de membrana enriquecido en bacterias N-damo

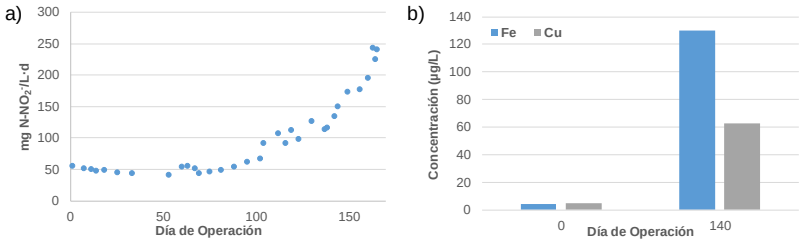
Fachal M.[1,*],Darwich A.[2],Martínez M.[1],Arias A.[1],Allegue T.[1],Omil F.[1],Garrido J.M.[1]
[1]Departamento de Enxeñaría Química y i-CRETUS, Universidade de Santiago de Compostela, Rúa Lope Gómez de Marzoa 15702, Santiago de Compostela, España
[2]Institut Européen des membranes, CC 047, Université de Montpellier. Site Triolet, 2, Place Eugène Bataillon, 34095, Montpellier Cedex 5, France.
**manuel.fachal.suarez@usc.es*

El tratamiento anaeróbico de las aguas residuales se utiliza ampliamente en países de clima cálido y templado (Brasil, Colombia, Méjico, La India…). Pese a sus numerosas ventajas, como la escasa producción de lodos y la generación de un biogás, que puede aprovecharse como fuente de energía; presenta dos importantes inconvenientes: una gran fracción de metano disuelto en el efluente y la escasa eliminación de nutrientes, lo que genera emisiones elevadas de Gases de Efecto Invernadero (GEI) y eutrofización de los medios receptores. Recientemente se han identificado microorganismos capaces de realizar la desnitrificación acoplada a la oxidación anaerobia del metano (bacteria n-damo) [1], por lo que el desarrollo de tecnologías que utilicen bacterias n-damo podrían solucionar, de forma simultánea, los problemas asociados al uso de sistemas de tratamiento anaerobio de aguas residuales.

La implantación de esta tecnología, sin embargo, presenta ciertas dificultades debido a la baja tasa de crecimiento de estos microorganismos (12 días) y las bajas velocidades de desnitrificación alcanzadas. Los estudios más recientes indican que el hierro y el cobre son dos elementos clave para el desarrollo de estos microorganismos [1]. Con el fin de evaluar el efecto de ambos micronutrientes sobre la actividad de los microorganismos, se ha operado un biorreactor de membrana previamente enriquecido en bacterias N-damo [2].

Durante el período de operación del reactor se ha incrementado de forma importante la biodisponibilidad de Fe y Cu mediante la adición de un agente quelante, ácido etilendiaminotetraacético (AEDT). Dicha acción causó un aumento notable de la actividad desnitrificante desde los 50 mg $N\text{-}NO_2^-/L\cdot d$ hasta alcanzar los 250 mg $N\text{-}NO_2/L\cdot d$ (Fig. 1)**.** Los resultados indican que la adición de estos metales es clave ya que se ha mejorado notablemente la actividad desnitrificante del biorreactor, en concordancia con los datos reportados en ensayos batch [1], suponiendo un avance significativo de cara a su implementación.

Figura 1. a) Evolución de la eliminación de nitrito. b) Biodisponibilidad de los metales en la alimentación



Agradecimientos
Los autores del estudio agradecen al ministerio de Economía y Competitividad por la financiación del proyecto COMETT (CTQ2016-80847-R). M. Martínez también quiere agradecer al ministerio por la concesión de la beca predoctoral (BES-2017-080503). Los autores pertenecen a la agrupación i-CRETUS (ED431E 2018/01).

Referencias

[1] L. Jiang, Z. Hu, Y. Wang, D. Ru, J. Li, J. Fan, Effect of trace elements on the development of co-cultured nitrite-dependent anaerobic methane oxidation and methanogenic bacteria consortium, Bioresour. Technol. 268 (2018) 190–196.
[2] T. Allegue, A. Arias, N. Fernandez-Gonzalez, F. Omil, J.M. Garrido, Enrichment of nitrite-dependent anaerobic methane oxidizing bacteria in a membrane bioreactor, Chem. Eng. J. 347 (2018) 721–730.

Can the impact associated with critical rare elements be reduced trough living macroalgae?

Thainara Viana[1,*], Bruno Henriques[1], Cláudia Lopes[2], Elaine Fabre[2], Nicole Ferreira[1], Marcelo Costa[1], José Soares[1], João Pinto[1], José Pinheiro Torres[3], Eduarda Pereira[1]

[1] Department of Chemistry, CESAM & REQUIMTE, University of Aveiro, 3810-193 Aveiro, Portugal
[2] Department of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
[3] N9VE – Nature, Ocean, Value, Porto, Portugal
**thainara@ua.pt*

We live in a highly technological world, where devices such as cell phones, televisions, computers and other technologies of our daily use play a key role. This modern technological innovation requires vital elements such as rare earth elements (REE) that are sometimes called "the seed of technology" due to their diverse chemical, electrical, metallurgical, magnetic, optical, and catalytic properties [1]. The REE rarely exist individually and in pure form, occurring naturally together in mineral deposits, with China holding 90% of the global production [2]. Neodymium and Dysprosium are two REE used in magnets for wind turbines, hybrid vehicles and hard disk drives [3] and together with remaining REE are considered critical rare elements (CREs) [4]. Due to the widespread application of Nd and Dy, their concentration in ecosystems is expected to increase with industrial effluents and e-wastes discharges.

The main objectives of this work are: a) to evaluate the possibility to remove and recover Nd and Dy, from contaminated waters using two species of aquaculture macroalgae (*Ulva lactuca* and *Gracilaria spp*); b) assess the influence of some operational parameters (salinity, mass and time of contact) on the bioaccumulation/biosorption efficiency of the process.

The results highlight the potential of these two macroalgae for REE removal and recovery, since the removal percentages varied between 70 to 90%. Algae mass was the most influence parameter for both elements, while salinity showed to be a relevant parameter for Dy removal yet it did not present a great relevance for Nd removal. The time of contact did not demonstrate relevance for the process removal efficiency, considering the periods evaluated (72 and 168 hours).

In conclusion, it was verified that the use of living macroalgae constitutes a simple, cost-effective and environmentally friendly process to remove and recover REE from waters even if these elements are at low concentrations.

Figure 1: Macroalgae used to remove and recover REE from contaminated waters: *Ulva lactuca* and *Gracilaria spp* (from left to right, respectively).

Agradecimientos
Bruno Henriques and Cláudia Batista Lopes benefited from a Research position funded by national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. Thanks are also due for the financial support to CESAM (UID/AMB/50017), to FCT/MEC through national funds, and the co-funding by the FEDER, within the PT2020 Partnership Agreement and Compete 2020. Work done in cooperation with the company N9VE.

Referencias

[1] J. Ponou, L. Wang, G. Dodbiba, K. Okaya, T. Fujita, K. Mitsuhashi, T. Atarashi, G. Satoh, M. Noda, Journal of Environmental Chemical Engineering, 2 (2014) 1070–1081.
[2] I. Anastopoulos, A. Bhatnagar, and E. C. Lima, Journal of Molecular Liquids, 221 (2016) 954–96,.
[3] D. Bauer, D. Diamond, J. Li, M. McKittrick, D. Sandalow, P.Tellen, U.S. Department of Energy, 2011.
[4] European Commission Technical Report, 39 (2010) 1–84.

3D tuned porous carbon monoliths as catalysts in wet peroxide oxidation of paracetamol

Fernanda F. Roman[1,2], Hendryk Steldinger[3], Jose L. Diaz de Tuesta[1,2], Adriano Henrique[1,2], Jose A. C. Silva[1,2], Jan Gläsel[3], Bastian J.M. Etzold[3], Helder T. Gomes[1,2,*]

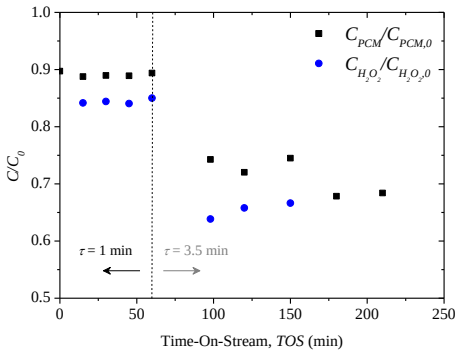
[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2]Laboratory of Separation and Reaction Engineering–Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[3]Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Alarich-Weiss-Straße, 64287 Darmstadt, Germany

**htgomes@ipb.pt*

In recent years, many pharmaceuticals have been identified at trace levels worldwide in the aquatic environment [1]. Municipal wastewater treatment plants (WWTPs) are considered the main sources of these pollutants as they are not generally prepared to deal with such complex substances and thus, they are usually ineffective in their removal [1]. Despite the low concentration of drugs contained in those effluents, the presence of pharmaceuticals, even in trace concentrations, affects the quality of water and constitutes a risk of toxicity for the ecosystems and living organisms [1-2]. Consequently, new regulation for micropollutants discharge and monitoring has been issued in Europe (Directive 2013/39/EU). Paracetamol (PCM) deserves particular attention, since it has recently been discovered as a potential pollutant of waters, largely accumulated in the aquatic environment [3]. This work deals with the treatment of PCM, used as a model pharmaceutical contaminant of emerging concern, by catalytic wet peroxide oxidation using carbon-based monoliths (Fig. 1a) as catalysts. Monoliths were prepared by stereolithographic 3D printing of a photoresin, which was later converted into porous carbon by oxidation in air (300 °C, 6 h) and subsequent pyrolysis in N_2 (900 °C, 15 min) as described elsewhere [4]. The materials revealed catalytic activity in the CWPO of PCM allowing to reach PCM conversions up to 30% with a residence time of 3.5 min (Fig. 1b).



(a) (b)

Fig.1. (a) Photograph of a monolith and (b) relative concentration of PCM and H_2O_2 upon *TOS*.

Acknowledgements

This work is a result of the Project "AlProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF); the Associate Laboratory LSRE-LCM - UID/EQU/50020/2019 - funded by national funds through FCT/MCTES (PIDDAC); and CIMO (UID/AGR/00690/2019) through FEDER under Program PT2020. The authors also acknowledge the joint financial support from Fundação para a Ciência e a Tecnologia (FCT) in Portugal and the Deutscher Akademischer Austauschdienst (DAAD) in Germany.

References

[1] Y. Luo, W. Guo, H.H. Ngo, L.D. Nghiem, F.I. Hai, J. Zhang, S. Liang, X.C Wang, Science of the Total Environment, 473-474 (2014) 619.

[2] B.I. Escher, R. Baumgartner, M. Koller, K. Treyer, J. Lienert, C.S. McArdell. Water Research 45 (2011) 75.

[3] C.P. Silva, G. Jaria, M. Otero, V.I. Esteves, V Calisto. Bioresource Technology 250 (2018) 888.

[4] H. Steldinger, A. Esposito, K. Brunnengräber, J. Gläsel, B.J.M. Etzold. Advanced Science (2019) 1901340.

Influence of agro-environmental conditions on phenolic compounds and biological properties of grape (*Vitis vinifera* L.) stems

Irene Gouvinhas[1], Rosa Pinto[1], Rafaela Santos[1], Maria José Saavedra[1], Ana Isabel Barros[1]

[1]Centre for the Research and Technology of Agro-Environmental and Biological Sciences, CITAB, UTAD, Vila Real, Portugal

**igouvinhas@utad.pt*

The winery industry is one of the most important industries worldwide, with an economical and social impact in Europe and specially in northern Portugal. This socio-economic activity entail large quantities of by-products generated annually, causing economical and environmental problems. In a close connection with the 40 years history of investigation on agro-food valorization, nowadays, a growing interest has wake up on recycling winery wastes boosted by the more and more reported putative health-promoting effects. Furthermore, the continuous emergence of multidrug resistant bacteria is becoming a huge threat to human, animal and environmental health (*One health approach*). Therefore, the research for new natural antimicrobial compounds is the most promising alternative to effectively control multidrug bacterial infections. Hence, qualitative and quantitative evaluation of polyphenolic extracts of grape stems as sources of individual phenolic compounds and their biological activity *in vitro* (radical scavenging power and antimicrobial activity) were assessed. Grape stems revealed to be a rich source of phenolic compounds, even after some months of storage. Furthermore, all extracts (with and without storage) were able to inhibit the bacterial growth of the Gram-positive bacteria and Gram-negative bacteria (except *E. coli* and *K. pneumoniae*), revealing the potential inclusion of these bioactive compounds in the food, cosmetic, and pharmaceutical industry as functional ingredients. Furthermore, and as expected, it was also verified a year-to-year variation proved by a significant increase of these parameters from 2017 to 2018, revealing the high influence of growing seasons in the phytochemical composition of these by-products. The antimicrobial activity determined in these samples demonstrated to be not severally affected by the climate conditions of each year of study, however, the high altitude induced generally a lower activity in the stem samples, results confirmed by the multivariate analysis.

Acknowledgments

This work was supported by National Funds by FCT - Portuguese Foundation for Science and Technology, under the project UID/AGR/04033/2019, and the I&D project Interact - Integrative Research in Environment, Agro-Chains and Technology (NORTE-01-0145-FEDER-000017), regarding the research line “Fostering viticulture sustainability for Douro Valley: multidisciplinary efforts from field to wine (VitalityWINE)”, and the research line “Innovation for Sustainable Agro-food Chains (ISAC)” co-founded by the European Regional Development Fund (FEDER) through NORTE-2020 (Programa Operacional Regional do Norte 2014/2020) and FEDER-Interreg España-Portugal programme for financial support through the project 0377_Iberphenol_6_E. R.A. Santos was supported by the grant SFRH/BD/ 131069/2017 . We also acknowledge Eng. Manuel Henriques from Rozés for the samples provided.

AMB09

Variación espacio-temporal de la concentración de Cr y Ni en suelos y sedimentos intermareales.

Paulina Guevara García[1,2*], Jaime Caza[2], Xose Luis Otero[2],

[1]Universidad de las Fuerzas Armadas ESPE, Av. El Progreso S/N, Sangolqui, Ecuador

[2] Departamento de Edafoloxía e Química Agrícola, Facultade de Bioloxía Universidade de Santiago de Compostela, 15782 Santiago de Compostela, España

**pvguevara@espe.edu.ec*

Las elevadas concentraciones de metales pesados encontrados en los sedimentos costeros son atribuidas frecuentemente a efectos antropogénicos. Los efectos de la actividad antropogénicas son visibles en los perfiles a diferentes profundidades marcando un histórico del auge industrial de este último siglo. En zonas costeras junto a complejos geológicos de composición litológica específica el enriquecimiento de metales pesados puede deber su origen a fuentes naturales como es el caso de complejo del cabo Ortegal (NO-Península Ibérica). Un complejo formado por rocas ultramaficas, con alto contendió de Mg, Cr, Ni, asociada a las dunitas serpentinizadas. Las dunitas son explotadas para uso industrial generando lodos con elevados contenidos de Cr y Ni. La presencia del Fe juega un papel importante en la movilidad del Cr y Ni en los sedimentos acumulados en la costa, por su facilidad de reacción en diferentes medios desde oxidante a fuertemente reductor.

Las marismas que forman parte de la ría de Ortigueira acumulan los sedimentos de origen continental-marino actuando como sumideros de carbono y metales pesados. La variabilidad de las condiciones redox que van de oxidantes en superficie a reductoras a los pocos centímetros aumentando su efecto en profundidad generan las reacciones de estabilización de metales con el Fe. Las formas de Fe dominantes en estos ambientes son oxihidroxidos de Fe en superficie y Fe-piritico en profundidad, produciéndose en la zona superior del suelos una continua alternancia entre estas dos firmas de Fe debido a cambios en las condiciones redox del sistema.

El objetivo de este trabajo es evidenciar la alteración antropogénica de los medios marino-costeros y su recuperación al cese del impacto. Para ello se realizó un monitoreo de perfiles de suelos de las marismas de Mera, Esteiro y Ladrido con presencia de ***Spartina Maritima*** como vegetación pionera y sedimentos superficiales de la Ria de Ortigueira por el canal principal. Se realizó analisis de Cr, Ni y Fe como metal total y por extracción secuencial asociados a las diferentes formas cristalinas del Fe.

Encontrándose que las concentraciones máximas se presentan en los suelos de la marisma de Esteiro 471 mg kg-1 Cr y 1323 mg kg-1 Ni entre los 20 a 25 cm de profundidad, asociados a los oxihidroxidos de hierro, más que la pirita. La abundancia de oxihidroxidos de Fe en los suelos de marismas y los sedimentos de la ria se debe al efecto oxidante que ejerce la *Spartina Maritima* sobre el suelos, cuyas raíces facilitan el transporte de oxígeno al interior del suelo, a la pérdida de agua de la parte superficial del suelo en baja mar y al proceso de evapotranspiración [1]. El reciclaje del Fe se da con la reacción de oxidación de la pirita en profundidad formando Fe2+ que fluye a superficie, donde se oxida y precipita en forma de oxihidroxidos de Fe reactivos (como ferrihidrita, lepidocrocita y goethita).

Los sedimentos de la marisma de Esteiro muestra un histórica enriquecimiento de Cr y Ni con un pico alto entre los 20 a 25 cm, más evidente en Ni que en Cr. Esta alta concentración fue comparable con la encontrada en muestras de la misma zona tomadas en 1996. El Cr y Ni permiten evidenciar el impacto de la actividad antropogénica en la zona producto de la explotación de las dunitas, y una vez cesada el proceso se evidencia la recuperación del suelos, observando una reducción de la concentración de Cr y Ni que le permitiría recupere su carácter prístino.

Agradecimientos

A la Universidad de las Fuerzas Armadas ESPE por la beca otorgada en el programa de Doctorados -2016.

Al Laboratorio de Edafología y Química Agrícola de la Universidad de Santiago de Compostela.

Referencias

tero, Biogeoquímica de Metales Pesados en Ambientes Sedimentarios Marinos, Santiago de Compostela: USC Tesis PHD, 2000.

Lipofilização de antocianinas baseado na retenção de enzimas em membranas porosas

M. Guimarães[1], M. Pérez-Gregorio[1], N. Mateus[1], V. de Freitas[1], C. Galinha[2], J. Crespo[2], C. Portugal[2], L. Cruz [1,*]

[1]Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal

[2]Departamento de Química e Bioquímica, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

[*] *Luis.cruz@fct.up.pt (L. Cruz)*

As antocianinas têm despertado o interesse da comunidade científica assim como da indústria cosmética, farmacêutica e alimentar, devido às suas características cromáticas apelativas e propriedades biológicas importantes. Todavia, a sua aplicabilidade tecnológica é ainda limitada devido à sua instabilidade e baixa solubilidade em matrizes lipídicas, entre outros fatores [1-3].

A esterificação de antocianinas com ácidos gordos surgiu como resposta à necessidade de melhorar a estabilidade destes compostos em matrizes lipofílicas. Através da esterificação enzimática foi possível não só aumentar a sua liposolubilidade como também foi observado o enaltecimento de algumas das suas propriedades biológicas, nomeadamente, a atividade antioxidante [4,5].

Com o objetivo de obter antocianinas lipofílicas de um modo mais eficiente e industrialmente viável, foi desenvolvido um novo método de esterificação. Assim, procedeu-se à imobilização de lipase B de *Candida antarctica* (*Ca*lB) em membranas porosas com diferentes capacidades de retenção. As membranas provaram serem bons suportes enzimáticos, retendo eficazmente a enzima. O catalisador enzimático retido neste suporte demonstrou igualmente a sua reusabilidade, não se observando diferenças nos fatores de conversão em três reações cíclicas consecutivas. Através deste método foi possível obter antocianinas lipofílicas mais rapidamente e com fatores de conversão 2,5 vezes superiores, comparativamente à síntese em bulk [6] (figura 1).

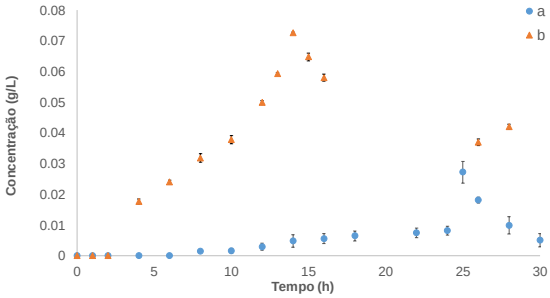


Fig 2. Reações de formação de antocianina lipofílica, Cy3glc-C8, (a) usando um extrato de enzima rico em *Ca*lB e (b) utilizando a enzima retida numa membrana de porosidade 10 KDa ao longo do tempo.

Agradecimentos

Este trabalho encontra-se inserido no projeto PTDC/OCE/ETA/31250/2017 financiado pela FCT/MCTES através do acordo PT2020 (UID/QUI/50006/2019 – POCI/01/0145/FEDER/007265).

Referências

[1] H. E. Khoo; A. Azlan; S. T. Tang; S. M. Lim, Food & Nutrition Research, 61 (2017) 1.
[2] X. H. Yang; E. Luo; X. Liu; B. Han; X. P. Yu; X. L. Peng, Bmc Cancer, 16 (2016).
[3] L. Xie; H. Su; C. Sun; X. Zheng; W. Chen, Trends in Food Science & Technology, 72 (2018) 13.
[4] L. Cruz; M. Guimaraes; P. Araujo; A. Evora; V. de Freitas; N. Mateus, Journal of Agricultural and Food Chemistry, 65 (2017) 6513.
[5] J. Mendoza; F. Pina; N. Basílio; M. Guimarães; V. de Freitas; L. Cruz, Dyes and Pigments, 151 (2018) 321.
[6] M. Guimarães; M. Pérez-Gregorio; N. Mateus; V. de Freitas; C. F. Galinha; J. G. Crespo; C. A. M. Portugal; L. Cruz, Food Chemistry, 300 (2019) 125167

Can the recycling of valuable europium from wastes be achieved through live macroalgae?

Bruno Henriques[1,*], Tiago Morais[1], Rosa Freitas[2], Marcelo Costa[1], João Pinto[1], José Soares, Thainara Viana[2], José Pinheiro Torres[3], Eduarda Pereira[1]
[1]Departament of Chemistry, LAQV-REQUIMTE & CESAM, University of Aveiro, 3810-193 Aveiro, Portugal
[2]Departament of Biology & CESAM, University of Aveiro, 3810-193 Aveiro, Portugal
[3]N9VE – Nature, Ocean, Value, Porto, Portugal
*brunogalinho@ua.pt

The expansion of modern industry, particularly related to technology, combined with mining activities, has contributed to the growing presence of europium (Eu) in aquatic systems, with negative environmental impact. Europium is a rare earth element, commonly used in computer and television screens (red colour on display comes from europium-yttrium compounds), fluorescent lamps and optical fibber [1]. Due to its strategic importance for European Union manufacturing industry, high economic value and high supply risk, Eu is classified as a critical raw material [2]. This problem open opportunities for innovation: the recovery and recycling of this element from waste(water) would bring clear economic and environmental benefits.

In this study, the ability of six different living macroalgae to concentrate and recover Eu from contaminated water was studied. Widely available in Portuguese coast, *Ulva intestinalis*, *Fucus spiralis*, *Ulva lactuca*, *Gracilaria sp.*, *Fucus vesiculosus* and *Osmundea pinnatifida* (3 g/L, fresh weight) were exposed to Eu saline solutions of 10, 152 and 500 µg/L.

U. lactuca and *Gracilaria sp.* proved to be the most effective in removing Eu from solutions, reaching values between 65 and 80% in 72 hours (Fig.1). Nevertheless, *U. intestinalis* showed the greatest bioconcentration factors (up to 2262 times higher than the initial concentration in solution). The potential toxic effect of Eu on *U. lactuca* was also studied, analysing four parameters (LPO, SOD, GPx and GSTs) related to oxidative stress [3]. No cellular damage was recorded.

The main results of this study point out that the biotechnological approach proposed for recovering and recycling Eu, based on living macroalgae, has an enormous potential. In addition to the decontamination of waters, it constitutes a simple, cheaper and environmentally friendly alternative of Eu supply to the conventional extraction methods from ores.

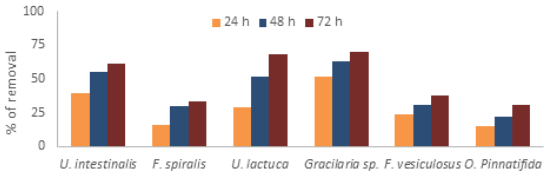


Fig.1. Percentage of Eu removed from a 500 µg/L enriched seawater by different living macroalgae.

Agradecimientos
Bruno Henriques benefited from a Research position funded by national funds (OE), through Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. Thanks are due for the financial support to CESAM (UID/AMB/50017), to FCT/MEC through national funds, and the co-funding by the FEDER, within the PT2020 Partnership Agreement and Compete 2020. Work done in cooperation with the company N9VE.

Referencias

[1] K. Rim, K. Koo, J. Park, Safety and Health at Work, (2013) 12–26.
[2] J. Jacinto, B. Henriques, A. Duarte, C. Vale, E. Pereira, Journal of Hazardous Materials, 344 (2018) 531–38.
[3] B. Henriques, F. Coppola, R. Monteiro, J. Pinto, T. Viana, C. Pretti, A. Soares, R. Freitas, E. Pereira, Science of the Total Environment 664 (2019) 626–34.

Monitorização de Pesticidas como Poluentes Emergentes em Rios do Nordeste de Portugal

G. Laender[1,2], P. Patrício[2], A. Ribeiro[1], P. Brito[1], A. Queiroz[1],*
1 Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
2 Centro Federal de Educação Tecnológica de Minas Gerais, Av. Amazonas, 5253, Nova Suíça, 30421-169 - Belo Horizonte, MG - Brasil
** amqueiroz@ipb.pt*

A monitorização da contaminação dos recursos hídricos é atualmente uma área de investigação cada vez mais relevante. Com o aumento demográfico mundial, e consequente aumento da quantidade de resíduos produzidos, os meios hídricos tornaram-se recetores privilegiados dos mais diversos tipos de poluentes, sejam eles provenientes de atividades industriais ou agrárias, resíduos hospitalares, entre outros. Estes resíduos têm-se tornado cada vez mais complexos e representam um perigo potencial não só para a fauna e a flora aquática, como também para o próprio ser humano. Atualmente, devido à evolução das técnicas de extração e de análise disponíveis, é possível detetar a presença destes poluentes emergentes em concentrações inferiores a mg/L ou mesmo ng/L. Neste contexto, é importante o desenvolvimento de novas metodologias ou a otimização/combinação das metodologias experimentais já existentes para a identificação e quantificação dos diferentes tipos de contaminantes emergentes nos meios hídricos [1].

Dentre os micropoluentes emergentes destacam-se os pesticidas, geralmente utilizados na agricultura [2]. Estes compostos são normalmente classificados em herbicidas, inseticidas, bactericidas e fungicidas, conseguindo migrar pelo solo, quer para alimentos, quer para aquíferos, contaminando toda a cadeia alimentar, ver Tabelas 1 e 2. Este estudo apresenta o desenvolvimento de uma metodologia experimental que combina de duas técnicas de extração e dois métodos instrumentais para a análise de diferentes classes de pesticidas em meios hídricos. A validação do método analítico é realizada através da análise de pesticidas em diferentes amostras recolhidas em 3 rios distintos da região do nordeste de Portugal.

A metodologia experimental baseia-se na utilização da extração em fase sólida (SPE) e/ou na microextração em fase sólida (SPME), seguida da análise por cromatografia líquida com detetor de arranjo de díodos (HPLC-DAD) e/ou por cromatografia gasosa com espetrometria de massas (GC-MS). **Tabela 1.** Exemplos de alguns pesticidas utilizados no nordeste de Portugal. [3]

Pesticidas	**Classe**
Acetocloro, Alacloro	Herbicida
Metolacloro, Terbutilazina	
Glifosato, MCPA	
Dimetoato, Heptacloro	Inseticida
Imidacloprida	
Epoxiconazol, Terbuconazol	Fungicida

Tabela 2. Legislação Brasileira para água potável. [4]

Pesticidas	**Valor máximo (ppb)**
Alacloro	20
Glifosato + AMPA	500
Diuron	90
Metolacloro	10
Tebuconazol	180

AMB13

Desenvolvimento de um sensor electroquímico para a deteção de compostos fenólicos em águas

L. A. Lema*, P. Bettencourt, F. Bento

Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
** id7395@alunos.uminho.pt*

Os compostos fenólicos foram identificados pela Agência de Proteção Ambiental dos Estados Unidos (USEPA) e pela União Europeia (UE) como poluentes de prioritários. Este reconhecimento está associado à sua elevada toxicidade, tanto para humanos como para animais, com efeitos graves a curto e a longo prazo [1]. A acorrência destes compostos no ambiente podem ter origem natural ou antropogénica, associada à sua utilização na produção de corantes têxteis, de aditivos não poliméricos, de plásticos e de resinas epóxi, em pesticidas, entre outras aplicações [1].

O desenvolvimento de um sensor sensível para a deteção de compostos fenólicos em água permitirá que a sua análise possa ser realizada por operadores não especializados, com custos de análise e tempos de resposta reduzidos. Por outro lado, a portabilidade destes dispositivos possibilita a sua utilização em medidas de campo [2].Os sensores eletroquímicos devido à sua elevada sensibilidade e capacidade para detectar reduzidas concentrações de analito são fortes candidatos à utilização nesta área [3].

Neste âmbito têm vindo a ser desenvolvidos sensores para a deteção de compostos fenólicos em águas utilizando materiais como GCE, nanodiamante-GCE, grafeno-GCE, nanocarbono-GCE, Nanoparticulas de níquel e de grafite screen-printed[3,4,5]. Apesar dos sensores eletroquímicos apresentarem limites de deteção baixos, a sua aplicação em análises de campo pode ser limitada pelo envenenamento da superfície do elétrodo e a consequente redução do tempo de vida útil do sensor.

Neste trabalho são apresentados resultados relativos ao desenvolvimento de um sensor eletroquímico para a deteção de compostos fenólicos em águas, baseado em nanoestruturas metálicas (Pt) e de carbono. Os resultados obtidos a partir da modificação da superfície de um elétrodo impresso de carbono (SPCE) mostram que a presença das nanoestruturas de Pt isoladamente na superfície do carbono não melhoram as características do sinal. No entanto, este sinal é intensificado quando se associa óxido de grafeno (GO) a estas nanoestruturas.

Os resultados obtidos com um composto fenólico modelo mostram um aumento significativo da sensibilidade de deteção e uma redução dos limiares analíticos, demonstrando que a estratégia adotada para modificação do SPCE é promissora.

Agradecimentos
L. A. Lema agradece o Governo Angolano, MESCT e ISCED do Uíge o financiamento da Bolsa de Doutoramento. Os autores agradecem ao Centro de Química da Universidade do Minho através do projeto UID/QUI/00686/2016 e UID/QUI/00686/2019(CQUM) financiado pela Fundação da Ciência e Tecnologia (FCT, Portugal)

Referências

[1] W. Anku, M. Mamo, P. Govender, in Phenolic Compounds - Natural Sources, Importance and Applications, M. Soto-Hernandez, M. Palma-Tenango, M. Garcia-Mateos(Eds), IntechOpen, 2017,17.
[2] A.Hayat J. Marty, Sensors, 14 (2014) 10433.
[3] L. Jiang, I. Santiago, J. Foord, Communications Chemistry 1 (2018) 43.
[4] M. Rahimi-Mohseni, J. Raoof, R. Ojani, Electroanalysis 31(2019) 2.
[5] J. R. Camargo, M. Baccarin, P. Raymundo-Pereira, A. Campos, G. Oliveira, O. Fatibello-Filho, O. Oliveira Jr., B. Janegitz, Analytica Chimia Acta 1034 (2018) 137.

Polymeric coatings containing new antifouling synthetic bile acid derivatives to prevent marine biofouling

Ana R. Neves[1,2], Joana R. Almeida[1], Jorge Antunes[1], Vitor Vasconcelos[1,3], Madalena. Pinto[1,2], Emília Sousa[1,2], Elisabete R. Silva[4,5*], Marta Correia-da-Silva[1,2*]

[1]CIIMAR/CIMAR - Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Terminal de Cruzeiros do Porto de Leixões Avenida General Norton de Matos, 4450-208 Matosinhos, Portugal.
[2]Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Rua Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal.
[3]Department of Biology, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4069-007 Porto, Portugal.
[4]BioISI - Biosystems & Integrative Sciences Institute, Faculdade de Ciências, University of Lisbon, Campo Grande, 1749-016 Lisboa, Portugal.
[5]CERENA - Centro de Recursos Naturais e Ambiente, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal
**m_correiadasilva@ff.up.pt, ersilva@fc.ul.pt*

Marine biofouling is a complex biological process involving the accumulation of microorganisms, algae, and animals on a submerged surface. Enormous economic and ecological problems result when biofouling occurs on artificial marine surfaces. Most conventional strategies rely on the continuous release of toxic agents from protective antifouling coatings, which imply significant ecotoxicity effects in the non-targeted biota. New non-toxic strategies to combat this phenomenon are sought.

In this work, we explored the bile acid scaffold as a new chemical platform to obtain new antifouling (AF) agents [1]. Seven bile acid derivatives were obtained by one or two step syntheses with simple methods from inexpensive reagents, and their structures were elucidated through spectroscopic methods. The AF activity was evaluated through the settlement inhibition of the mussel *Mytilus galloprovincialis* larvae [2] and the growth inhibition of five biofilm-forming marine bacteria and four benthic marine diatoms [3]. The most promising compound was incorporated in two polymeric coating systems [4].

One of these synthetic derivatives presented a broad spectrum AF activity inhibiting the settlement of *Mytilus galloprovincialis* larvae with an EC_{50} of 7.47 µM, the growth of the biofilm-forming marine bacteria *Roseobacter litoralis* with an EC_{50} of 9.94 µM, as well as the growth of four benthic marine diatoms with EC_{50} values between 5 and 10 µM. The marine polyurethane-based coating containing the selected compound was more effective after 40h in contact with *Mytilus galloprovincialis* larvae than the ECONEA®-containing coating. Considering the polydimethylsiloxane based coatings containing ECONEA® or the selected compound, no mussel larvae settlement was observed at a long-term exposure. These results showed that this compound can be turned in the future into a commercially valuable product for marine biofouling.

Acknowledgments:
Support for this work was provided by FCT through UID/MULTI/04046/2019 (BioISI) and UID/Multi/04423/2019 (CIIMAR), and the European Regional Development Fund (ERDF) in the framework of PT2020 and under the project PTDC/AAG-TEC/0739/2014 (FCT/MCTES and Technology and Higher Education (PIDDAC) and European Regional Development Fund (ERDF) through the COMPETE (POCI-01-0145-FEDER-016793) and RIDTI - Project 9471). A. R. Neves, J. Almeida and E. R. Silva acknowledge FCT for the Grants SFRH/BD/114856/2016, SFRH/BD/99003/2013 and SFRH/BPD/88135/2012, respectively.

References

[1] F. Carvalhal, M. Correia-da-Silva, E. Sousa, M. Pinto, A. Kijjoa, J. Mol Endocrinol. 61 (2018) 211.
[2] J.R. Almeida, M. Correia-da-Silva, E. Sousa, J. Antunes, M. Pinto, V. Vasconcelos, I. Cunha, Sci. Rep. 7 (2017) 42424
[3] J.R. Almeida, J. Moreira, D. Pereira, S. Pereira, J. Antunes, A. Palmeira, V. Vasconcelos, M. Pinto, M. Correia-da-Silva, H. Cidade, Sci. Total Environ. 643 (2018) 98.
[4] E.R. Silva, O. Ferreira, P.A. Ramalho, N.F. Azevedo, A. Igartua, J.C. Bordado, M. J. Calhorda, Sci. Total Environ., 650 (2019) 2499.

Pharmaceutical Drugs as Environmental Emerging Pollutants

A. Oliveira[1], A. Ribeiro[1,2], P. Brito[1], A. Queiroz,[1,*]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2] Laboratory of Separation and Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal
* amqueiroz@ipb.pt

Pharmaceutical drugs have been considered in recent years as one of the groups belonging to emerging contaminants regarding environmental pollution. Their presence in aqueous matrices is mainly related to emissions in their production, direct disposal in environment and human and/or animal excretion [1]. These pollutants can be found in rivers and other aqueous matrices, in very low concentrations, below the ppm level. As, normally, they occur in trace concentrations, their identification and quantification were complex tasks since they require very expensive and not so available analytical methods. Additionally, the actual European Legislation is still scarce for this called “emergent contaminants”. Nowadays, there is a strong interest in the development of inexpensive and acute determination methods for these compounds, to overcome the huge lack of information about the potential harmful effects in the living beings and in the environment.

In this study, it will be presented the development of a complete analytical methodology and its validation, for the detection and quantification of a set of eight different pharmaceutical drugs. The studied pharmaceutical drugs, azithromycin, sulfamethoxazole, caffeine, paracetamol, acetylsalicylic acid, ketoprofen, diclofenac, and carbamazepine, are representative drugs of several different therapeutic classes: two antibiotics, one central nervous system stimulant, two analgesics, two non-steroidal anti-inflammatories and one anticonvulsant, respectively.

Experimental results will include solid phase extraction (SPE) as an extraction/concentration technique followed by detection and quantification using high performance liquid chromatography with diode array detector (HPLC-DAD) [2]. The complete separation of all the studied compounds requires the use of two different columns and the optimization of two mobile phase compositions. For compounds with low pKa values a Nucleosil 100-5 C18 column is used with a solvent composed of acetonitrile:water:trifuoracetic acid. For compounds with higher pKa values a SiliaChrom XT C18 column is used with a methanol:water:diethylamine solvent composition. SPE recoveries, calibration curves, limits of detection and quantification will be presented. Several samples were collected from three different rivers from the Bragança region and the developed methodology was implemented to measure drugs concentration.

References

[1] I. Baranowska, B. Kowalski. Polish Journal of Environmental Studies, 20 (2011) 21.
[2] A. Nemoto, M. Gonçalves, A. Ribeiro, P. Brito, A. Queiroz. Proc. of XXIV Encontro Luso-Galego de Química, 2018, QAMB56.

White winery wastewater treatment by coagulation/flocculation optimized by a Simplex Lattice Design and O_3/Fe^{2+}/UV process

Nuno Jorge[1*]; André Cunha[2]; Ana R. Teixeira[2]; Marco S. Lucas[2]; José A. Peres[2]

[1] *Campus da Auga, Campus Universitário de Ourense, Universidad de Vigo, As Lagoas, 32004, Ourense, España*

[2] *Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5001-801, Vila Real, Portugal*

**e-mail: njorge@uvigo.es*

White winery wastewater (WWW) is very problematic due to organic carbon high content, polyphenols and other recalcitrant compounds [1]. In this work it was developed a statistical model for coagulation-flocculation-decantation process (CFD) by performance of a Simplex Lattice Design (SLD) with application of oenological coagulants: potassium caseinate (X_1), bentonite (X_2) and PVPP (X_3). Furthermore, it was carried out a study which combined ozonation and irradiation with UV-C mercury lamp emitting at 254 nm and addition of iron to increase removal efficiency.

By the results obtained on the SLD design (Fig.1a) there was 98.3, 97.6, 87.8, 44.6 and 48.0% removal of turbidity, total suspended solids (TSS), total polyphenols, total organic carbon (TOC) and chemical oxygen demand (COD), respectively. It was also observed a decrease of red ($\Delta a^* = -1.2$) and yellow color ($\Delta b^* = 0.2$). Ozonation best operational conditions (pH 4, 1.0 mM Fe^{2+}, UV-C 254 nm) achieved 49.4 and 55.7% TOC and COD removal, with an operational cost of 0.17 €/m^3. The combined process CFD→O_3 was selected as the best treatment process for water reuse with 60.7 and 65.6% of TOC and COD removal. In addition, it was discerned the whole removal of total anthocyanins and total tannins which was reflected on the removal of red ($\Delta a^* = -1.90$) and yellow color ($\Delta b^* = -3.29$) and increase of luminosity (100%), which was reflected on the complete discoloration of the wastewater, with an operational cost of 0.20 €/m^3, lower than 1.31 €/m^3 observed by Lucas et al. 2010 [2] and high germination index (GI) of different seeds (GI≥80%), observed on Fig.1b. In conclusion, this work proved the efficiency of combined CFD/ozonation process on white winery wastewater reuse for crops irrigation.

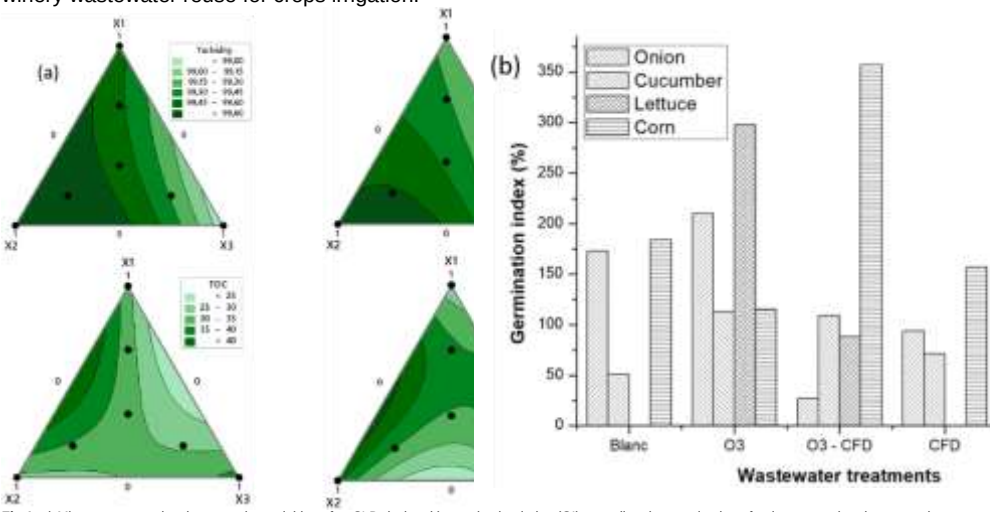


Fig.1. a) Mixture contour plots between the variables after SLD design; b) germination index (GI) regarding the germination of onion, cucumber, lettuce and corn after different treatments.

Acknowledgements

The authors thank the financial support of the Project I&D Interact – Integrative Research in Environment, Agro-Chain and Technology, operation number NORTE-01-0145-FEDER-000017. Marco S. Lucas acknowledges also the Investigador FCT project (IF/00802/2015).

References

[1] R. Braz, A. Pirra, M.S. Lucas, J.A. Peres, Desalination, 263 (2010) 226–232.

[2] M.S. Lucas, J.A. Peres, G. Li Puma, Separation and Purification Technology, 72 (2010) 235–241.

Evaluation of the potential of marine macroalgae for gadolinium removal from aquatic systems

José Pinheiro Torres[1,*], Bruno Henriques[2], Adriana Ferreira[2], Marcelo Costa[2], João Pinto[2], José Soares[2], Cláudia Lopes[3], Nicole Ferreira[3], Eduarda Pereira[2]

[1]N9VE – Nature, Ocean, Value, Porto, Portugal

[2]Departament of Chemistry, LAQV-REQUIMTE & CESAM, University of Aveiro, 3810-193 Aveiro, Portugal

[3]Departament of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

**jose@clinicapinheirotorres.com*

The use of rare earth elements (REE) in its several applications has been increasing [1] and, as a result, contamination of aquatic systems has also increased. It is therefore a growing concern to find new processes to remove these elements from wastewaters. Gadolinium (Gd) is a REE, widely used in the medical field, as contrast agent in magnetic resonance imaging (e.g. Gadoteric acid and Gadodiamide). After use, Gd is released in the urine of patients, in concentrations up to 350 mg/L, ending up in estuaries and rivers [2] since wastewater treatment plants are no capable of removing it.
Knowing the high capacity of living macroalgae to remove classical contaminants (e.g. Hg, Cd, Pb) [3] from waters, the present study aims to evaluate their potential in the removal and recovery of Gd from aquatic systems.
Experiments with a duration of 72 hours were performed with 6 different macroalgae (3 g/L, fresh weight), collected at Aveiro estuary, Portugal. Two green (*Ulva intestinalis* and *Ulva lactuca*), two brown (*Fucus spiralis* and *Fucus vesiculosus*) and two red macroalgae (*Gracilaria sp.* and *Osmundea pinnatifida*) were studied. Various contamination scenarios were evaluated, including single-contaminant solutions (10, 157 and 500 µg of Gd per L of saline water) and multi-contaminant solutions (mixture of Gd with several classical contaminants).
The data obtained indicate that the macroalgae with the highest surface area (*U. intestinalis*, *U. lactuca* and *Gracilaria sp.*) led to the most relevant decreases of Gd in solution - up to 79% of reduction. Overall, neither the initial concentration nor the presence of other contaminants was a relevant limiting factor in the removal performance.
Since Gd is currently a critical raw material due to its high demand, difficulty of extraction and separation from ores, and high price, the recovery and recycling of this element for further application is pertinent. The results showed that the marine macroalgae, particularly those of the genus Ulva, have a high capacity to concentrate Gd in their tissues (up to 2000 times higher than the initial concentration in solution). Thereafter all Gd is recovered into a small volume of solution by acidic algal digestion.

Fig.1. Macroalgae studied, from left to righ respectively: U. *intestinalis, U. lactuca, F. spiralis, F. vesiculosus, Gracilaria sp. and O. pinnatifida*

Agradecimientos

Bruno Henriques benefited from a Research position funded by national funds (OE), through Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. Thanks are due for the financial support to CESAM (UID/AMB/50017), to FCT/MEC through national funds, and the co-funding by the FEDER, within the PT2020 Partnership Agreement and Compete 2020. Work done in cooperation with the company N9VE.

Referencias

[1] V. Balaram, Geosci. Front. 10 (2019) 1285–1303

[2] B. Henriques, F. Coppola, R. Monteiro, J. Pinto, T. Viana, C. Pretti, A. Soares, R. Freitas, E. Pereira, Science of the Total Environment 664 (2019) 626–34.

[3] B. Henriques, A. Teixeira, P. Figueira, A.T. Reis, J. Almeida, C. Vale, E. Pereira, Science of the Total Environment, 652 (2019) 880-888.

AMB18

Asparagopsis armata: a nightmare for Azores coast biodiversity

Diana C.G.A. Pinto[1,*], Marie L. Lesenfants[2], Ana M.L. Seca[1,3], Artur M.S. Silva[1]
[1]QOPNA & LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
[2]Faculty of Sciences and Technology, University of Azores, Rua Mãe de Deus, 9501-321 Ponta Delgada, Portugal.
[3]cE3c- Centre for Ecology, Evolution and Environmental Changes/ Azorean Biodiversity Group, Rua Mãe de Deus, 9501-321, Ponta Delgada, Portugal
**diana@ua.pt*

Asparagopsis armata Harvey is a red alga belonging to the Rhodophyta division. In Azores, is considered a biological invader due to its presence in large amount of biomass, particularly in São Miguel coast. Its overall impact still needs to be evaluated and economically valuable applications are welcomed.

Some previous studies showed that *A. armata* extracts exhibit some antibacterial activity against *Bacillus subtilis* [1] and anti-aging, antioxidant and anticholinesterasic activities, were recently presented [2,3].

The knowledge of this species chemical composition is utmost importance not only to find some valuable utilization but also to discovery its mechanisms of defense that can explain its invasive behavior.

In our effort to contribute to this problem solution we establish the chemical profiles of both the non-polar and polar extracts. The main compounds in the lipophilic extract were palmitic acid and
1-monopalmitin and brominated compounds (Fig. 1). The polar extract is also dominated by the presence of halogenated phenols. These recent results will be presented and discussed.

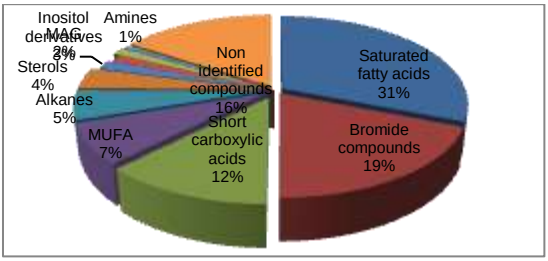


Fig.1. Organic compounds families in *A. armata* dichloromethane extract.

Acknowledgments
This study was financed by ASPAZOR project (DRCT: ACORES-01-0145-FEDER-00060- ASPAZOR); Portuguese National Funds through FCT – Fundação para a Ciência e a Tecnologia, co-financed by the FEDER within the PT2020 Partnership Agreement; by funding the Organic Chemistry Research Unit (QOPNA) (UID/QUI/00062/2013) and the cE3c centre (UID/BIA/00329/2013, 2015 - 2018) and UID/BIA/00329/2019).

Referencias

[1] S. Pinteus, C. Alves, H. Monteiro, E. Araújo, A. Horta, R. Pedrosa, World J. Microbiol. Biotechnol. 2015, 31, 445.
[2] M.L. Lesenfants, G.P. Rosa, C. Barreto, A.M.L. Seca, 1st Seaweed for Health Conference, Galway, 2018, pp 13.
[3] A.R. Fonseca, J. Ponte, C. Barreto, D.C.G.A Pinto, A.M.L. Seca, 1st Seaweed for Health Conference, Galway, 2018, pp 50.

A new biotecnological-based iron-fertilizer formulation for environmental sustainable correction of chlorosis of soybean plants grown in calcareous soils

Carlos M.H. Ferreira.[1,2,3], Sandra Lopez-Rayo[2], Juan Lucena[2], Eduardo V. Soares[3,4], Helena M.V.M. Soares[1,*]

[1]REQUIMTE/LAQV, Departmento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Portugal

[2]Departamento de Química Agrícola y Bromatología, Facultad de Ciencias, Universidad Autónoma de Madrid, Spain

[3]CEB-Centro de Engenharia Biológica, Universidade do Minho, Braga, Portugal

[4] Laboratório de Biengenharia-CIETI, Departmento de Engenharia Química, ISEP, Porto, Portugal

*hsoares@fe.up.pt

Iron (Fe) is an essential element for the proper development of life. Plants require Fe for chlorophyll synthesis. However, due to the lack of Fe, plants grown in alkaline calcareous soils are very susceptible to a symptomatic array named iron-deficiency induced chlorosis (IDIC). The inappropriate chlorophyll production results in the reduction of crop yields with major implications in many agricultural regions worldwide. Organic chelating agents, namely aminopolycarboxylic acids (APCAs), are adequate for IDIC amending. However, the low biodegradability of such compounds raises several environmental concerns. Therefore, the replacement of APCAs by new more environment-friendly alternatives is needed.

The main objective of this work was to develop environmentally-friendly alternatives to current APCAs used in agriculture to amend IDIC. As an alternative, in this work, a new green freeze-dried iron fertilizer containing siderophores [high Fe(III) affinity chelators produced by several microorganisms in Fe-deficient conditions] able to bind Fe at pH 9 was produced biotechnologically from a culture of *Azotobacter vinelandii* in Fe-deficient conditions and its potential for correcting Fe deficiency of soybean plants grown in calcareous soil conditions was studied [1, 2].

For this purpose, the ability of the freeze-dried product for maintaining Fe in solution, without being displaced by other cations or being retained by soil surfaces was evaluated in alkaline soils or some of its relevant constituents; lower amounts of Fe were lost to soil in the three day experiments. Then, the efficiency of the freeze-dried formulation in mending IDIC in soybean plants grown in calcareous soil was studied by measuring plant development (dry mass), chlorophyll production (measured by the SPAD index), and plant tissue Fe content. For comparison, *o,o*- ethylenediaminedi(*o*-hydroxyphenylacetic acid (*o,o*-EDDHA) was used as positive control and no Fe treatment was used as negative control. Plants treated with *A. vinelandii* iron fertilizer developed a dry mass comparable to that of *o,o*-EDDHA and a significant increase of the SPAD levels when compared to the negative control plants. On average, iron content was also greater on green iron-fertilizer treated plants than on negative control treated ones but lower than on positive control.

In conclusion, the overall results pointed out that the freeze-dried product prepared from *A. vinelandii* has potential for application in IDIC amendment in calcareous soils.

Acknowledgments

This work was financially supported by: Project PTDC-AGR-TEC-0458-2014 - POCI-01-0145-FEDER-016681 - funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES and project RTI2018-096268-B-I00 by the State Research Agency, Ministry of Science, Innovation and Universities of Spain. Carlos Ferreira would like to thank the support from his grant with reference SFRH/BD/95490/2013 from FCT.

References

[1] HMVM Soares, CMH Ferreira, EV Soares, JJ Lucena, S Lopez-Rayo, “Freeze-dried fertilizing compositions containing siderophores, their preparation processes and their uses for treating plants”. Provisional patent submitted (December 2018).

[2] CMH Ferreira, S. López-Rayo, JJ Lucena, EV Soares, HMVM Soares. Evaluation of the efficacy of two new biotechnological-based freeze-dried fertilizers for sustainable Fe deficiency correction of soybean plants grown in calcareous soils. Frontiers in Plant Science (accepted for publication).

BIOQUÍMICA Y BIOTECNOLOGÍA

Intermediate molecular weight poly(ethylene glycol) inhibits protein aggregation

Andreia Barbosa[1], Sara S. Ribeiro[2], João C. Marcos[1,*]
[1]Centre of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[2]Institute of Physical and Theoretical Chemistry, Technical University of Braunschweig, Rebenring 56, D-38106 Braunschweig, Germany
* *jcmarcos@quimica.uminho.pt*

In recent years, advances in production and purification methodologies lead to an exponential boom in protein drugs commercialization. However, their manufacture is riddled with obstacles, such as physical and chemical protein instabilities. Amongst these, protein unfolding, which leads to aggregation and consequently its inactivation, is undoubtedly the most common and troublesome phenomenon [1], [2]. This also occurs in living cells where it is usually avoided by complex cellular quality control mechanisms, which have evolved to ensure proper protein homeostasis. However, proteins drugs are isolated and constantly exposed to the alteration of several environmental factors such as pH, temperature and ionic strength which makes them prone to instability, leading to unfolding, and exposition of their hydrophobic patches that could interact amongst themselves resulting in aggregation [2], [3].

In this context, understanding protein unfolding, and aggregation is of utmost importance to unveiling these processes and solving many problems that may occur in the production of protein drugs. Several synthetic additives are known for their stabilizing effect in proteins, leading usually to the reduction of protein aggregation. Some of them are also used in protein drug formulations. For instance, poly(ethylene glycol) (PEG) is one of the most commonly used, despite there being some contradictory results about its action on protein stabilization [4]. In this work, myoglobin was tested as a model protein to further explore the effects of PEG on protein thermal unfolding and aggregation.

Thermal unfolding of myoglobin was followed in the presence of PEG with different molecular weights (400, 600, 3350, 8000 and 10,000). Mid-temperature of denaturation (Tm), mid-temperature of aggregation (Ta) and the reversibility of the process were determined. It was observed that both Tm and Ta decreased in the presence of all PEGs but with a steeper decline for lower molecular weights (400 and 600). The reversibility shows a different trend, decreasing for lower and higher molecular weights (400, 600 and 10000), whereas for intermediate molecular weights (PEG 3350 and 8000) there's an increase that reaches 17% for higher PEG concentration (10% w/w). This corresponds to 93% of global reversibility. The data suggests that, although PEG 3350 and 8000 decrease the thermal stability of the protein, they shield the interaction of neighbour proteins, preventing their irreversible aggregation. The mechanisms involved in this protective effect are currently under study, but it can already be concluded that when using PEG as a stabilizing additive in protein drug formulations, a proper molecular weight has to be used.

Acknowledgements
The authors acknowledge the Foundation for Science and Technology, FCT- Portugal, for financial support through Centre of Chemistry of University of Minho (CQ-UM) (project UID/QUI/00686/2016).

References
[1] V. Kumar, N. Sami, T. Kashav, A. Islam, F. Ahmad, and Md. I. Hassan, 'Protein aggregation and neurodegenerative diseases: From theory to therapy', *Eur. J. Med. Chem.*, vol. 124, pp. 1105–1120, Nov. 2016.
[2] H.-C. Mahler and A. Allmendinger, 'Stability, Formulation, and Delivery of Biopharmaceuticals', in *Protein Therapeutics*, Wiley-Blackwell, 2017, pp. 469–491.
[3] W. Wang, 'Protein aggregation and its inhibition in biopharmaceutics', *Int. J. Pharm.*, vol. 289, no. 1–2, pp. 1–30, Jan. 2005.
[4] S. Piszkiewicz and G. J. Pielak, 'Protecting Enzymes from Stress-Induced Inactivation', *Biochemistry*, Aug. 2019.

Avaliação do efeito de extratos da polpa de *Cucurbita ficifolia* Bouché no stresse oxidativo celular

Tiago E. Coutinho[1,2,*],Calos Martins-Gomes[1,4], Fernando M. Nunes[2,3], Amélia M. Silva[1,4]

[1]Departamento de Biologia e Ambiente, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal

[2]CQ-VR, Centro de Química de Vila Real, UTAD, Vila Real, Portugal

[3]Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Vila Real, Portugal

3

[4]CITAB, Centro Investigação em Tecnologias Agro-Ambientais e Biológicas, UTAD, Vila Real, Portugal

**tecoutinho@utad.pt*

A *Cucurbita ficifolia* Bouché (abóbora chila) é nativa do México, contudo hoje encontra-se dispersa por vários pontos do globo, entre eles Portugal, onde é cultivada e consumida. Nos países de onde é originária, tem sido utilizada para fins medicinais, no tratamento da diabetes tipo 2, de feridas e no tratamento de febre, sendo também utilizada na alimentação humana principalmente na preparação de doces cristalizados e de sobremesas. A abóbora chila é rica em compostos fenólicos, terpenos e açúcares, podendo estes ser os responsáveis pelas atividades anti-inflamatórias, antidiabéticas e antioxidantes atribuídas a este elemento.

O objetivo deste trabalho foi a avaliação do efeito das frações aquosa e metanólica do extrato hidro-etanólico da polpa da abóbora chila na proteção contra o stresse oxidativo celular, na linha celular Caco-2 (adenocarcionoma colorretal humano), usando a citometria de fluxo e a microscopia de fluorescência. Os métodos encontram-se descritos em [1].

As células Caco-2 foram previamente expostas aos diferentes extratos, durante 24 h, à concentração de 500 e 750 µg/mL. Por citometria de fluxo avaliou-se o conteúdo em espécies reativas de oxigénio (ROS) intracelulares, com a sonda DCFDA, o nível de peroxidação lipídica com a sonda DHPE-FITC, o conteúdo intracelular de GSH através da sonda *Mercury Orange* e o potencial mitocondrial através da sonda Rodamina 123. Por microscopia de fluorescência, avaliou-se a integridade do DNA das células expostas aos extratos, com recurso à sonda Hoechst [1].

Observou-se que a pré-exposição das células à fração aquosa aumentou o conteúdo em GSH, a energização da mitocôndria, mantendo os níveis de ROS e de peroxidação lipídica em relação ao controlo. Por outro lado, a exposição à fração metanólica da polpa aumentou o conteúdo em ROS, o conteúdo em GSH, a peroxidação lipídica e despolarização mitocondrial em relação ao controlo. Verificou-se ainda que a exposição às diferentes frações produziu uma ligeira diminuição do número de células, depende da concentração de extrato. Contudo não se verificou danos no DNA celular, em relação ao controlo.

Conclui-se, portanto, que a fração aquosa demonstra ter um poder protetor celular. Por outro lado, a fração metanólica ao induzir um elevado aumento de ROS e peroxidação lipídica, acompanhados do aumento de GSH, não apresenta um efeito protetor direto, contudo pode exercer efeito estimulador. Estas diferenças poderão ser justificadas pela natureza dos compostos presentes em cada uma das frações (aquosa e metanólica) do extrato hidro-etanólico da polpa da *C. ficifolia*.

Referências:

[1] C. Martins-Gomes, E.B. Souto, F. Cosme, F.M. Nunes, A.M. Silva (2019). Journal of Functional Foods 54, 128–135.

BB02

Voláteis, α e β- ácidos em lúpulo: um estudo da planta à cerveja

Hugo Goes[1,3], Cátia Magalhães[3], Jorge Sá Morais[1,3], Luís Pedro[2], Mª João Sousa[1,3]
[1]Centro de Investigação de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, Apartado 117, 5301-855 Bragança, Portugal
[2]Centro de Estudos do Ambiente e do Mar (CESAM), Faculdade de Ciências da Universidade de Lisboa, Centro de Biotecnologia Vegetal (CBV), C2, Piso 1, Campo Grande, 1749-016 Lisboa, Portugal
[3]Istituto Politécnico de Bragança- Escola Superior Agraria de Bragança, Portugal
e-mail: hugoggoesmail.com

Da família Cannabaceae o *Humulus lupulus* L., produz compostos com ação bactericida, particularmente contra bactérias Gram-negativas e de ter aumentado a demanda por novos aromas, fez com que o lúpulo fosse cada vez mais estudado. [1]

Os extratos voláteis e α e β ácidos de lúpulo espontâneo na região de Bragança foram comparados com variedades comerciais (Nugget, Cascade, Chinooke e Centennial). Os voláteis extraídos do lúpulo (cones femininos, partes vegetativas e pellets) usando o sistema LikensNickerson, e analisados por GC e GC-MS. Os ácidos α e β, foram extraídos e analisados por HPLC. As amostras de cervejas que foram testadas, pela metodologia LN, das quais obtivemos dados não conclusivos com 90% de níveis de álcoois, desta forma a metodologia será alterada de forma a obtermos dados mais precisos.

As amostras tem semelhanças na componente monoterpenica, com β-mirceno como principal composto (na variedade Cascade 61,4% e valores parecidos nas pellets, na parte vegetativa é que foram reduzidos, em Nugget e Centennial os valores formam idênticos e na variedade Chinook obteve-se valores mais baixos) e trans-β-farneseno (9% na espontânea, em Cascade foi detetado 3,7% nos cones e 4,7% nas pellets, não detetado na cultivar Nugget).

Nas análises por HPLC, a amostra de lúpulo espontâneo apresentaram valores totais de ácidos α e β 7,30% e de 8,60%, já na variedade Nugget apresenta valores médios de 13,27 % e 3,65% , na variedade Cascade (flor) de 4,53% e 5,63% semelhante nas pellets já em relação a variedade Chinook flor 14,4% e 4,58% nas pellets 9,25% e 3,01% e nas amostras Centennial (pellets) de 7,07% e 3,14%.

Palavras chave: lúpulo, ácidos α e β, compostos voláteis, espontâneos, cultivares

[1] Heale J. B., Legg T., Brar J., Fabb A., Bainbridge B., (1989) Application of plant tissue culture and molecular biology techniques to “progressive” wiltof hops caused by Verticillium albo-atrum. Eur. Brew. Conv. Monogr., XV, Symposium on Plant Biotechnology, Helsinki, 70:83.

BB03

Drought stress effects on cowpea polyphenolic composition and antioxidant activity

Márcia Carvalho[1,*], Irene Gouvinhas[1], Isaura Castro[1,2], Eduardo Rosa[1], Valdemar Carnide[1,2], Ana Barros[1]

[1] Centre for the Research and Technology of Agro-Environmental and Biological Sciences (CITAB), University of Trás-os-Montes and Alto Douro (UTAD), 5000-801 Vila Real, Portugal

[2] Department of Genetics and Biotechnology, University of Trás-os-Montes and Alto Douro (UTAD), 5000-801 Vila Real, Portugal

**marciac@utad.pt*

Climate change is considered as one of the major threats to agriculture sustainability. Drought is a severe environmental stress with major impacts on plant development and productivity. The use and improvement of crops with the ability to mitigate the effects of drought will be a key step for future crop sustainability. Cowpea (*Vigna unguiculata* L. Walp) is a warm-season grain legume, considered an interesting crop, due to its high adaptability to heat and drought, as well as to its association with nitrogen fixing rhizobia. This legume is an incredible source of nutrients as proteins, minerals, vitamins, fibers and phenolic compounds. Besides all the advantages, this crop can be consumed during all stages of plant development (as young leaves, immature pods and immature and dry seeds). The main objective of this study was to understand the effects of drought stress on polyphenolic composition and antioxidant activity in plant tissue at different stages of cowpea development.

In a greenhouse, plants of two cowpea genotypes (Bambey21 and IT97K-499-35) grown until the anthesis under well-irrigate, were submitted to two watering regimens (0% and 100% of field capacity, FC) during one week. Immature pods and seeds and dry seeds were collected and the polyphenolic extracts were prepared. The phenolic composition (total phenols, flavonoids and *ortho*-diphenols contents) and antioxidant activity (ABTS and DPPH) were evaluated by spectrophotometry.

In general, differences between genotypes and plant tissue at different plant development stage were observed. A variation of all phenolic contents and antioxidant activity has been detected in both cowpea genotypes and plant tissues at different development stages. The Immature pods showed the highest values in all the parameters evaluated, while the dry seed presented the lowest values. The genotype IT97K-499-35 showed the highest values for all the parameters evaluated assessed in the three development stages. The samples submitted to drought stress showed a slight decrease in all the parameters evaluated compared to control (100% FC) samples. The multivariate analysis resulted in a grouping of samples based on plant tissue type/plant development stage.

Acknowledgements
This study was supported by EUROLEGUME project. This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no 613781 and from National Funds by FCT – Portuguese Foundation for Science and Technology, under the project UID/AGR/04033/2019.

Oligomerización enzimática de rutina en sistemas acuosos bifásicos biocompatibles

Abel Muñiz-Mouro[1,*], Ana M. Ferreira[2], João A. P. Coutinho[2], Mara G. Freire[2], Gemma Eibes[1], Beatriz Gullón[1] e Ana P. M. Tavares[2]
[1]Departamento de Enxeñaría Química, Instituto de Investigacións Tecnolóxicas, Universidade de Santiago de Compostela, 15782, Santiago de Compostela, España
[2]CICECO – Aveiro Institute of Materials, Departamento de Química, Universidade de Aveiro, 3810-193, Aveiro, Portugal
**abel.muniz@usc.es*

A rutina (quercetina-3-O-glicósido) posúe propiedades beneficiosas para a prevención de diferentes enfermidades. Sen embargo, as súas propiedades físico-químicas non conducen a unha boa biodispoñibilidade da mesma, principalmente debido á súa baixa solubilidade acuosa [1]. A súa polimerización enzimática preséntase como un método eficiente para a obtención de produtos con propiedades melloradas. Non obstante, é habitual o uso disolventes tóxicos que, se ben favorecen a solubilidade do substrato, restrinxen as posibles aplicacións do produto final [2,3].

Os sistemas acuosos bifásicos (ABS) preséntanse como posibles medios de reacción alternativos interesantes en procesos de biocatálise, xa que posibilitarían a reacción enzimática nun medio que, ante o cese de axitación e/ou mediante a aplicación dun estímulo externo (cambios na temperatura, no pH, etc.) xeraría dúas fases inmiscibles que levarían á separación dos produtos e do enzima, permitindo así re-utilizar o biocatalizador durante varios ciclos de produción [4,5].

Neste traballo estudouse a síntese de oligorutina catalizada por lacasa de *Trametes versicolor*, empregando como medio de reacción sistemas acuosos bifásicos biocompatibles, compostos de diferentes mesturas de polietilenglicol (PEG) de distintos pesos moleculares (600 e 1000 Da) con dihidroxenofosfato de colina ([Ch][H_2PO_4]). A reacción levouse a cabo a diferentes valores de pH (4,4, 5,5, 6,5 e 7,0) para observar a influencia deste parámetro no proceso. Tras observar que un valor de pH de 6.5 levaba aos mellores resultados, os ABS escollidos caracterizáronse mediante a obtención das súas curvas de solubilidade e rectas de reparto a ese pH. Posteriormente estudouse a re-utilización da fase enriquecida en biocatalizador en novas sínteses consecutivas, analizando os rendementos acadados, así coma a perda de actividade enzimática existente. A pesar de que a caída de actividade enzimática acadou valores próximos a un 40-45% tras tres sínteses seriadas, os rendementos de produción de oligorutina só se reduciron a un ~85% no terceiro ciclo consecutivo (Táboa 1). Asemade, o bo reparto de produtos nas fases ricas en polímero (~70%), xunto co aínda mellor reparto do enzima nas fases opostas, as ricas en líquido iónico (~96%), demostra que estes ABS constitúen medios de reacción biocompatibles que posibilitan non só a integración da síntese enzimática e separación de biomoléculas, senón a re-utilización do catalizador en sucesivos procesos produtivos sen comprometer en gran medida o rendemento acadado nos mesmos.

Táboa 1. Conversión (%) de rutina en oligómeros acadada nos diferentes ciclos de produción.

ABS	Síntese 1	Síntese 2	Síntese 3
PEG600 – [Ch][H_2PO_4]	95.20 ± 3.10	90.50 ± 1.70	89.20 ± 1.60
PEG1000 – [Ch][H_2PO_4]	95.50 ± 5.30	89.80 ± 4.20	83.60 ± 5.90

Agradecementos
Este traballo foi financiado polo Goberno Español (RTI2018-094482-J-I00) e Portugués (FCT/MCTES). O traballo enmárcase no proxecto CICECO-Aveiro Institute of Materials, (UID/CTM/50011/2019). Os autores AMM e GE pertencen ao grupo galego de investigación competitiva GRC-ED431C 2017/29 e ao grupo estratéxico CRETUS (AGRUP2015/02), cofinanciados por FEDER. A.P.M. Tavares agradece ao Programa Investigador FCT (IF/01634/2015). AMM agradece á Xunta de Galicia pola súa axuda á etapa predoutoral.

Referencias

[1] B. Gullón, T. A. Lú-Chau, M. T. Moreira et al., Trends Food Sci. Technol., 2017, 67, 220–235.
A. Muñiz-Mouro, B. Gullón, T. Lú-Chau, et al., Catalysts, 2018, 8, 321.
[2] M. Kurisawa, J. E. Chung, H. Uyama, et al., Biomacromolecules, 2003, 4, 1394–1399.
[3] Ferreira, A. M.; Passos, H.; Okafuji, A.; Tavares, A. P. M.; Ohno, H.; Freire, M. G.; Coutinho, J. A. P., Green Chem. 2018, 20 (6), 1218–1223.
[4] Quental, M. V.; Caban, M.; Pereira, M. M.; Stepnowski, P.; Coutinho, J. A. P.; Freire, M. G., Biotechnol. J. 2015, 10 (9), 1457–1466.

L-asparaginase recovery through supported ionic liquid materials based on silica

João C. F. Nunes*, Mafalda R. Almeida, Margarida Rosmaninho, Margarida Castro Ribeiro, Márcia C. Neves, Mara G. Freire, Ana P. M. Tavares

CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
**jcfn@ua.pt*

Acute lymphoblastic leukemia (ALL) accounts with approximately 6500 new cases in the United States each year [1]. The first-line biopharmaceutical being used to treat ALL, Oncaspar, is based on L-asparaginase (LA), with annual sales of approximately USD $100 million [2]. The main problem related to the therapeutic use of LA is the difficulty in its purification, accounting for up to 80% of total production costs [3]. Therefore, it is crucial to find new strategies to purify LA in order to decrease its current cost and allow its routinely use by a widespread population.

Supported ionic liquid materials based on silica (SILs) are reported in the literature for the separation of natural compounds from vegetable biomass [4]. Although SILs represent a class of materials with high potential in protein purification, this specific application has been scarcely considered [5]. In this work, the search for SILs able to establish (non-covalent) specific interactions with LA, which subsequently allow its purification from the fermentation broth in which it is produced, was studied.

In a first set of experiments, commercial LA was used in order to understand the adsorption behaviour of the enzyme onto SILs. Experimental conditions, such as pH, contact time and SILs/LA ratio were evaluated and optimized in what concerns the LA recovery yield. LA activity was assessed by the Nessler reaction, which quantifies the amount of ammonium released after the enzymatic reaction [6]. The results show that the ideal conditions for LA are pH 8 and a contact time with SILs of 30 min. With the envisioned strategy, process costs, energy consumed, and waste generated, can be considerably reduced, which can lead to the LA cost decrease and wider application. Further investigations on the purification of LA from the fermentation broth are ongoing.

Acknowledgements
This work was developed within the scope of the project CICECO (UID/CTM/50011/2019), financed by national funds through the FCT/MCTES, and project POCI-01-0145-FEDER-031268 - funded by FEDER, COMPETE2020, POCI and OE. A.P.M. Tavares and M.C. Neves acknowledge FCT for the research contract IF/01634/2015 and CEECIND/00383/2017, respectively.

References

[1] T. Terwilliger and M. Abdul-Hay, Blood Cancer J., 7 (2017) 577.
[2] Bioscience B. Baxter, BioScience to Expand Global Oncology Footprint with Acquisition of Oncaspar ®; Portfolio for Leukemia., (2015).
[3] L. L. Tundisi et al., Sep. Purif. Rev., 46 (2017) 35–43.
[4] M. M. Pereira, J. A. P. Coutinho, and M. G. Freire, RSC Green Chemistry., 36 (2016) 227–257.
[5] M. J. Jacinto et al., J. Chromatogr. A., 1532 (2018) 246–250.
[6] Magri, Agnes et al., Analytical and Bioanalytical Chemistry., (2018) 6985-6990.

CATÁLISIS Y FOTOCATÁLISIS

Bidirectional Synergy between POMs and ZIFs in POM@ZIF Nanocomposites for an Improved OER Electrocatalysis

Víctor K. Abdelkader-Fernández*, Diana M. Fernandes, Salete S. Balula, Luís Cunha-Silva, Cristina Freire

REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdadade de Ciéncias, Universidade de Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal

**victor.fernandez@fc.up.pt*

The continuous increase of global demand for energy resources makes it urgent to develop affordable nanostructured materials to act as efficient electrocatalysts (ECs) in the energy-related reactions. Specifically, the efficient electrocatalysis of the oxygen evolution reaction (OER), the half-reaction for the water splitting process, will be crucial for the real implementation of fuel cells, regenerative batteries, and electrolyzer systems. Some oxides containing platinum group metals (PGMs), e.g., ruthenium and iridium oxides (RuO_2 and IrO_2), have been reported as the materials with the best electrocatalytic performances for the OER process. However, the extremely elevated costs of PGMs, along with the scarceness and lack of reliable suppliers, strongly encouraged the research on development of alternative and affordable OER electrocatalysts[1].

Regarding this challenge, the desirable features shown by Zeolitic Imidazole Frameworks – ZIFs – (RT synthesis, high and ordered porosity, N-containing ligands and different metal compositions) and PolyOxoMetalates – POMs – (anions consisting of three or more transition metal atoms linked together by oxygen atoms, exhibiting attractive electrocatalytic properties) makes that the efficient integration of POMs anions into the ZIF cavities in order to produce electrocatalytic nanocomposites became a hot topic during the last years[2]. For this reason we have successfully prepared several novel guest@host POM@ZIF nanocomposites via RT 'in situ' approach, synthesizing ZIF-8(Zn) and ZIF-67(Co) in the presence of two different Co-containing POMs - $SiW_{11}Co(H_2O)O_{39}$ and $SiW_9Co_3(H_2O)O_{39}$ – at different concentrations. This has allowed us to assess the effect of the Co atoms interactions on the electrocatalytic activity exhibited by these new nanomaterials, as well as, the influence of the POM loading on their structural and electrocatalytic features.

Interestingly, in the context of this study we have detected a new synergistic effect with bidirectional nature: a charge transfer from the ZIF-67 host to the encapsulated POM clusters (ZIF-67 → POM) and the POM-induced generation of unsaturated Co nodes (active sites) into the ZIF-67 skeletons (POM → ZIF-67).This positive interaction results in a remarkable improvement of the OER performances of the nanocomposites in relation of the 'pure' ZIFs, especially for the cases of the highly-loaded POM@ZIF-67 samples:

Tabla 1. OER parameters for the prepared POM@ZIF nanocomposites

Sample	Overpotential (V)	Current density[a] (mA/cm^2)	Tafel slope (mV/dec)
ZIF-8	6.88	0.2	81.5
ZIF-67	0.58	7.2	144.3
$SiW_{11}Co$@ZIF-8	4.13	0.3	73.7
$SiW_{11}Co$@ZIF-67	0.46	15.0	141.6
$SiW_{11}Co$(↑)@ZIF-67	0.43	23.0	95.3
SiW_9Co_3@ZIF-8	2.73	0.5	69.4
SiW_9Co_3@ZIF-67	0.47	14.1	113.6
SiW_9Co_3(↑)@ZIF-67	0.42	28.9	93.9

[a] At potential equal to 1.75 V vs. RHE.

Agradecimientos
The work was funded by Fundação para a Ciência e a Tecnologia de Portugal (FCT)/MEC under FEDER under Program PT2020 - project UID/QUI/50006/2019 and project "UniRCell", with the reference POCI-01-0145-FEDER-016422. Víctor K. Abdelkader Fernández thanks UniRCell project for the post-doctoral grant.

Referencias
[1] V. K. Abdelkader-Fernández *et al*., ACS Appl. Energy Mater., 3 (2019) 1854.
[2] C. Freire *et al*., Chem. Cat. Chem., 10 (2018) 1703.

Bifunctional Co_xNi_yP nanowires for electrocatalysis of the oxygen and hydrogen evolution reactions and energy-saving of overall water splitting using a bipolar membrane

Isilda Amorim[1,2], Junyuan Xu[1], Fátima Bento[2], Lifeng Liu[1,*]
[1]International Iberian Nanotechnology Laboratory (INL), Avenida Mestre José Veiga, 4715-330 Braga, Portugal
[2] Centro de Química, Universidade do Minho, Campus de Gualtar, Braga, 4710-057, Portugal
**lifeng.liu@inl.int*

Electrochemical water splitting enabled by renewable energy sources represents a promising approach to the generation of clean and high-purity hydrogen (H_2) fuels because unlike steam reforming of hydrocarbons this process does not emit any pollutants. Despite the advantages, the cost of water electrolyzers prohibits their market penetration and makes electrolysis not an economically viable approach for mass production of H_2. Transition metal phosphides (TMPs) have in the past few years attracted considerable research interest for use as a class of emerging electrocatalysts to expedite the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), and show substantial promise to substitute the expensive and scarce platinum and iridum/ruthenium-based catalysts [1,2].

In this talk, ternary Co_xNi_yP nanowires (NWs) and their catalytic performance for both OER and HER will be presented. Firstly, the effect of the ratios of Co and Ni in the form of powders was studied, showing that the introduction of a secondary metal in a binary TMP substantially improves both the OER and HER performance. Increasing the content of nickel helps to boost the reactions, with the best catalytic performance obtained at the Co:Ni ratio of 1:1. The performance (OER: η_{10} = 260 mV in NaOH; HER: η_{10} = 77 mV in NaOH and η_{10} = 65 mV in H_2SO_4) can be further improved by *in-situ* growth of the CoNiP NWs on three-dimensional Ni foam current collectors.

Finally, we demonstrate that using a bipolar membrane and self-supported bifunctional Co_xNi_yP NWs electrodes, we can accomplish water splitting in acid-alkaline dual electrolytes with a voltage of 0.89 V to deliver 10 mA cm^{-2}, which is 0.83 V lower than that of the membrane-free alkaline water electrolyzer working at the same current density.

Acknowledgements
Acknowledgements to the financial support from the Portuguese Foundation of Science and Technology (FCT) under the projects “IF/2014/01595” and “PTDC/CTM-ENE/2349/2014" (grant agreement No. 016660). Isilda Amorim acknowledges the FCT for the Ph.D. Grant (SFRH/BD/137546/2018).

Referencias
[1] Tan, Y. W.; Wang, H.; Liu, P.; Cheng, C.; Zhu, F.; Hirata, A.;Chen, M. W., Adv. Mater., 28 (2016) 2951.
[2] Xu J.; Li J.; Xiong D.; Zhang B.; Liu Y.; Wu K-H.; Amorim I.; Li W.; Liu L., Chem. Sci., 9 (2018), 3470.

Wet peroxide oxidation of paracetamol using natural clay-based materials as catalysts

Adriano S. Silva[1,2,3], Jose L. Diaz de Tuesta[1,2,*], Juliana G. Sgorlon[3], Marzhan S. Kalmakhanova[4], Helder T. Gomes[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2]Laboratory of Separation and Reaction Engineering–Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[3]Universidade Tecnológica Federal do Paraná, R. Marcílio Dias, 635 - Jardim Paraiso, Apucarana - PR, 86812-460, Brasil

[4]M.KH. Dulati Taraz State University, Taraz. Department of Chemistry and Chemical Engineering, Tole bi 63, Taraz, Kazakhstan

**jl.diazdetuesta@ipb.pt*

In recent years, many pharmaceutical compounds have been identified worldwide at trace levels (in the order from $ng \cdot L^{-1}$ to $mg \cdot L^{-1}$) in the aquatic environment [1]. The presence of pharmaceutical contaminants in water, even at low concentrations, could bring harmful toxicological consequences to human beings and animals that ingested the contaminated water [2]. This work deals with the treatment of water containing paracetamol (PCM) by catalytic wet peroxide oxidation (CWPO) using clay-based materials as catalysts. PCM was considered as a model pharmaceutical emergent pollutant. For the preparation of the catalysts, natural clays from four different regions of Kazakhstan were used Akzhar, Asa, Karatau, and Kokshetau. From the clay obtained in kokshetau deposit, three catalysts were prepared: 1) natural one (KON), 2) calcined clay at 600 ºC for 5 h (KOC), and 3) a pillarized clay (KOP) with a pillaring solution containing 0.25 M $CoCl_2$, 0.5 M $FeCl_3$ and 0.5 M NaOH, resulting in OH/(Fe+Co) = 2:1. Additionally, three clays were prepared by the same procedure of pillarization from the Akzhar, Asa and Karatau natural clays, resulting in AKP, ASP, and KAP, respectively. The concentration of PCM, H_2O_2 and total organic carbon (TOC) were followed during the CWPO experiments (Fig. 1). All materials revealed high catalytic activity, the non-pillared samples allowing to remove more than 33.4% of PCM after 24 h of reaction time under the following operating conditions: 80 °C, initial pH 3.5, $C_{catalyst}$ = 2.5 g L^{-1}, C_{PCM} = 100 mg L^{-1} and $C_{H_2O_2}$ = 472 mg L^{-1}. The CWPO runs done with the pillared clay catalysts resulted in more than 90% of removal of the pollutant after 24 h of reaction. The best catalyst was KOP since it leads to the complete removal of the pollutant after 8 h of reaction time and to the highest abatement of TOC (>60%) under the same operational conditions.

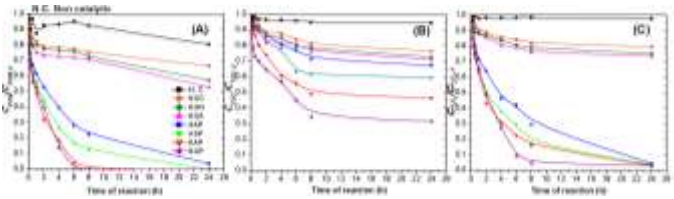


Fig.1 Concentration of A) PCM, B) TOC and C) H_2O_2 against time of reaction.

Acknowledgements

This work is a result of Project "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by ERDF; and the Associate Laboratory LSRE-LCM - UID/EQU/50020/2019 - funded by national funds through FCT/MCTES (PIDDAC); and CIMO (UID/AGR/00690/2019) through FEDER under Program PT2020.

References

[1] Y. Luo, W. Guo, H.H. Ngo, L.D. Nghiem, F.I. Hai, J. Zhang, S. Liang, X.C. Wang, Science of The Total Environment 473–474 (2014) 619.

[2] K. Fent, A.A. Weston, D. Caminada. Aquatic Toxicology 76 (2006) 122.

CAT04

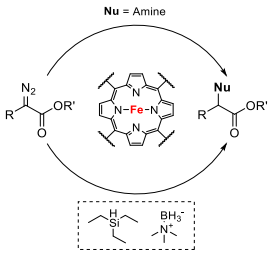
Why not Iron? Revisiting the Carbene Insertion Reactions

Vasco F. Batista[1,*], Diana C.G.A. Pinto[1], Artur M.S. Silva[1]
[1]*QOPNA & LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal*
**vfb@ua.pt*

Carbene chemistry is widely established as an important toolbox for the organic chemist. The last decades saw the implementation of a diverse set of metal complexes for carbene-mediated insertion reactions, either with noble metals (Rh, Ir, Ru, Au, Ag, etc…) or Copper. While a vast number of catalysts are reported for these reactions, most have limited reactivity, are expensive and/or not selective. Nevertheless, they allow the insertion of any given nucleophile, as well as the synthesis of cyclopropanes and several multicomponent reactions.[1,2]

A common feature to all the aforementioned transition metals is their limited availability in the earth's crust. As so, it is surprising that Fe(II), a suitable alternative centre for carbene reactivity, has been so far overlooked. Only a handful of articles report the use of iron porphyrins in a set of carbene insertions using standard carbene precursors.[4]

In this work we revisited this versatile transition metal, searching for new and improved reactivity in carbene insertion. The scope of the more common amination of diazoesters with Fe(III) porphyrins was expanded, aiming at the synthesis of high-value heterocyclic compounds. More so, the synthesis of silanes and boranes was attempted with very limited success **(Fig. 1)**. A thorough computational analysis was performed to reveal the concerted mechanism of these insertions, allowing an assessment of significant factors that affect overall reactivity and possible barriers to its success. This work may provide some guidelines towards future endeavours in the field and make the case for a future with widespread and more sustainable Iron-catalysed carbene reactions.



Agradecimientos

Thanks are due to the University of Aveiro and FCT/MCT for the financial support for the QOPNA research Unit (UID/QUI/00062/2019) through national funds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement, and to the Portuguese NMR Network. Vasco F. Batista also thanks FCT for his PhD grant (PD/BD/135099/2017). A special thank you is due to Dr. Sónia Pires for its expertise in the metalation of porphyrins and to Dr. Paulo Ribeiro-Claro for its help and expertise with the *in silico* study.

Referencias

[1] Ford, H. Miel, A. Ring, C. N. Slattery, A. R. Maguire, M. A. McKervey, Chem. Rev., 115 (2015), 9981-10080.
[2] H. Keipour, V. Carreras, T. Ollevier, Org. Biomol. Chem., 15 (2017), 5441-5456.
A. Fürstner, ACS Cent. Sci., 2 (2016), 778-789.
[3] M. M. Q. Simões, D. T. G. Gonzaga, M. F. C. Cardoso, L. S. M. Forezi, A. T. P. C. Gomes, F. C. Silva, V. F. Ferreira, M. G. P. M. S. Neves, J. A. S. Cavaleiro, Molecules, 23 (2018), 792.

Solvent-free desulfurization system to produce low-sulfur diesel using hybrid monovacant Keggin-type catalyst

F. Mirante,[1*] M. C. Corvo,[2] B. Castro,[1] C. M. Granadeiro[1] and S. S. Balula[1]

[1] LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal
[2] CENIMAT/I3N, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Monte da Caparica, and AD Física, ISEL/IPL, R. Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal
*e-mail fatima.mirante@fc.up.pt

Over the last years, one of worries all over the world is the emissions of SOx casued by the combustion of fuels, which has become a serious environmental problem. The sulfur compounds present in fuels are responsible for several undesired issues, such as acid rain, air pollution, respiratory disorders; as well as irreversible catalyst poisoning. Strict environmental policies were implemented worldwide limiting the sulfur level in fuels to 10 ppm [1]. Therefore, the production of ultra-clean fuels has become of the most challenging subjects for petroleum refining industry and it has been attracting researchers attention developing of novel methods for the deep-desulfurization of fuels as alternatives and complementary to the conventional desulfurization hydrotreating process (HDS) [2,3]. In particular, the oxidation desulfurization (ODS) process offers very promising advantages due to its cost-effectiveness and mild operational conditions while being able to efficiently remove the most refractory sulfur-compounds from fuels [4]. Among such materials, polyoxometalates have proved to form robust catalysts, able to efficiently oxidize the sulfur compounds of diesel [3-6].

In this work, we prepared quaternary ammonium catalysts based on the monovacant polyoxotungstate ($[PW_{11}O_{39}]^{7-}$, abbreviated as PW_{11}). The desulfurization performances of the organic-inorganic hybrid PW_{11} ($TBAPW_{11}$ and $ODAPW_{11}$), the potassium salt compound ($K_7PW_{11}O_{39}$, abbreviated as KPW_{11}) and the peroxo- compound ($TBA\text{-}PO_4[WO(O_2)_2]$, abbreviated as $TBAPW_4$) were compared as catalysts in the ODS system using a multicomponent model diesel. The ODS studies were performed using solvent-free systems and aqueous H_2O_2 as oxidant.

The nature of the cation in the catalyst PW_{11} showed to have an important influence in the catalytic performance. The hybrids catalysts showed higher catalytic efficiency than the other tested catalysts. $TBAPW_{11}$ revealed a remarkable desulfurization performance with 96% of sulfur compounds removed in the first 120 min. The reusability and stability of the catalyst was also investigated for three consecutive ODS cycles. A treated diesel could be recovered without sulfur compounds performing a liquid/liquid extraction diesel/H_2O and diesel/EtOH mixture (1:1) after catalytic oxidative step.

Acknowledgments
This work was partly funded through the project REQUIMTE-LAQV (Ref. UID/QUI/50006/2019) and the project GlyGold, PTDC/CTM-CTM/31983/2017, financed by national funds through the FCT/MCTES and when appropriate co-financed by FEDER (Fundo Europeu de Desenvolvimento Regional) under the PT2020 Partnership Agreement. This work is funded by national funds (OE), through FCT in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19 (to LCS and CMG).

References

[1] Z. Ismagilov, S. Yashnik, M. Kerzhentsev, V. Parmon, A. Bourane, F.M. Al-Shahrani, A.A. Hajji, O.R. Koseoglu, Cat. Rev. - Sci. Eng., 53 (2011) 199-255.
[2] H. Lü, Y. Zhang, Z. Jiang, C. Li, Green Chem., 12 (2010) 1954-1958.
[3] S. Ribeiro, C.M. Granadeiro, P. Silva, F.A. Almeida Paz, F.F. de Biani, L. Cunha-Silva, S.S. Balula, Catal. Sci. Technol., 3 (2013) 2404-2414
[4] C.M. Granadeiro, L.S. Nogueira, D. Juliao, F. Mirante, D. Ananias, S.S. Balula, L. Cunha-Silva, Catal. Sci. Technol., 6 (2016) 1515-1522.
[5] S.O. Ribeiro, D. Julião, L. Cunha-Silva, V.F. Domingues, R. Valença, J.C. Ribeiro, B. de Castro, S.S. Balula, Fuel, 166 (2016) 268-275.
[6] F. Mirante, L. Dias, M. Silva, S.O. Ribeiro, M.C. Corvo, B. de Castro, C.M. Granadeiro, S.S. Balula, Catal. Commun., 104 (2018) 1-8.

ENSEÑANZA DE LA QUÍMICA

A ciência cidadã e as atitudes dos alunos face à disciplina de Físico-Química

Araújo, J. L.[1,*], Morais, C.[1], Paiva, J. C.[1]
[1] CIQUP, Unidade de Ensino das Ciências, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007, Porto, Portugal
** jl.arauj@gmail.com*

A literatura revela dificuldades de nível afetivo e atitudes negativas em relação à Química [1, 2] bem como barreiras cognitivas pela complexidade dos conteúdos abordados nesta disciplina. A ciência cidadã emergiu, à partida, com o objetivo de envolver ativamente os cidadãos no processo de produção científica [3]. Estes projetos são muito bem sucedidos junto das comunidades e o seu potencial pedagógico é grande [4, 5] uma vez que se baseiam em contextos específicos e socialmente relevantes capazes de promover a motivação e o interesse dos alunos pela aprendizagem da ciência, em geral, e pela química, em particular. Contudo, não há ainda muitos estudos acerca da avaliação do impacto na motivação e na aprendizagem dos alunos resultantes da sua participação nestes projetos.

É no seguimento de alguns estudos já realizados sobre as potencialidades ciência cidadã como ferramenta pedagógica [4, 5], que surge o projeto *PVC – Perceive the Value of Chemistry behind water and microplastics*. No ano letivo de 2018/2019, participaram neste projeto cerca de 500 estudantes do ensino básico, realizando a monitorização de parâmetros de qualidade das águas costeiras na região norte de Portugal (como, por exemplo, pH, temperatura, turbidez, salinidade, concentração de nitratos e de nitritos) e identificando a presença de microplásticos nessas águas. Os dados recolhidos serão partilhados na plataforma *EarthEcho Water Challenge*. Um dos objetivos do projeto PVC é avaliar de que forma a participação dos alunos promove atitudes mais positivas face à disciplina de Físico-Química. Para tal, uma escala previamente validada para o efeito [6], foi respondida pelos alunos antes e depois da sua participação no projeto de ciência cidadã. Realizaram-se também entrevistas a professores e alunos para se obterem informações complementares.

Os dados recolhidos através da aplicação da escala de atitudes respondida antes da participação no projeto foram sujeitos a uma análise de componentes principais através do software SPSS. Da análise fatorial exploratória da escala de atitudes emergiram quatro dimensões: (i) comportamental [M=4.52, SD±1.24] onde se inclui, e.g., a questão "Percebo a aplicação prática da Físico-Química" com a média mais elevada dentro da dimensão comportamental [M=4.84], (ii) cognitiva [M=5.46, SD±1.18] onde a questão "A expressão "Físico-Química" provoca-me uma sensação agradável." [M=5.68], (iii) afetiva face à disciplina [M= 4.33, SD±1.32] tendo esta dimensão questões que se destacam tanto pela positiva (e.g., "Ir às aulas de Físico-Química é agradável" [M=5.03]) como pela negativa ("Penso que a disciplina de Físico-Química deveria ser obrigatória para todos os cursos" [M=3.64]) e (iv) afetiva face ao estudo da disciplina [M=4.79, SD±1.26] onde as respostas dos alunos às questões desta dimensão foram mais homogéneas, e.g., a questão "Penso que a Físico-Química é útil no dia-a-dia" foi a que obteve uma média mais elevada [M=4.90]. A comparação ainda preliminar destes resultados da escala respondida como pré-teste com os dados do pós-teste, parecem evidenciar uma melhoria mais significativa das atitudes dos alunos face às dimensões (iii) afetiva face à disciplina e (iv) afetiva face ao estudo da disciplina. As entrevistas realizadas dão ainda indicadores que corroboram a ideia de que o envolvimento dos alunos no projeto PVC promoveu uma maior motivação e empenho à disciplina e ao seu estudo.

Agradecimentos
J. L. Araújo é apoiado pela bolsa FTC: SFRH/BD/132482/2017

Referencias

[1] Bennett, J., Hogarth, S. International Journal of Science Education, 31 (2009), 1975-1998.
[2] Osborne, J., & Collins, J. International Journal of Science Education, 23 (2001), 441-467.
[3] Bulte, A., Westbroek, H., De Jong, O., Pilot, A. International Journal of Science Education, 28 (2014), 1063-1086.
[4] Tulloch, A., Possingham, H., Joseph, L., Szabo J., Martin, T. Biological Conservation, 165 (2013), 128-138.
[5] Ferreira, M. A., Soares, L., Andrade, F. Journal of Coastal Conservation, 16 (2012), 567-574.
[6] Neto, A., Candeias, A., Rebelo, B., Varelas, & Diniz, A. M. (2013). Validade estrutural do questionário de atitudes face às ciências físico-químicas: estudo com alunos de 9.º ano do ensino básico português. XII Congresso Internacional Galego-Português de Psicopedagogia.

Experimentos comestibles ¿Se puede degustar la ciencia?

Ángel Vidal-Vidal[1,2*]
[1]Departamento de Química Orgánica, Facultade de Química, Universidade de Vigo. Lagoas Marcosende s/n 36310 Vigo, España.
[2]CITACA - Clúster de Investigación y Transferencia Agroalimentaria del Campus Auga, Universidad de Vigo, 32004-Ourense, España.
**a.vidal.vidal@uvigo.es*

A la hora de hablar de la educación actual, observamos cómo la memorización sistemática de contenidos y su aplicación directa a problemas modelo es uno de los métodos más empleados tanto en educación secundaria como en educación superior. Sin embargo, existe poca vinculación entre la formación teórica que recibe el alumnado y la capacidad que poseen al finalizar sus estudios, para la aplicación de estos conceptos en situaciones desconocidas y en la vida cotidiana. Otro de los grandes problemas a los que nos enfrentamos es la falta de motivación generalizada del alumnado hacia la adquisición de nuevos conocimientos, por ello es necesario buscar nuevas estrategias innovadoras y contenidos atractivos que interesen a los estudiantes. Con el fin de motivar al alumnado, en esta comunicación se muestra una propuesta educativa en la que se trabaja la relación entre la química y la cocina buscando en todo momento la interconexión de conocimientos teóricos con la vida cotidiana.

Tradicionalmente no se prestaba demasiada atención a los saberes científicos culinarios a pesar de la existencia de una gran cantidad de fenómenos físico-químicos en la cocina. En la actualidad la vinculación entre la cocina y la química es más conocida por el público general gracias a numerosos reality shows en los que se emplean técnicas de vanguardia procedentes del campo de la cocina molecular para realizar diferentes platos. No obstante, lo que quizás es más desconocido es el uso de la cocina como contexto y pretexto para el aprendizaje de la química en el aula. Existen numerosos experimentos culinarios muy sencillos de realizar gracias a los cuales se pueden tratar una infinidad de conceptos del currículo de química de todos los niveles educativos. Algunos ejemplos de temáticas son los polímeros, las técnicas de extracción sólido-líquido, los coloides, la termodinámica, la química ácido-base…

Habitualmente, las actividades de aula en las que existe relación química-cocina se centran en explicar la ciencia oculta en una elaboración culinaria, por ejemplo, las reacciones químicas que ocurren en el horneado de un bizcocho o en la elaboración de un flan. No obstante, en esta comunicación se va un paso más allá y se pretende crear elementos útiles para la ilustración de conceptos científicos en el laboratorio de química y que además sean comestibles. Uno de los experimentos que se recogen en esta comunicación es la creación de unas sondas para la medida del pH de sustancias desconocidas en base a unas esferificaciones de un indicador ácido-base comestible.

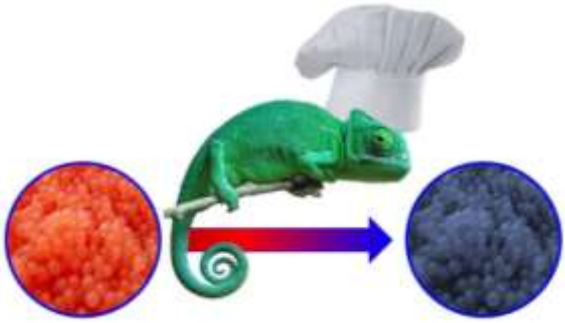


Fig.1. Esquema gráfico de uno de los experimentos comestibles

Diseño de un Sistema Automático para la Manipulación de Gases en el Aula.

José Antonio Murillo, José Miguel Murillo y Pablo Murillo.
Departamento de Química Analítica y Tecnología de Alimentos, Facultad de Ciencias y Tecnologías Químicas, UCLM, Avda. Camilo José Cela 10, 13004 Ciudad Real, España
joseantonio.murillo@uclm.es

Uno de los principales problemas que nos encontramos en la Didáctica y la Divulgación de la Química es el uso de reactivos irritantes y tóxicos, muy especialmente, cuando éstos son gases. Esto condiciona el uso de algunas experiencias magistrales en el aula o laboratorios sin vitrina de gases, en museos científicos y en demostraciones en ferias de las ciencias o situaciones similares.

En este trabajo se muestra un diseño sencillo, controlado por Arduino, que nos permite realizar reacciones con gases que pueden ser molestos o peligrosos para la salud.

Hoy en día, el mundo en el que vivimos depende cada vez más de la tecnología [1]. Muchas de estas nuevas tecnologías son interactivas, lo que hace posible la creación de entornos en los que se facilita el aprendizaje [2].

Arduino es una plataforma de código abierto [3] basada en una simple placa de microcontrolador y un entorno de desarrollo que implementa el lenguaje de procesamiento. Además proporciona un entorno de fácil acceso para usuarios no especializados, placas de hardware de bajo coste y capacidad de expansión con placas adicionales.

El sistema se basa en utilizar un frasco lavador de gases donde se genera el gas, un recipiente transparente herméticamente cerrado, donde tiene lugar la reacción objeto de estudio, y, por último, otro lavador de gases donde se coloca un reactivo que transforma el gas peligroso en un producto soluble en agua y, a ser posible, exento de toxicidad como se muestra en la Fig 1. La automatización consiste en controlar el tiempo en el que se está pasando el gas para la producción de la reacción y el tiempo en el que se pasa aire para eliminarlo del sistema o bien para volver a las condiciones iniciales.

Fig.1. Sistema diseñado para el uso de amoniaco gas

Referencias
[1] A.A. Galadima, 11th International Conference on Electronics Computer and Computation 2014; pp 1-1-4.
[2] The computer as an educational tool: Productivity and problem solving. R.C. Forcier, D.E. Descy, Ed. Prentice-Hall, 2007.

ELECTROQUÍMICA

Preparation of AuNPs nanocomposites for electroanalytical sensors development

João Braga[1,*], Sofia G. Meirinho[1,2], M. Cristina Oliveira[1]

[1]CQ-VR, Departamento de Química, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal;
[2]Life and Health Sciences Research Institute (ICVS), School of Medicine, University of Minho, Braga, Portugal
**jfbraga88@gmail.com*

In the present study, a new strategy is exploited to synthesize gold nanoparticles (AuNPs). The work is motivated by the recent finding that electrogenerated carbon-based material exhibits a high reducing ability [1]. The synthesis approach differs from conventional procedures in that the carbon-based nanomaterial plays simultaneously the role of reducing agent and substrate on which the AuNPs are deposited, giving rise to an AuNPs-carbon composite.

The as-prepared composite was characterized by UV-Visible spectrophotometry, transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDS), dynamic light scattering (DLS) and Zeta potential. Envisaging the application of this composite in the development of electrochemical sensors, the as-prepared AuNP composite, without further modification, was immobilized on a glassy carbon electrode. The electrode electroactive area and metal loading were evaluated by cyclic voltammetry, as well as the chemical stability of the nanomaterial and the immobilization effectiveness.

The behaviour of the AuNP-carbon composite on the preparation of aptasensors integrating biotin-labeled and thiol-labeled aptamers for osteopontin specific detection (a common tumor marker in various types of cancer, namely breast cancer [2]) was appraised. In addition, it was investigated the ability of the nanocomposite for the electrocatalytic reduction of hydrogen peroxide and oxygen reduction. The new synthetic route provides a very simple method for the fabrication of nanoparticles composite for catalytic and sensing applications.

Aknowledgements
The authors thank FCT (Portugal's Foundation for Science and Technology) for financial support through the CQ-VR Research Unit (UID/QUI/00616/2013).

References
[1] A.D. Veloso, A.M. Ferraria, M. Botelho, P.B. Tavares, P. Valento, D.D. Pereira, P.B. Andrade, A.J. Fernandes, M.C. Oliveira, R.A. Videira, ChemMedChem. 14 (2019) 1–14.
[2] S.G. Meirinho, L.G. Dias, A.M. Peres, L.R. Rodrigues, Analytica Chimica Acta 987 (2017) 25-37.

Síntesis fotoquímica de clústeres de platino.

Reigía B. Mónica[1,*], Buceta F. David[1], López-Quintela M. Arturo[1]
[1]Nanomag, USC, Santiago de Compostela, España
*monica.reigia.blanco@usc.es

Los clústeres de átomos metálicos son materiales formados por un pequeño número de átomos, con un tamaño comparable a la longitud de onda de Fermi del electrón, lo que les concede unas propiedades únicas debidas a efectos cuánticos que los diferencian de nanomateriales y materiales en estado masivo, como por ejemplo sus propiedades catalíticas o fotoluminiscencia [1]. El estudio del presente trabajo se centra en la obtención de clústeres de Platino por un método fotoquímico.

Los clústeres de Pt sintetizados fueron caracterizados por las siguientes técnicas: espectrofotometría UV-Vis y fluorescencia, así como espectrometría de masas. La figura adjunta muestra el espectro de masas experimental y el teórico de los clústeres sintetizados que muestran la presencia de clústeres formados por solamente dos átomos de Pt.

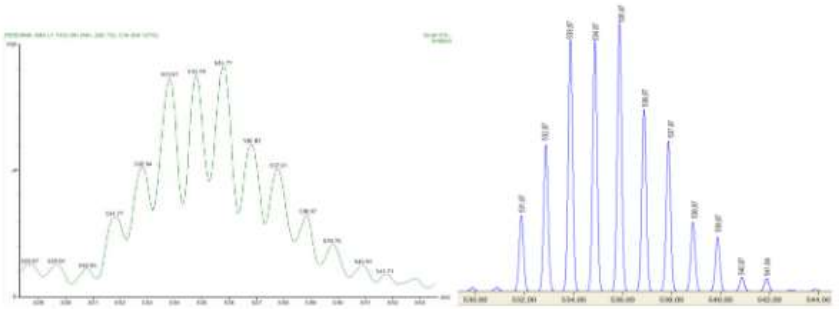


Fig. 1. Espectro de masas experimental (izquerda) teórico (derecha) aducto que forma el clúster $Pt_2Cl_3(H2O)_2(H)_2$

Agradecimientos
Consellería de Cultura, Educación e Ordenación Universitaria, Xunta de Galicia, Spain (Grupos Ref. Comp. ED431C 2017/22). Consellería de Educación, Universidad y Formación Profesional, Xunta de Galicia, por la concesión a la USC la Agrupación Estratégica en Materiales – AEMAT, con el código ED431E 2018/08.

Referencias

[1] Buceta Fernandez, D. Caracterización y propiedades catalíticas de clústeres cuánticos subnanométricos. 203 (2011).

QUÍMICA INDUSTRIAL E INGENIERÍA QUÍMICA

Adsorption dynamics of $CO_2/CH_4/N_2$ mixtures in zeolite 4A for Biogas Upgrading

Carmem N.P. Gonçalves[1], Lucas F. A. S. Zafanelli[1], J.A.C. Silva[1*]

[1] Grupo de Processos e Produtos Sustentáveis, Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal
**jsilva@ipb.pt*

Biogas is mainly composed by methane (CH_4, 60 to 70%) and carbon dioxide (CO_2, 30 to 40%) or nitrogen (N_2, 10 to 20%) and to obtain a high energy content, CO_2 needs to be separated from CH_4 and N_2. To this end, a variety of solid physical adsorbents have been considered, as well as molecular sieve zeolites and a new class of adsorbents named Metal-Organic Frameworks (MOFs). The technology for biogas upgrading using adsorbents is called Pressure Swing Adsorption (PSA). With this technique, CO_2 is separated from the biogas by adsorption under elevated pressure. The adsorbing material is regenerated by a sequential decrease in pressure before the column is reloaded again, hence the name of the technique.

In this work, we will present a series of breakthrough experiments performed in a fixed bed with ternary mixtures of $CO_2/CH_4/N_2$ and single component experiments with CO_2 at 313, 343, and 373 K with a pressure up to 4.5 bar using binderless 4A zeolite as the adsorbent. This data could be used in the design (simulation) of a cyclic adsorption processes (PSA) for the purification of biogas. Figure 1 (b) shows an example of a breakthrough curve at 313 K and 1 bar where it can be seen a complete separation between CO_2 and CH_4/N_2 proving that zeolite 4A can be an effective adsorbent to be used in strategies for BIOGAS upgrading by removing CO_2 from the gas stream.

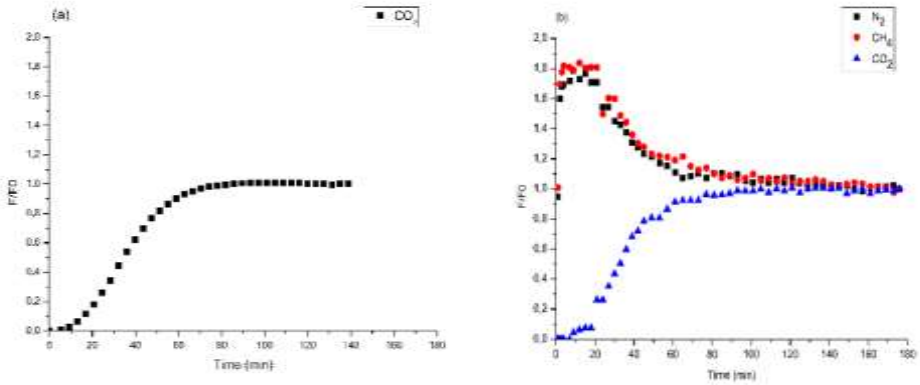


Figure 1. Single component (a) and multicomponent (b) breakthrough curves of mixtures $CO_2/CH_4/N_2$ at 313 K and 1 bar in zeolite 4A.

Acknowledgments
We acknowledge a research grant awarded under project "VALORCOMP" (ref.0119_VALORCOMP_ 2_P), financed through INTERREG V A Spain Portugal (POCTEP) 2014-2020, under the European Regional Development Fund by FCT. This work has also been funded by Project POCI-01-0145-FEDER-006984 − Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) − and by national funds through FCT - Fundação para a Ciência e a Tecnologia.

Fixed Bed Dynamics of Multicomponent Adsorption of Pentane and Hexane Isomers in ZIF-8

P. Brântuas[1,2,*], A. Henrique[1,2], A. Rodrigues[1], J. Silva[1,2]
[1]Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE/LCM), Department of Chemical Engineering, Faculty of Engineering University of Porto, Rua Dr. Roberto Frias, S/N, 4200-465 Porto, Portugal
[2]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
**pedrobrantuas@ipb.pt*

The separation of hydrocarbon mixtures is one of the most important topics in the petrochemical industry, including the separation of paraffins isomers in the C5/C6 range for the octane upgrading of gasoline. These processes separate low Research Octane Number (RON) linear paraffins, n-hexane (nC6) and n-pentane (nC5), from their respective branched isomers with higher RON content: 3-methylpentane (3MP), 2-methylpentane (2MP), *iso*-pentane (iC5), 2,3-dimethylbutane (23DMB) and 2,2-dimethylbutane (22DMB). In this context, metal organic frameworks (MOFs) have been studied for this process [1]. Due to their chemical and thermal stability, Zeolite Imidazolate Frameworks are of interest, specially ZIF-8 [2].

Septenary fixed bed breakthrough experiments of pentane and hexane isomers were performed with ZIF-8. The equimolar septenary studies were performed between 373 – 473 K and at a total hydrocarbon pressure of 25 kPa resulting in the following sorption hierarchy: nC6 > nC5 > 2MP > 3MP > iC5 > 23DMB > 22DMB as can be seen in **Fig. 1** for the breakthrough experiment at 423 K. Results also show that the sorption of the linear nC5 and nC6 is equilibrium based in contrast with the sorption of branched isomers which is kinetically controlled. The equilibrium data were modelled by the Sips isotherm and the fitted parameters were used to simulate the breakthrough data through a mathematical model developed in a Matlab code using the method of lines (MOL).

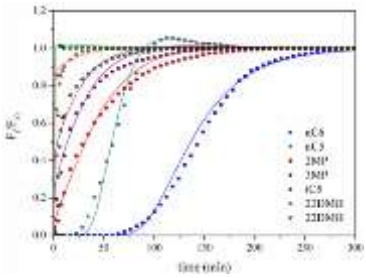


Fig.1. Experimental (points) and numerical (lines) breakthrough curves for a septenary (nC5/iC5/nC6/2MP/3MP/23DMB/22DMB) equimolar mixture of C5/C6 isomers in ZIF-8 at hydrocarbon total pressure of 25.0 kPa and at 423 K.

Agradecimientos
We acknowledge financial support from (1) Project ref POCI01-0145-FEDER-016517 (PTDC/QEQ-PRS/3599/2014) funded by FEDER through COMPETE2020 and FCT; (2) AIProcMat@N2020-Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020, with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF), and (3) by Project POCI-01-0145-FEDER006984-Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020, Programa Operacional Competitividade e Internacionalização (POCI), and by national funds through FCT - Fundação para a Ciência e a Tecnologia.

Referencias

[1] Separation of Hexane Isomers in ZIF-8 by Fixed Bed Adsorption. A. Henrique, A. Rodrigues, J. Silva, Ind. Eng. Chem. Res. 58 (2019) 378–394.
[2] Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. K. Park, Z. Ni, A. Cote, J. Choi, R. Huang, F. Uribe-Romo, H. Chae, M. O'Keeffe, O. Yaghi, Proc. Natl. Acad. Sci. 103 (2006) 10186–10191.

Supercritical CO_2 extraction as green technology for obtainig coffee oil

Javier Andrés Dávila[1,*], Carlos Julio Santacruz[1]
[1]Universidad Jorge Tadeo Lozano, Cra 4 No. 22-61, Bogotá, Colombia
**e-mail: javiera.davilar@utadeo.edu.co*

Supercritical extraction (Fig. 1) of green coffee oil from defective coffee beans was studied in this research. The supercritical CO_2 extraction was carried out under different conditions of pressure (2800 - 4100 psia), temperature (40 - 60 °C) and cosolvent (ethanol):sample ratio (5 - 15 % W/W), thus determining its influence on the antioxidant activity (AA) and total phenolic content (TPC). The methods of DPPH and Folin Ciacolteau were used to quantify the AA and TPC, respectively [1]. A directly proportional relationship was observed between the AA and TPC.

The addition of a cosolvent allows a maximum AA of 15.54 µmol trolox equivalent per milliliter of oil and the highest TPC was 6.03 mg gallic acid equivalent per gram of oil, both obtained at the superior levels of the factors analyzed (4100 psia, 60°C and 15% W/W). The oil extracted with supercritical technology was compared with one obtained using soxhlet extraction and etanol as solvent, obtaining an AA four times higher for supercritical extraction, thus demonstrating the potential of this technology in the extraction of TPC with an AA.

Finally, a sample of green coffee was analysed before (Fig 2 left) and after (Fig 2 righ) the supercritical extraction. Before supercritical extraction a soft surface with uniform undulations was found, while after supercritical extraction a rough morphology with edges of irregular characters was found. This morphology was may be due to the effect of the mass transfer of solutes from inside the plant matrix to the supercritical CO_2 [2].

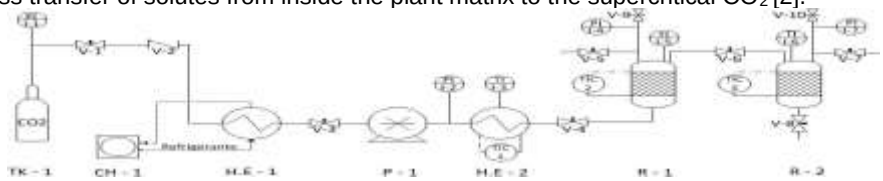


Fig 1. Process diagram - Supercritical extraction unit

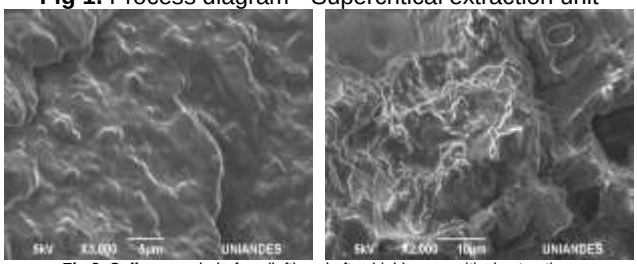


Fig 2. Coffee sample before (left) and after (righ) supercritical extraction.

References

[1] P. M. A. de Oliveira, R. H. de Almeida, N. A. de Oliveira, S. Bostyn, C. B. Gonçalves, and A. L. de Oliveira, "Enrichment of diterpenes in green coffee oil using supercritical fluid extraction – Characterization and comparison with green coffee oil from pressing," J. Supercrit. Fluids, vol. 95, pp. 137–145, 2014.X. Author, Y. Author, Z. Author, Proc. of congress name, City, Country, 2014, 10.

a. Belbaki, W. Louaer, and A. H. Meniai, "Supercritical CO2 extraction of oil from Crushed Algerian olives," J. Supercrit. Fluids, vol. 130, no. June, pp. 165–171, 2017.

Lipofilização de antocianinas baseado na retenção de enzimas em membranas porosas

M. Guimarães[1], M. Pérez-Gregorio[1], N. Mateus[1], V. de Freitas[1], C. Galinha[2], J. Crespo[2], C. Portugal[2], L. Cruz [1,*]

[1]Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal

[2]Departamento de Química e Bioquímica, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

[*]Luis.cruz@fct.up.pt *(L. Cruz)*

As antocianinas têm despertado o interesse da comunidade científica assim como da indústria cosmética, farmacêutica e alimentar, devido às suas características cromáticas apelativas e propriedades biológicas importantes. Todavia, a sua aplicabilidade tecnológica é ainda limitada devido à sua instabilidade e baixa solubilidade em matrizes lipídicas, entre outros fatores [1-3].

A esterificação de antocianinas com ácidos gordos surgiu como resposta à necessidade de melhorar a estabilidade destes compostos em matrizes lipofílicas. Através da esterificação enzimática foi possível não só aumentar a sua liposolubilidade como também foi observado o enaltecimento de algumas das suas propriedades biológicas, nomeadamente, a atividade antioxidante [4,5].

Com o objetivo de obter antocianinas lipofílicas de um modo mais eficiente e industrialmente viável, foi desenvolvido um novo método de esterificação. Assim, procedeu-se à imobilização de lipase B de *Candida antarctica* (*Ca*lB) em membranas porosas com diferentes capacidades de retenção. As membranas provaram serem bons suportes enzimáticos, retendo eficazmente a enzima. O catalisador enzimático retido neste suporte demonstrou igualmente a sua reusabilidade, não se observando diferenças nos fatores de conversão em três reações cíclicas consecutivas. Através deste método foi possível obter antocianinas lipofílicas mais rapidamente e com fatores de conversão 2,5 vezes superiores, comparativamente à síntese em bulk [6] (figura 1).

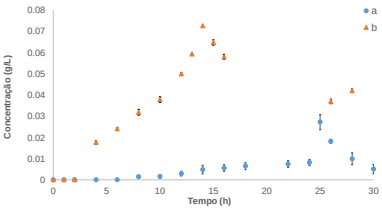


Fig 3. Reações de formação de antocianina lipofílica, Cy3glc-C8, (a) usando um extrato de enzima rico em *Ca*lB e (b) utilizando a enzima retida numa membrana de porosidade 10 KDa ao longo do tempo.

Agradecimentos

Este trabalho encontra-se inserido no projeto PTDC/OCE/ETA/31250/2017 financiado pela FCT/MCTES através do acordo PT2020 (UID/QUI/50006/2019 – POCI/01/0145/FEDER/007265).

Referências

[1] H. E. Khoo; A. Azlan; S. T. Tang; S. M. Lim, Food & Nutrition Research, 61 (2017) 1.
[2] X. H. Yang; E. Luo; X. Liu; B. Han; X. P. Yu; X. L. Peng, Bmc Cancer, 16 (2016).
[3] L. Xie; H. Su; C. Sun; X. Zheng; W. Chen, Trends in Food Science & Technology, 72 (2018) 13.
[4] L. Cruz; M. Guimaraes; P. Araujo; A. Evora; V. de Freitas; N. Mateus, Journal of Agricultural and Food Chemistry, 65 (2017) 6513.
[5] J. Mendoza; F. Pina; N. Basílio; M. Guimarães; V. de Freitas; L. Cruz, Dyes and Pigments, 151 (2018) 321.
[6] M. Guimarães; M. Pérez-Gregorio; N. Mateus; V. de Freitas; C. F. Galinha; J. G. Crespo; C. A. M. Portugal; L. Cruz, Food Chemistry, 300 (2019) 125167.

Optimization of Nanoemulsion Formulations using Saponin from Quillaja Bark, a Natural Surfactant

Tatiana B. Schreiner[1-3*], António M. Peres[1,2], Madalena M Dias[3], Simão P. Pinho[1,2], M. Filomena Barreiro[1,2]
[1]CIMO, Polytechnic Institute of Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal
[2]LSRE-LCM, Polytechnic Institute of Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal
[3]LSRE-LCM, Department of Chemical Engineering, Faculty of Engineering of University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
*tatianas@ipb.pt

Nanoemulsions are systems comprising three constituents, hydrophilic, lipophilic and amphiphilic compounds, forming a single macroscopic phase with reduced particle size. Nowadays, an important topic under study is the introduction of natural products as surfactants. This is partly motivated by consumer's demands for more sustainable products, leading industry and researchers to search for alternatives with natural-friendly connotation, avoiding the large utilization of the synthetic forms. In this context, recent studies have focused the use of saponins, highlighting its physicochemical properties, and commercial potential for the development of natural-based emulsions [1,2]. Thus, the objective of this work is to optimize a nanoemulsion formulation incorporating saponin as surfactant, through response surface methodology (RSM).

The systems were formed with the natural surfactant, pure saponin from Quillaja Bark, and glycerol as co-surfactant. Sweet almond oil was used as the lipophilic component. To produce the nanoemulsions, a high energy technique was chosen, namely high-pressure homogenization (HPH). The produced emulsions were characterized by measuring the zeta potential, droplet size (by laser diffraction) technique), pH and viscosity. In order to select the best formulation, a 2k full-factorial design with 3 factors and 3 replicates at the central point was implemented. The chosen parameters were oil/water ratio (10/90, 20/80, 30/70, w/w), surfactant content in the mixture (0.5, 1 and 1.5%, w/w) and the surfactant/co-surfactant ratio (50/50, 75/25, 100/0, w/w). The results obtained with the produced formulations showed zeta potential to vary between -40.3 and -46.0 (evidencing high stability) and a particle size in volume comprised in the range 111.9-431.4 nm. These two parameters were selected to perform the experimental design to find the most stable systems.

Nanoemulsions with pure saponin were successfully produced, where the formulations with better long term stability were those prepared with the lower amount of oil, which is 10%. It is important to point out that taking into consideration final product applications, to have less than 10% of the lipophilic component it is not suitable. Regarding the amount of surfactant, smaller droplet sizes, and consequently lower zeta potentials, were achieved at its highest content. The co-surfactant glycerol showed to have no significant impact in zeta potential, even it showed to slightly increase droplet's size.

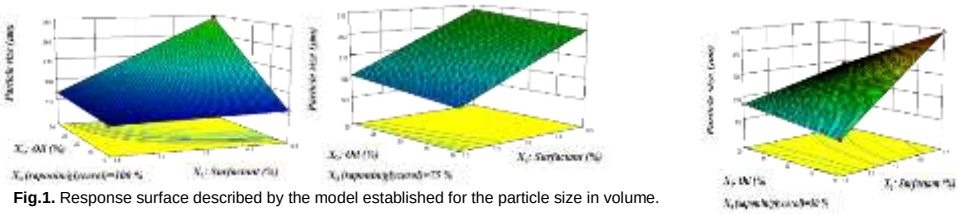


Fig.1. Response surface described by the model established for the particle size in volume.

Acknowledgments
This work is financed by POCI-01-0145-FEDER-006984 (LA LSRE-LCM) and UID/AGR/00690/2013 (CIMO), funded by FEDER, through POCI-COMPETE2020 and FCT; Project NORTE-01-0145-FEDER-000006, funded by NORTE2020 under PT2020.

References

[1] T. Ralla, H. Salminen, M. Edelmann, C. Dawid, T. Hofmann, J. Weiss, J Agric Food Chem, 20 (2017) 65.
[2] D. Kregiel, J. Berlowska, I. Witonska, H. Antolak, C. Proestos, M. Babic, L. Babic, B. Zhang, in Application and Characterization of Surfactants, R. Najjar, Rijeka, InTechOpen, 2017, 1.

One-step conversion of Eucalyptus globulus wood into platform chemicals under microwave irradiation using biphasic systems

Mar López[1*], Valentín Santos[1], Juan C. Parajó[1]

[1]University of Vigo (Campus Ourense), Chemical Engineering Department, Polytechnical Building, 32004 Ourense, Spain
**e-mail: marlopezr@uvigo.es*

The traditional economy, basically based on the consumption of fossil fuel resources (coal, petroleum, natural gas), is not sustainable in the long term [1]. Multiple researches on the field of renewable sources have been done and lignocellulosic biomass (LB) has been selected as one of the best alternatives to deal with this change. The reason is not only because LB does not compete with food resources but also because it is the most abundant carbon source on Earth. A lot of products and platform molecules can be obtained directly from LB, such as furans (5-hydroxymethylfurfural and furfural) and acids (levulinic acid, formic acid and acetic acid).

Biphasic systems for the production of furans with high yields have been widely investigated. A biphasic system is comprised of an aqueous reactive phase and an organic extraction solvent phase. Biphasic reaction systems offer advantages over monophasic reaction systems because in the former, the organic solvent acts as an extractant, inhibiting the formation of humins and thus improving yields [2]. One of the most preferred extraction solvents widely employed in biphasic systems is methyl isobutyl ketone (MIBK), a green solvent whose use is recommended by the CHEM21 guide [3].

Eucalyptus globulus wood samples were mixed with aqueous H_2SO_4 solutions and organic MIBK, and processed under microwave irradiation (MARS 6, CEM Corporation). The influence of the main experimental variables taking part in the reaction (temperature, reaction time, liquid to solid ratio, catalyst concentration and organic to aqueous ratio) were assessed in order to identify the optimal operation conditions.

The experimental results obtained under the selected operational conditions lead to favourable yields of the target products, which were obtained directly from the raw wood, being in accordance with the ones exposed in the bibliography. The direct conversion of products from *Eucalyptus globulus* wood results in fewer steps in the overall process, which implies a reduction in energy consumptions and enables shorter process time. The concentrations obtained in a one-step reaction are slightly lower if compared with a two-step reaction.

Acknowledgements
The authors are grateful to the Spanish Ministry of Economy and Competitivity for supporting this study in the framework of the research project “Modified aqueous media for wood biorefineries” (reference CTQ2017-82962-R), partially funded by the FEDER program of the European Union. Ms. Mar López thanks for her predoctoral grant (reference ED481A-2017/316) with financial support from the “Xunta de Galicia” and the European Union (European Social Fund – ESF).

References

[1] S. Peleteiro, V. Santos, J.C. Parajó, Carbohydrate Polymers, 153 (2016) 421.
[2] N. Sweygers, J. Harrer, R. Dewil, L. Appels, Journal of Cleaner Production, 187 (2018) 1014.
[3] D. Prat, A. Wells, J. Hayler, H. Sneddon, C.R. McElroy, S. Abou-Shehada, P.J. Dunn, Green Chemistry, 18:1 (2015), 288.

Heavy Metals Removal on Leachate for Use as Fertilizers

Jonathan S. Cardoso[1,*], Maria T. Vertonha[1], David Cabral[1], Adriano S. Silva[1], Fernanda F. Roman[1], José L. Díaz de Tuesta[1], Margarida Arrobas[1], Paulo Brito[1], Helder T. Gomes[1]
[1]Centro de Investigação de Montanha – CIMO, Instituto Politécnico de Bragança, Campus Santa Apolónia,
5300-253 Bragança, Portugal
* *jonathancardoso@ipb.pt*

Municipal landfill leachates typically contain high ammonium and organic concentration which could contribute to its use in agriculture, leading to the reduction of costs for the respective waste treatment plants. However, due to the nature of the leachates, they may contain phytotoxic substances. The landfill leachate samples differ by many factors such as the composition of the treated waste, elapsed time, geochemical and weather conditions [1–3]. Taking into account these considerations, leachate samples from a storage tank at the "Resíduos do Nordeste, EIM" mechanical and biological treatment plant, were collected in February 2019, and stored at 4°C. The leachate samples were processed using activated carbon adsorbents produced from the compost of the referred company, and H_2SO_4 activated clays obtained from a partnership with a Kazakhstan institution. The leachate samples were mixed with the adsorbents for 48 hours, centrifugated and the supernatant was reserved. TOC analysis in a Shimadzu TOC-L equipment and metals quantification by atomic absorption spectroscopy using a Varian SpectrAA 220 apparatus were carried out. Selected results are presented in Fig. 1.

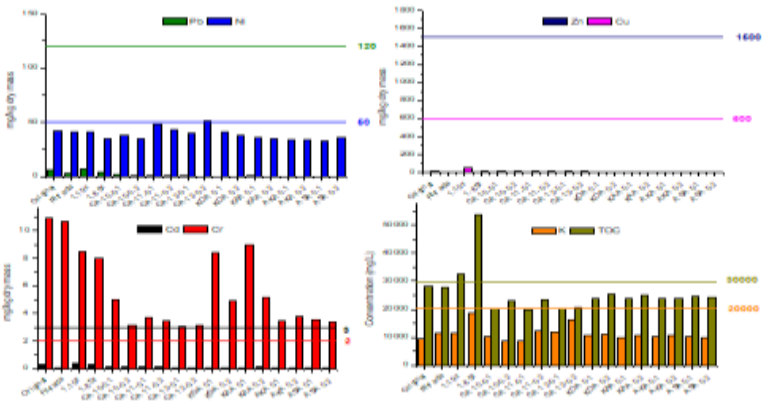


Fig. 1. Total Organic Carbon (TOC) and metals content.

The original leachate presents an organic carbon content closer to the requirements of the EU legislation for liquid organo-mineral fertilizers. The activated carbon promoted greater TOC removal in comparison with the activated clays. Both materials showed interaction with the heavy metals. However, Cr still remains present in higher contents and K presents lower values than the legislation requirements. Overall, the activated carbons presented a greater potential for heavy metals removal. However, ion-exchange resins will be tested for a more efficient heavy metals removal to minimize possible secondary elimination of components such as nutrients and organic carbon.

Acknowledgments
This work was financially supported by: Project VALORCOMP, funded by FEDER through Programme INTERREG V-A Spain − Portugal (POCTEP) 2014–2020 and Associate Laboratory LSRE-LCM UID/EQU/50020/2019 - funded by national funds through FCT/MCTES (PIDDAC).

References
[1] European Comission, *European Parliament and European Council Proposal for the Regulation of fertilizers products with the CE marking and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009*. 2016.
[2] J. Cardoso, H. Gomes, P. Brito, *Recycling*, 4 (1) (2019), paper 8.
[3] M. Zhao, Y. Xu, C. Zhang, H. Rong, G. Zeng, *Appl. Microbiol. Biotechnol.*, 100(15) (2016) 6509.

NANOQUÍMICA E NANOTECNOLOXÍA

Nanomateriais versátiles baseados na magnetita para aplicacións teragnósticas.

Arnosa Prieto Ángela[1,*], González Gómez Manuel A.[1], Yáñez Vilar Susana[1], Piñeiro Redondo Yolanda[1], Rivas Rey José[1]
[1]Grupo NANOMAG, Instituto de Investigacións Tecnolóxicas, Santiago de Compostela, España
**angela.arnosa@usc.es*

Na actualidade, un dos temas máis destacados dentro do campo da biomedicina é a detección precoz de enfermidades. Con este obxectivo, empréganse técnicas como a imaxe por resonancia magnética (IMR). Os principais axentes de contraste empregados conteñen compostos organometálicos de gadolinio, os cales levan asociada certa toxicidade ao almacenarse no fígado[1]. Por este motivo cobra importancia a busca de alternativas.

As nanopartículas de magnetita constitúen unha alternativa como base para a ensamblaxe de novas estruturas con múltiples aplicacións na detección de enfermidades.

Neste traballo, empréganse nanopartículas compostas por un núcleo de magnetita (Fe_3O_4) e un recubrimento de sílice (SiO_2). A sílice caracterízase pola súa biocompatibilidade, a formación de recubrimentos con distribución homoxénea e a súa posibilidade de funcionalización[2]. Con esta funcionalización conséguese a unión ás nanopartículas de distintos materiais: óxido de manganeso (Mn_3O_4) para a obtención de axentes de contraste en MRI, compostos fluorescentes para o uso como biomarcadores, radioisótopos como o ^{18}F para o uso en terapias como PET (tomografía por emisión de positróns) ou a fixación de anticorpos e proteínas.

A perspectiva xeral amosa diferentes posibilidades no deseño e síntese de nanopartículas baseadas en magnetita de cara á aplicación en diagnóstico e tratamento de enfermidades.

Agradecementos
Este traballo conta co apoio da Comisión Europea proxecto PANA (Call H2020-NMP-2015- two-stage, N. 686009) e proxecto MADIA (732678-MADIA-H2020-ICT-2016), e o Programa da Consellería de Educación para o Desenvolvemento da Agrupación Estratéxica en Materiais (AEMAT) na Universidade de Santiago de Compostela (N. ED431E2018/08) e o Programa para Consolidación de Grupos de Referencia Competitiva GRC2017 (N. ED431C2017/22) da Xunta de Galicia

Referencias
Deben usarse los siguientes ejemplos para su formato: [Arial 9 pt]

[1] S. Mura, P. Couvreur, Z. Author, Advanced drug delivery reviews, 64 (2012) 1394.
[2] E. Taboada, R. Solanas, E. Rodríguez, R. Weissleder, A. Roig, Advanced Functional Materials, 19 (2009) 2319

Nuevos materiales poliméricos termoplásticos reforzados con micro y nanopartículas de celulosa

M. M. Castro López[1*], V. López Puente[1], R. Noguerol Cal[1], J. A. Vázquez[2]

[1]I CETIM, Parque empresarial de Alvedro, c/ H 20, 15180- Culleredo (Coruña). España
[2]Grupo ABN, Estrada Baños de Arteixo. 28, Parque Empresarial AGrela, 15008, A Coruña
**mcastro@cetim.es*

Actualmente, la sociedad exige un cambio y el mundo está inmerso en una carrera hacia un modelo de desarrollo eco-sostenible, promoviendo el consumo y uso responsable de todo aquello que nos rodea, siendo una de las líneas de mayor interés la apuesta por los recursos renovables. En este sentido, los polímeros son un material de uso diario y presentes en un sinfín de aplicaciones, y la mayor parte de los mismo se obtiene a partir del petróleo, lo que ha llevado a la búsqueda de materiales de baja huella de carbono e igualmente competitivos en el mercado. Existen múltiples estudios y avances tecnológicos en cuanto a nuevas matrices, así como un amplio interés y dedicación al uso de fibras naturales. Estas fibras tienen un precio bajo (si la fuente es local), baja densidad y altas propiedades mecánicas específicas. Además, estas fibras son generalmente biodegradables y no abrasivas. Sin embargo, estos materiales tienen limitaciones, como la baja estabilidad térmica o la incompatibilidad con los polímeros derivados del petróleo. Estas limitaciones reducen la posibilidad de uso y limitan el potencial de estas fibras [1].

Dentro del proyecto NOVACELL, financiado por la convocatoria CIEN 2017 se ha propuesto el desarrollo y empleo de nanofibras de celulosa y su modificación para el desarrollo de aplicaciones de alto valor añadido basadas en termoplásticos con propiedades mejoradas. En este sentido, la inclusión de nanopartículas de celulosa en porcentajes variables entre 2 y 40 % ha sido evaluada con el objetivo último de conseguir mejoras en las propiedades térmicas, mecánicas y barrera de los nuevos desarrollos alcanzados, todo ello con reducción del material polimérico empleado y con la inclusión de dichas fibras de origen natural, dado así lugar a un material medioambientalmente más sostenible.

Propiedades destacables de los nuevos materiales poliméricos han sido, por ejemplo, la mejoría en cuanto a estabilidad térmica, ya con la incorporación de un 2% de nanocelulosa modificada y variación del espectro de TGA en matrices con un contenido superior al 5% en partículas de celulosa, respecto a matrices vírgenes y/o comerciales, así como la mejora de las propiedades mecánicas de los nuevos materiales desarrollados.

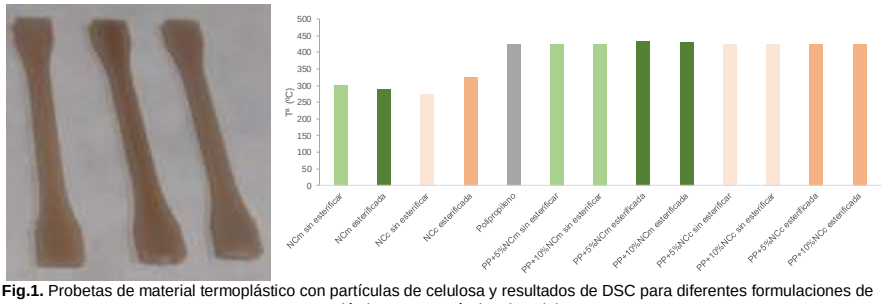


Fig.1. Probetas de material termoplástico con partículas de celulosa y resultados de DSC para diferentes formulaciones de termoplásticos con partículas de celulosa

Agradecimientos

Agradecemos a CDTI la ayuda recibida para la realización del proyecto "Investigación de nuevas generaciones de micro y nanopartículas de celulosa para su uso en productos industriales estratégicos" (IDI-20171076) y al Grupo ABN por facilitar la presentación de los resultado alcanzados.

Referencias

[1] H. Kargarzadeh, J. Huang, N. Lin, I. Ahmad, M. Mariano, A. Dufresne, S. Thomas, Andrzej Gałeski; Progress in Polymer Science 87 (2018) 197 – 227

Development of polysaccharide-based nanosystems using marine-based polymers

Flórez-Fernández N.[1,2*], Afonso I.[1], Pontes J. F.[1], Domínguez H.[2], Grenha A.[1]
[1]Centre for Marine Sciences (CCMAR), Universidade do Algarve, 8005-139 Faro, Portugal
[2]Department of Chemical Engineering, Science Faculty, University of Vigo, 32004 Ourense, Spain
**noelia.florez@uvigo.es*

Polymers from seaweeds often have great biological potential, an attractive characteristic to apply these compounds in biomedicine. Particulate systems, such as nanoparticles, introduce the possibility to create vehicles allowing the delivery of drugs in a controlled way [1]. Based on these premises, polysaccharides from brown seaweeds have been proposed to compose these carriers. Fucoidan, a sulphated polysaccharide present in brown seaweeds, has been gathering increased interest in the field of drug delivery, owing to beneficial biological characteristics conferred by its structure and composition [2]. Chitosan is another polysaccharide of marine origin, which can be used in the preparation of the nanosystems. It is extracted from the exoskeleton of crustaceans and is chemically comprised of *N*-acetylglucosamine and D-glucosamine units. Chitosan's low toxicity and biocompatibility make it suitable for biomedical applications [3]. The preparation of nanoparticles relies on several different methods, one of the most popular being polyelectrolyte complexation. This mild method requires the contact between two polymers of opposite charges, the interaction leading to the formation of the nanocarriers almost instantaneously. The aim of this work was to prepare nanoparticles composed by fucoidan and chitosan using polyelectrolyte complexation. Different polymeric compositions were tested to analyse their influence on the physicochemical characteristics of the carriers, such as size and zeta potential.

Fucoidan from *Fucus vesiculosus* and chitosan were dissolved in ultrapure water and acetic acid at 1% (v/v), respectively, and filtered (0.45 µm and 5-13 µm) before use. Fucoidan/chitosan (FUC/CS) nanoparticles were prepared according to a previously described method [4]. The variables studied to evaluate the differences between formulated nanoparticles were polymer mass ratio, ranging from 4/1 to 1/4, and the pH of the prepared solutions (adjusted to the value 4.0 or not adjusted). Size and zeta potential of freshly prepared nanoparticles were characterised by diluting the samples in deionised water (Zetasizer Nano ZS, Malvern Panalytical, UK). The experiments were done at least in triplicate.

The nanoparticle formulations with adjusted pH (4.0) showed sizes under 300 nm and zeta potential values that are ruled by the carriers' composition. This work allowed to establish the optimal parameters for the preparation of the polymeric nanocarriers, showing promising results for drug delivery applications. The next step will comprise the encapsulation of a model drug, so that a biomedical approach can be envisaged.

Acknowledgements
N.F.F. acknowledges Xunta de Galicia for her postdoctoral grant (ED481B 2018/071). The Ph.D. scholarship to Jorge F. Pontes (PD/BD/137064/2018) is also acknowledged to Fundação para a Ciência e a Tecnologia - Portugal.

References

[1] G. Archana, A. S. Priyanka, S. S. Pranav, International Journal of Pharmaceutics 561 (2019) 244-264.
[2] J. Venkatesan, B. Lowe, S. Anil, P. Manivasagan, A. A. Al Kheraif, K-H. Kang, S-K. Kim, Starch/Stärke, 66 (2015) 1-10.
[3] Grenha, B. Seijo, C. Remuñán-López, European Journal of Pharmaceutical Sciences 25 (2005) 427-437.
[4] Grenha, M. E. Gomes, M. Rodrigues, V. E. Santo, J. F. Mano, N. M. Neves, R. L. Reis, Journal of Biomedical Materials Research A, 92A, (2010) 1265–1272.

Photophysical characterisation of post-modified carbon dots obtained from olive mill wastewaters, and sensing behaviour toward *p*-nitroaniline

Alexandra I. Costa,[1,2] Mário N. Berberan-Santos,[3] José V. Prata[1,2*]
[1]Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007, Lisboa, Portugal; [2]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal; [3]Centro de Química-Física Molecular and Institute of Bioengineering and Biosciences, Instituto Superior Técnico, Universidade de Lisboa, Portugal
**jvprata@deq.isel.ipl.pt*

Carbon dots (C-dots) are a very recent class of nanosized carbon materials that are finding widespread prospective applications in fluorescent bioimaging and nanomedicine, chemo/biosensing, photocatalysis and optoelectronics, potentiated by several remarkable properties which include tunable photoluminescence, outstanding photostability and negligible cytotoxicity [1].
Through simple one-pot green thermochemical methodologies we have recently shown that olive mill wastewaters can be directly converted into luminescent C-dots using easily scalable-up processes [2], thereby contributing to mitigate the current environmental impacts associated with such effluents. Our pursuit to deepening the knowledge about the origins of photoluminescence in C-dots led us to evaluate the effects of post-synthesis thermal treatment on their photoluminescent properties and, inter-alia, the impact on their ability to behave as high sensitive chemosensors.
Upon thermal treatment of as-synthesized C-dots (AS-C-dots) at *ca.* 250 ºC in air, a significant change in their photophysical properties was observed. In the absorption spectrum, instead of a well-defined band near 340 nm, usually assigned to an edge/molecular band (n-π and/or mixed n-π and π-π transitions) in C-dots, a near continuous structureless absorption is observed, accompanied overall by an hyperchromic effect and an increase of lower energy states (> 400 nm) from surface groups. The quantum yield (Φ_F) of post-modified C-dots (PM-C-dots) was severely diminished in comparison to AS-C-dots (from Φ_F = 0.26 to Φ_F = 0.02). The time-resolved fluorescence (TRF) experiments for PM-C-dots revealed a significant shorter average lifetime decay (τ_{ave}) of 6.6 ns as compared to pristine AS-C-dots (τ_{ave} = 13.2 ns). On the other hand, surface analysis by FTIR has indicated the maintenance of amide and carboxylate functional groups and a reduction of *O*-substituted aliphatic components, an outcome also observed by ^{1}H/^{13}C NMR. Albeit with a strong reduction in Φ_F, PM-C-dots show an even greater sensitivity for *p*-nitroaniline (K_{SVcorr} = 9.74 x 10^3 M^{-1}) in buffered aqueous media (pH =7.2) as compared to AS-C-dots (K_{SVcorr} = 7.64 x 10^3 M^{-1}). The rationale beyond the observed photophysical changes and the mechanism of fluorescence quenching of C-dots by *p*-nitroaniline will be discussed based on TRF, UV-Vis and ^{1}H NMR spectroscopy titration experiments.

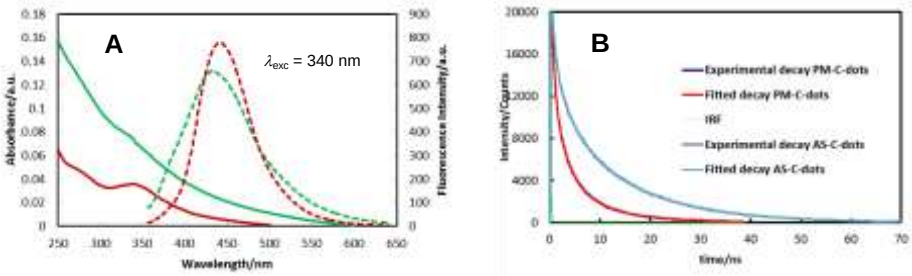


Fig.1. A - UV-Vis (full lines) and emission (dashed lines) spectra of AS-C-dots (red) and PM-C-dots (green); **B** - TRF decay curves of AS-C-dots and PM-C-dots (λ_{exc} = 340 nm; λ_{em} = 442 nm).

Acknowledgements
This work was supported by IPL/2017/NANOCHIRAL/ISEL project funded by IPL and FCT/MCTES under UID/QUI/00616/2019 project. We also thank Dr. A. Fedorov (CQFM/Instituto Superior Técnico/Universidade de Lisboa) for his assistance with the fluorescence lifetime measurements.

References

[1] P. Zuo, X. Lu, Z. Sun, Y. Guo, H. He, Microchimica Acta, 183 (2016) 519.
[2] D. A. Sousa, A. I. Costa, M. R. Alexandre, J. V. Prata, Sci. Total Environ., 647 (2019) 1097.

P-doped glucose-derived carbon/carbon nanotube hybrids for supercapacitors application

Natalia Rey-Raap*, José Luís Figueiredo, Manuel Fernando R. Pereira
Associate Laboratory LSRE-LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, R. Dr Roberto Frias s/n, 4200-465 Porto, Portugal
nataliarey@fe.up.pt

Biomass-derived carbon materials have attracted enormous attention for supercapacitor applications. However, their poor cycling stability and rate capability still hinder their real application. The introduction of carbon nanotubes (CNT) and heteroatoms have proved effective in enhancing the electrochemical properties of carbon-based electrodes [1]. However, the effect of phosphorus heteroatoms has not yet been extensively studied and their role on supercapacitor performance is still unclear. Herein, a simple method is developed to synthesize P-doped carbon hybrids with adequate electrochemical properties. Glucose-derived carbon/CNT hybrids were prepared by i) hydrothermal carbonization followed by phosphoric acid activation and ii) by introducing phosphoric acid during the hydrothermal polymerization of glucose followed by conventional carbonization.
The role played by phosphoric acid on the final textural and chemical properties of the samples was thoroughly investigated by varying the temperature of activation/carbonization. It was observed that temperatures higher than 700 ºC were needed to chemically activate the samples with phosphoric acid. In addition, 800 ºC seems to be the optimum temperature to generate the largest amount of micropores. In contrast, the addition of H_3PO_4 during the polymerization of glucose gave rise to materials with specific surface areas similar to those of common porous carbon materials. Regardless of the method of preparation, the treatments with H_3PO_4 resulted in the incorporation of oxygen and phosphorus functionalities. However, the results obtained show that most of the incorporated oxygen in the chemically activated samples was linked to phosphorus forming functional groups, which were mainly located in the bulk of the carbon structure, while the addition of H_3PO_4 during the polymerization of glucose gave rise to materials with a high degree of oxidation of the carbon surface. The temperature employed also results in different phosphorus functionalities. At 700 ºC only C-O-P-O_3 and C-P-O_3 groups were observed, while C-P=O and C-P groups appeared at 800 ºC and 900 ºC, respectively.
In addition, the effect of the physicochemical properties on the supercapacitor performance was also examined. The oxygen functionalities anchored to carbon seem to contribute greatly to the pseudocapacitance, while the oxygen groups linked to phosphorus enhance the electrostatic charge. Regarding their application as electrode materials in supercapacitors, it can be concluded that higher surface areas along with a higher amount of phosphorus increase the total capacitance. Higher content of phosphorus allows increasing the current density applied, while the formation of C-P groups on the surface of the carbon increases the capacitance retention. Thus, the sample activated with H_3PO_4 at 800 ºC showed the most interesting properties as electrode material, with a capacitance of 110 F g^{-1}, an energy density of 10 Wh kg^{-1}, a power density of 9 kW kg^{-1} and a very stable electrochemical performance with capacitance retention of 93 % after 10000 cycles at 10 A g^{-1}. Therefore, it can be concluded that the addition of phosphorus functionalities is a successful strategy to enhance the electrochemical performance of low-cost glucose-derived carbon/carbon nanotube hybrids.

Acknowledgement
This work was financially supported by Project UNIRCELL – POCI-01-0145-FEDER-016422 – funded by European Structural and Investment Funds (FEEI) through - Programa Operacional Competitividade e Internacionalização - COMPETE2020, Project SmarText4Storae – POCI-01-0145-FEDER-031271 – funded by FCT – Fundação para a Ciência e a Tecnologia, P2020|COMPETE - Projetos em Todos os Domínios Científicos and by national funds through FCT - Fundação para a Ciência e a Tecnologia, I.P; and Associate Laboratory LSRE-LCM - UID/EQU/50020/2019 - funded by national funds through FCT/MCTES (PIDDAC).

References

[1] N. Rey-Raap, M. Enterria, J.I. Martins, M.F.R. Pereira, J.L. Figueiredo, ACS Appl. Mater. Interfaces 11 (2019) 6066-6077.

Synthesis of carbon nanostructures by chemical vapour deposition over Ni-Al co-oxides using plastic solid waste as precursor

Ana P. Ferreira da Silva[1,2,3], Jose L. Diaz de Tuesta[1,2,*], Aulus R.R. Bineli[3], Adrián M.T. Silva[2], Helder T. Gomes[1,2]

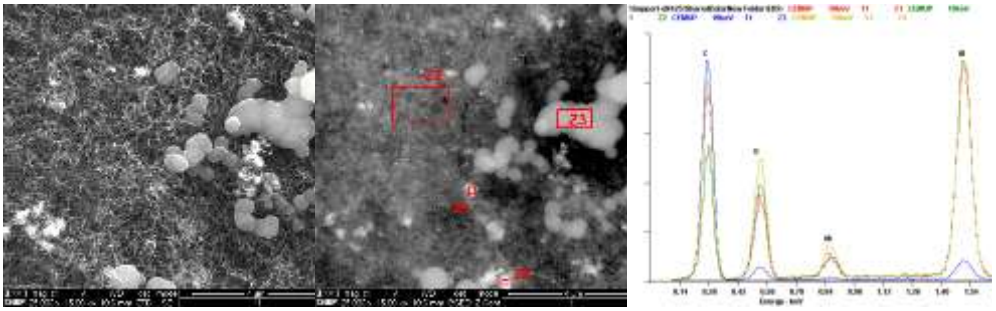
[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2]Laboratory of Separation and Reaction Engineering–Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[3]Universidade Tecnológica Federal do Paraná (UTFPR), Campus de Londrina, Av. dos Pioneiros, 3131 - Jardim Morumbi, Londrina - PR, 86036-370, Brasil

**jl.diazdetuesta@ipb.pt*

Europe contributed with 18.5% of the almost 350 Mton of plastics produced worldwide in 2017. Polypropylene (PP) and light and heavy density polyethylene (LDPE and HDPE, respectively) represents near 49.1% of the plastics produced in Europe. Packaging is the main application of these plastics, so typically they have one-single use. In 2014, 25.8 Mton of post-consumer plastic solid wastes (PSWs) ended up in the official waste streams (54.0% of the demanded quantity), 69.2% being recovered through recycling (7.7 Mton) and energy recovery processes (10.2 Mton), the remaining 30.8% sent to landfill [1]. Concerns about usage and disposal are diverse and include accumulation of PSWs in landfills and in natural habitats, physical problems for wildlife resulting from ingestion or entanglement in plastic and the leaching of chemicals from plastic products [2]. The incineration of PSWs contributes to pollution due to harmful and toxic emissions and both incineration and mechanical recycling are costly and may or may not be economically viable in different situations [3]. More attractive strategies are the production of carbon nanomaterials using PSWs as carbon precursors [4]. In this work, Ni-Al co-oxide nanoparticles were synthesized by co-precipitation and employed as catalysts in the chemical vapour deposition of CNTs when using LDPE as carbon precursor and as model compound of plastic solid waste. Fig. 1 shows the scanning electron micrographs of the carbon nanostructures prepared at 1000 ºC during 1 h in a tubular furnace under 10 $NmL \cdot min^{-1}$ nitrogen flow. As can be observed, CNTs and carbon nanospheres were produced.



(a) (b) (c)

Fig.1. Scanning electron micrographs obtained in (a) secondary electron mode and (b) electron backscattered diffraction, and (c) local elemental analysis.

Acknowledgements

This work is a result of Project "PLASTIC_TO_FUEL&MATs - Upcycling Waste Plastics into Fuel and Carbon Nanomaterials", with the reference POCI-01-0145-FEDER-031439, through the Competitiveness and Internationalization Operational Program, supported by the European Regional Development Fund (ERDF); the Associate Laboratory LSRE-LCM - UID/EQU/50020/2019 - funded by national funds through FCT/MCTES (PIDDAC); and CIMO (UID/AGR/00690/2019) through FEDER under Program PT2020.

References

[1] Plastics – the facts 2018, Plastic Europe Association of Plastics Manufactures, 2018.
[2] R.C. Thompson, C.J. Moore, F.S. Vom Saal, S.H. Swan. Philosophical Transactions of the Royal Society B. 364 (2019) 2153.
[3] J. Aguado, D.P. Serrano, J.M. Escola. Industrial & Engineering Chemistry Research 47 (2008) 7982.
[4] C. Zhuo, Y.A. Levendis. Journal of Applied Polymer Science 131 (2014) 1001.

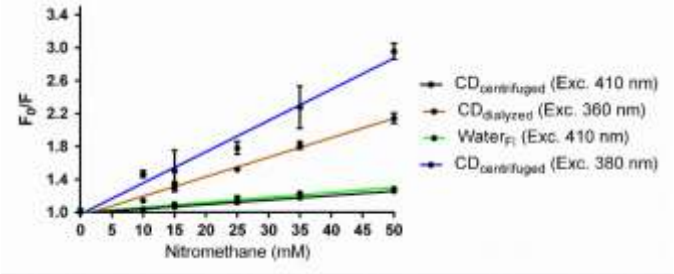
Study of the interaction between fluorescent Carbon dots and the fluorescent by-products that result from their synthesis

Ricardo M.S. Sendão[1,*], Joaquim C.G. Esteves da Silva[1], Luís Pinto da Silva[1]
[1]Chemistry Research Unit, Faculty of Sciences – University of Porto, Porto, Portugal
**ricardo241196@hotmail.com*

Carbon dots (CDs) are carbon-based nanoparticles that possess several advantageous optical and electronic properties, including a high photoluminescence, broadband optical absorption, biocompatibility, high photostability, low toxicity, and good water solubility. [1] Although CDs are already used for several purposes, the origin and mechanism of their photoluminescence remains to be clarified, with different authors proposing mechanisms based in the role of quantum confinement effects, self-trapped excitons, edge states, delocalized surface states and exciton-hole recombination. [2] More recently, some reports have demonstrated that an important part of the photoluminescence commonly ascribed to CDs can in fact result from strongly fluorescent molecular by-products that are formed during the CD synthesis and are capable of masking the CD true photoluminescence. [2]

Herein, we studied the effects caused by these fluorescent by-products on the photochemical properties of CDs. Towards this end, we synthesized a citric acid and urea-based CD through a microwave-assisted approach. Purification by dialysis followed and resulted in the obtention of two fluorescent fractions: the CD itself and the fluorescent molecular by-products that resulted from the CD synthesis. Different techniques, such as XPS, mass spectrometry, FT-IR analysis and UV-Vis absorption and fluorescence studies, were employed to characterize the samples. Studies regarding the photochemical response of both components (CD and by-products) towards neutral and ionic species (electron-donors and electron-withdrawing molecules) revealed that while the fluorescent by-products themselves have no response towards these molecules, they are capable of increasing the CDs' photochemical response to them. [3] Interestingly, when co-existing in the same solution, the CD and the fluorescent by-products do not behave as two separate species but instead display a synergistic effect in which the fluorescent by-products influence the photochemical properties and reactivity of the CD (Fig. 1) and vice-versa. [3] This could be exploited for the making of novel hybrid materials, useful for the development of the CD-based applications.

Fig.1 – F_0/F values in the presence of different concentrations of nitromethane (0-50 mM) and excitation wavelengths for co-existing CD and fluorescent by-products excited at 410 nm (black); CD excited at 360 nm (orange); fluorescent by-products excited at 410 nm (green); co-existing CD and fluorescent by-products excited at 380 nm (blue).



Acknowledgements
We thank the Fundação para a Ciência e Tecnologia for financial support (NORTE-01-0145-FEDER-00028; POCI-01-0145-FEDER-006980; CEECIND/01425/2017; PTDC/QEQ-QAN/5955/2014).

References

[1] Malyukin, Y.; Viagin, O.; Maksimchuk, P.; Dekaliuk, M.; Demchenko, A. *Nanoscale* 10 (2018) 9320.
[2] Kasprzyk, W.; Swiergosz, T.; Bednarz, S.; Walas, K.; Bashmakova, N.V.; Bogdat, D. *Nanoscale* 10 (2018) 13889.
[3] Sendão, R., Crista, D., Afonso, A., Martínez de Yuso, M., Algarra, M., Esteves da Silva, J., Pinto da Silva, L., *Phys. Chem. Chem. Phys.* (2019) DOI: 10.1039/C9CP03730F

Energy Storage for Fashion Applications: Fluorescent Textile Supercapacitors

Joana S. Teixeira[1,*], André M. Pereira[2], Clara Pereira[1]
[1] REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.
[2] IFIMUP-IN, Department of Physics and Astronomy, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.
**joanafsteixeira@hotmail.com*

In the current Era of the Internet of Things, the Society is continuously surrounded by the development of smart technologies that allow the interconnection between devices and with the world. The production of miniaturized technologies, which include smartphones, smartwatches, biochemical sensors, digital cameras, medical electronic devices, among others, is expanding due to their capability to be incorporated on clothes/body. However, the vast use of smart technologies created an energy problem, increasingly demanding the inclusion of energy storage devices, such as supercapacitors (SC) and batteries [1]. A promising strategy for wearable applications is the design of textile SCs based on the use of nanomaterials that allow the upgrading of the SCs performance, while maintaining intrinsic properties of the fabrics such as flexibility, lightness and comfort [2]. In the fashion world, the modification of textiles with functional carbon and/or nanomaterials with optical properties allows imparting new advanced properties to the fabrics, such as electrical conductivity and light-responsive features.

In this work, nanomaterials with luminescent and electrical properties were used to develop a dual-function textile SC that presents fluorescent properties by the action of UV light and simultaneously stores energy. To achieve that goal, textile substrates were coated with a conductive carbon nanomaterial (CN) and a fluorescent pigment (FluoP) and used as electrodes to produce the smart textile photo-SC (SC_CN_FluoP). For comparison, a non-fluorescent SC was also produced (SC_CN). Characterization techniques including XRD, FTIR-ATR and SEM-EDS confirmed the successful preparation of the functional textile electrodes. Both textile SCs revealed a double layer capacitive behavior. The SC_CN_FluoP presented lower internal resistance of 556.0 Ω than SC_CN (743.3 Ω) and higher specific capacitance of 8.98 F g^{-1} (*vs.* 8.10 F g^{-1} for SC_CN). The energy and power densities of SC_CN_FluoP were 3.24 W h kg^{-1} and 383.0 W kg^{-1}, respectively, while the SC_CN device afforded 3.06 W h kg^{-1} at 328.7 W kg^{-1}. The exposure of the SC_CN_FluoP to UV light (λ = 254 and 365 nm) triggered a change of its color from black to orange – Fig. 1 –, highlighting the versality of these devices to the fashion area.

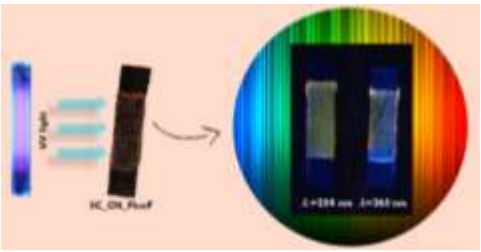


Fig.1. Response of the fluorescent textile supercapacitor device to UV light (λ = 365 nm and 254 nm).

Acknowledgements
Work was funded by FEDER through COMPETE 2020-POCI and by FCT/MCTES under Program PT2020 in the framework of the projects PTDC/CTM-TEX/31271/2017, UID/QUI/50006/2019 and UID/NAN/50024/2013. JST thanks FCT for MSc. grant in the project PTDC/EME-SIS/31575/2017. CP thanks FCT for FCT Investigator contract IF/01080/2015.

References
[1] Q. Xue et al., Small, 13 (2017) 1701827.
[2] U. Gulzar et al., J. Mater. Chem. A, 4 (2016) 16771.

The intrinsic redox ability of Electrogenerated Hydrophilic Carbon Nanomaterials

Andreia D. Veloso, Maria C. Oliveira
CQ-VR and Chemistry Department, University of Trás-os-Montes e Alto Douro, Vila Real, Portugal
**mcris@utad.pt*

The inherent electrochemistry of carbon-based nanomaterials in aqueous solution, i.e, their ability to be oxidized or reduced at relatively mild potentials (within the range ± 0.5 V), dictates their potential use in cutting-edge technological therapeutic applications. Thus, it is most important to fully characterize the intrinsic electrochemical properties of the carbon-based materials and, to understand how it depends on the synthesis conditions.

Typically, electrochemical studies of carbon-based materials are focused on their characterization using surface sensitive redox probes in solution (e.g. $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$), wherein the carbon-based material is immobilized on a glassy carbon electrode (drop-cast procedure) [1-2]. In such studies, it is not elucidated the intrinsic redox ability of the carbon-based materials, neither their electrochemical behavior in aqueous medium.

The main goal of this work is to evaluate the redox ability, in aqueous solution, of a recently developed carbon-based material, the Electrogenerated Hydrophilic carbon (EHC) nanomaterial, making use of its remarkable ability to dissolve in water. In addition, this study aims to investigate if the electrochemical properties of the EHC material are dependent on the buffer electrolyte used on the EHC synthesis.

To pursue these objectives, the EHC was generated in three different electrolytes, namely phosphate, citrate, and glycine buffers, and the resulting nanomaterials (EHC@phosphate, EHC@citrate, EHC@glycine) were electrochemically characterized by cyclic voltammetry in a micro three-electrode cell using a glassy carbon electrode.

The obtained results allow concluding that the EHC ability to donate and/or accept electrons, and corresponding electron transfer mechanism, can be selectively tuned by the nature of the electrolyte used in the electrochemical synthesis of the EHC nanomaterial.

Acknowledgments

FCT/MEC (UID/QUI/00616/2013), FEDER (Partnership Agreement PT2020) ERDF (NORTE-01-0145-FEDER-000024); A. D. Veloso (SFRH/BD/138425/2018) thank FCT/MEC.

References

[1] D. A. Brownson, G. C. Smith, C. E. Banks, R. Soc. open sci., 4 (2017) 171128.
[2] A. Ambrosi, A. Bonanni, Z. Sofer, J. S. Cross, M. Pumera, Chem. Eu. J., 17, (2011) 10763.

QUÍMICA DE POLÍMEROS

Remediación ambiental en vías férreas: captación de metales pesados a través del uso de polímero impresos iónicamente (IIPs)

M. M. Castro-López[1,*], A. Bañón-Goiriz[1], R. Noguerol-Cal[1]

[1]CETIM, Parque empresarial de Alvedro, c/ H 20, 15180- Culleredo (Coruña). España
** mcastro@cetim.es*

La contaminación asociada al transporte ferroviario, la cual abarca tanto la propia vía, como terrenos aledaños y zonas subterráneas, es de especial importancia y presenta efectos nocivos preocupantes, ya que durante la circulación de los trenes se produce la liberación de metales pesados e hidrocarburos, lo que supone un riesgo tóxico para la salud y el medio ambiente. Su reducido estudio, así como la ausencia de legislación ambiental específica, llevaron al desarrollo del proyecto RECOVER, focalizado en el desarrollo de soluciones anticontaminantes dirigidas principalmente a vías férreas. Entre las diferentes soluciones propuestas, el desarrollo de compuestos específicos encargados de captar los metales pesados liberados sobre el balasto de las vías (polímeros impresos iónicamente o IIPs), así como una solución (adhesivo o recubrimiento) capaz de portar los IIPs sobre el balasto han sido consideradas.

Los IIPs son materiales nanoporosos que presentan una alta afinidad por los analitos de interés: una vez lixiviado el ión de impresión, pueden volver a unir, detectar o transportar el analito diana en presencia de iones inorgánicos. De forma general, se basan en la formación de un complejo entre un ligando específico y el ión metálico de interés para producir sitios de unión específicos, tras la lixiviación del metal, basándose así en una reticulación de la plantilla (ión metálico) con el monómero funcional [1]. Para el desarrollo de IIPs para captación de metales pesados se empleó la técnica de polimerización por precipitación. En cuanto a la solución portadora, se evaluaron diferentes sistemas poliméricos de diferente naturaleza (poliuretano, epoxi, acrílico).

Los resultados de laboratorio fueron validados mediante la realización de pruebas en campo, mediante la aplicación de diferentes soluciones y recabando resultados tras un período de 8 meses de validación. El análisis de resultados puso de manifiesto la retención de metales en el sistema IIP + sistema portador aplicado al balasto y con elución máxima respecto al metal reenlazado de 1,2%, indicando la retención del metal en la solución del IIP aplicado en el balasto y, por lo tanto, la validad de la tecnología desarrollada, la cual, de este modo permite una clara reducción de la contaminación en metales pesados que se emitiría al medio en vías férreas, logrando porcentajes de reducción superiores al 50% para gran parte de los metales de mayor presencia (reducción del Cu: 92%; Zn: 81%; Ni: 78%; Cr: 72%; Pb: 60%).

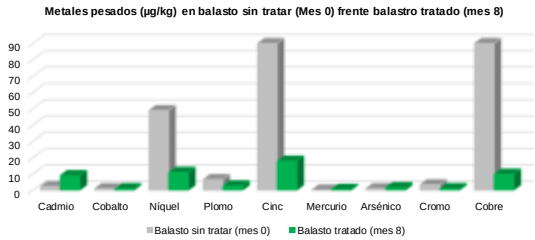


Fig.1. Balasto con solución en vías; concentración de metales en lixiviados de balasto en validación

Agradecimientos
Los autores expresan su agradecimiento al Ministerio de Economía y Competitividad por su financiación al proyecto RECOVER (RTC-2015-4043-4) bajo la convocatoria RETOS-Colaboración.

Referencias

[1] Taher Alizadeha, Mohamad Reza Ganjalib, Mashaalah Zareb, Analytica Chimica Acta, 689 (2011) 52-59.

Poly(diphenylacetylene)s: optical properties and structural analysis

Juan José Tarrío[1,*], Emilio Quiñoá, Félix Freire[2]
[1]Departamento de Química Orgánica/CIQUS, Santiago de Compostela, España
[2]Departamento de Química Orgánica/CIQUS, Santiago de Compostela, España
*juanjose.tarrio@usc.es

In nature, helical structure is present in a lot of biomolecules such as proteins, nucleic acids or polysaccharides. It's also known this secondary structure is directly related with the properties of those molecules. For this reason, scientific community has expended time and effort to obtain new molecules that can adopt the helical structure to be able of emulating the functions and properties of biomolecules. Thus, helical polymers borned.

Dynamic helical polymers have been widely studied due to the potential of these materials to act as sensors, chiral stationary phases to chromatographic separation or chiral catalyst because of the helical sense control via external stimuli. [1]

In order to find new structures and new functions in helical polymers, this work addressed the synthesis of a novel family of materials denominated poly(diphenylacetylene)s. These polymers are a special class of conjugated polymers that present the abilities of fluorescence emission and a high thermal stability. [2]

Until now, researching groups only have prepared achiral poly(diphenylacetylene)s or chiral with a one preferred helical sense. Maeda *et al* has obtained a symmetric poly(diphenylacetylene) that presents both helical senses modifying the ratio of chiral/achiral amine used as pendant moiety obtaining something similar to a copolymer. [3]

In this work, the synthetized polymers have thermochiral properties induced by a solvent because of the presence of a chiral pendant based on methylester aminoacids. This is the first time a poly(diphenylacetylene) presents a dynamic behaviour obtaining both helical sense via external stimuli. Moreover, some of the emission properties are analysed and, it is the first time that AFM images of these kind of polymers have been obtained.

ACKNOWLEDGMENTS:
We thank Ministerio de Ciencia Innovación y Universidades (CTQ2015-70519-P, CTQ2014-61470-EXP), Xunta de Galicia (Centro singular de investigación de Galicia accreditation 2016-2019, GRC2014/040), the European Union (European Regional Development Fund – ERDF) for financial support and Ministerio de Educación y Formación Profesional for an FPU predoctoral fellowship.

References

[1] F. Freire, J. M. Seco, E. Quiñoá, & R. Riguera, R., *J. Am. Chem. Soc.*, 134 (2012) 19374-19383.
[2] Y. J. Jin, & G. Kwak, *Polym. Rev.*, 57 (2017) 175-199.
[3] K. Maeda, M. Maruta, Y. Sakai, T. Ikai & S. Kanoh. *Molecules*, 21 (2016), 1487.

Cellulose based gel polymer electrolytes for energy storage

Tiago G. Paiva[1*], Teresa Cordeiro[2], Madalena Dionísio[2], Eurico J. Cabrita[3], Marta C. Corvo[1]

[1]CENIMAT/i3N Dep. Materiais Fac. Ciências e Tecnologia, UNL 2829-516 Caparica, Portugal
[2]LAQV-REQUIMTE/CQFB, Dep. Química, Fac. Ciências e Tecnologia – UNL, 2829-516 Caparica, Portugal[3]UCIBIO, REQUIMTE, Dep. Química Fac. Ciências e Tecnologia, UNL 2829-516 Caparica Portugal *t.paiva@campus.fct.unl.pt*

The transition to carbon free technologies demands for diverse energy storage (ES) solutions, motivating the search for new materials with high capacity, including safe, electro and thermal stable electrolytes for lithium Ion batteries. This is crucial for several fields such as small electronic devices, electrical/hybrid transports and power grids.[1]. Ionic liquid (IL) derived materials such as polymeric electrolytes and gel polymer electrolytes (GPE) are viable alternatives[2] to the conventional systems that contain volatile and flammable organic solvents with several safety risks.

The main shortcoming of polymeric electrolytes is their low conductivity at room/low temperatures. GPE blend their polymeric qualities of safety enhancement with the better conductivity of liquid electrolytes.[3] ILs can be used as polymeric materials to form gels or as monomers to enhance the conductivity of GPEs formed with neutral polymers.[4,5] These materials, with their usual low vapor pressure and non-flammability can be tailored to have the necessary electrochemical and thermal stability to be used in electrolytes.

Cellulose is one of the most abundant polymers in nature and because it is a renewable, biodegradable, and biocompatible material it is the focus of many research efforts because of the desirability of large-scale applications. However, its low solubility in common organic solvents impairs a widespread application.

Herein we present our latest efforts on the development of cellulose/IL derived GPEs. The chemical modification of cellulose allowed the disrupting the H-bonding network, and an easier processability. GPEs were obtained by the sequential dissolution and gelation of the derivatized polymers.[6] Li-ion electrolytes were also formed by doping the solutions with a lithium salt. The ion dynamics of the GPEs and respective precursors was studied using Nuclear Magnetic Resonance (NMR)[7] exploiting the fact that abundant NMR active isotopes, such as ^{1}H, ^{7}Li or ^{19}F are present . Relaxation measurements and pulsed field gradient diffusion experiments allowed probing ion motions in different timescales and Nuclear Overhauser experiments were used to measure interactions within the electrolyte components. The information about the different species in the material was used to rationalize the properties of the gel, providing an insight to the lithium ions transport.

Acknowledgments

This work has been carried out with financial aid from FEDER funds through the COMPETE 2020 Programme and National Funds through FCT, the Portuguese Foundation for Science and Technology (POCI-01-0145-FEDER-007688, Reference UID / CTM / 50025) and SFRH/BD/133447/2017. The NMR spectrometers are part of The National NMR Facility, supported by Fundação para a Ciência e a Tecnologia (ROTEIRO/0031/2013 - PINFRA/22161/2016) (co-financed by FEDER through COMPETE 2020, POCI, and PORL and FCT through PIDDAC).

References

[1] A. A. Tidblad, H. Berg, K. Edström, *Swedish Hybrid Veh. Cent.* **2015**, 1–88.
[2] M. Moreno, E. Simonetti, G. B. Appetecchi, M. Carewska, M. Montanino, G.-T. Kim, N. Loeffler, S. Passerini, *J. Electrochem. Soc.* **2017**, *164*, A6026–A6031.
[3] P. Wang, H. Zhang, J. Chai, T. Liu, R. Hu, Z. Zhang, G. Li, G. Cui, *Solid State Ionics* **2019**, *337*, 140–146.
[4] M. Brinkkötter, E. I. Lozinskaya, D. O. Ponkratov, Y. Vygodskii, D. F. Schmidt, A. S. Shaplov, M. Schönhoff, *J. Phys. Chem. C* **2019**, *123*, 13225–13235.
[5] M. Kostag, O. A. El Seoud, *Carbohydr. Polym.* **2019**, *205*, 524–532.
[6] C. Echeverria, S. N. Fernandes, P. Lucio, M. D. E. Almeida, M. H. Godinho, M. C. Corvo, T. G.Paiva, I. Rosete, *PT 110572 A*, **2019**.
[7] M. M. Lopes, R. V. Barrulas, T. G. Paiva, Ferreira, Ana S D, M. Zanatta, M. C. Corvo, *IntechOpen* **2019**, DOI 10.5772/intechopen.89182.

QUÍMICA ANALÍTICA

Determinación de sustancias tóxicas en superficies elaboradas con caucho reciclado mediante GC-MS/MS

Daniel Armada[1*], María Celeiro[1], Thierry Dagnac[2], María Llompart[1]

[1]Laboratorio de Investigación y Desarrollo de Soluciones Analíticas (LIDSA), Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Química, E-15782, Santiago de Compostela, España

[2]Agencia Galega da Calidade Alimentaria, Centro de Investigaciones Agrarias de Mabegondo (AGACAL-CIAM), Unidad de Contaminantes Orgánicos, Apartado 10, 15080, A Coruña, España

*daniel.armada@rai.usc.es

El caucho de neumático es un material que se reutiliza para fabricar superficies deportivas, superficies de parques infantiles, pavimento para suelos urbanos (ej: retención de raíces de árboles) y como relleno en los campos de fútbol de hierba artificial. Esto representa un riesgo para la salud humana debido a la presencia de sustancias tóxicas en el caucho [1].

Debido a la preocupación surgida en los últimos tiempos por el uso de caucho reciclado en superficies deportivas de recreo, este estudio evalúa la presencia de cuarenta y dos compuestos incluyendo hidrocarburos policílicos aromáticos (PAHs), plastificantes (ftalatos y adipatos), antioxidantes y aditivos vulcanizantes. Los compuestos objeto de estudio fueron seleccionados de acuerdo a estudios previos realizados sobre campos de fútbol de césped artificial [2] y superficies infantiles de juego [3].

El método seleccionado para determinar estos compuestos se basa en la extracción asistida por ultrasonidos (UAE), obteniendo resultados satisfactorios, seguida de un análisis mediante cromatografía de gases acoplada con espectrometría de masas en tándem (GC-MS/MS). Siendo esta la primera vez que se utiliza esta técnica para analizar este tipo de muestras.

Las muestras fueron tomadas en diferentes ayuntamientos de la provincia de A Coruña. Fueron tomadas de instalaciones tanto interiores como exteriores y algunas de ellas fueron adquiridas en tiendas especializadas.

El análisis confirmó la presencia de un gran número de sustancias tóxicas entre las que se incluyen, PAHs, ftalatos, adipatos, antioxidantes y aditivos vulcanizantes, incluyendo compuestos cancerígenos como criseno, benzo[a]pireno y benzo[a]antraceno. Estos contaminantes han sido detectados en todas las muestras analizadas excluyendo dos de ellas: un granulado de corcho utilizado como relleno en un campo de fútbol y una muestra de arena de juego tomada de un parque situado en una zona urbana de alta densidad de tráfico.

Agradecimientos

Este trabajo ha sido apoyado por el Proyecto UNST10-1E-491 (Programa de Infraestructuras, MINECO, España) y RED2018-102522-T (Ministerio de Ciencia, Innovación y Universidades, España). Los autores pertenecen al Grupo de Investigación Competitivo de Galicia GPC 2017/04, GPC 2019/13 y a la Asociación Estratégica de CRETUS (ED431E 2018/01). Estos programas se encuentran cofinanciados por FEDER (UE).

Referencias

[1] J. G. M. Van Rooij, F. J. Jongeneelen, *Int. Arch. Occup. Environ.Health*, *83* (2010) 105-110.
[2] M. Celeiro, T. Dagnac, M. Llompart, *Chemosphere,* 195 (2018) 201-211.
[3] M. Llompart, L. Sanchez-Prado, J.P. Lamas, C. Garcia-Jares, E. Roca, T. Dagnac, *Chemosphere*, *90* (2013) 423-431.

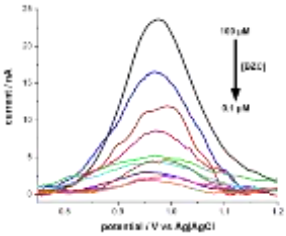
Electrochemical sensing of benzocaine for cocaine profiling via molecularly imprinted polymers

Alnilan Lobato[1], Renata Antunes Grothe[1], Nikola Tasić[1], Thiago RLC Paixão[1], Luís Moreira Gonçalves[1,*]

[1]Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo (USP), São Paulo, SP, Brazil
**lmgoncalves@iq.usp.br*

Benzocaine (BZC) is an anaesthetic widely used for medical and dentistry purposes, however it is often found in cocaine samples as a volume boosting adulterant [1,2]. Thus, quantitative and qualitative BZC determination can allow the authorities to identify the origin of apprehended drugs. An electrochemical sensor for BZC was developed based on the electropolymerization of 3-amino-4-hydroxybenzoic acid (3,4-AHBA) in a medium with BZC as the template molecule. Electropolymerized molecularly imprinted polymers (MIPs) hold several advantages like portability, speed, low reagent consumption and selectivity [3,4]. The sensor worked by measuring the BZC oxidation signal through square-wave voltammetry (SWV) or electrochemical impedance spectroscopy (EIS) after an incubation period of 45 minutes. The analytical methodology was validated (LOD below 2.9 µmol L^{-1}) and suitable sample studies in urine and cocaine samples provided by the Brazilian Federal Police (PF) were performed. This opportunity was also seized to comprehensively study the BZC electrochemical oxidation and develop computer simulations concerning the MIP's chemical interactions.

Fig.1. Calibration curve



Acknowledgements
Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP: 2018/14425-7, 2019/11214-8 and 2018/13922-7), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq: 117865/2019-2) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES: 001) are acknowledged for financial support.

References

[1] J.M. Freitas, D.L.O. Ramos, R.M.F. Sousa, T.R.L.C. Paixão, M.H.P. Santana, R.A.A. Muñoz, E.M. Richter, Sensors Actuators B Chem. 243 (2017) 557–565.
[2] M.O. Salles, W.R. Araujo, T.R.L.C. Paixão, J. Braz. Chem. Soc. 27 (2016) 54–61.
[3] J.G. Pacheco, P. Rebelo, F. Cagide, L.M. Gonçalves, F. Borges, J.A. Rodrigues, C. Delerue-Matos, Talanta. 194 (2019) 689–696.
[4] R.A.S. Couto, S.S. Costa, B. Mounssef, J.G. Pacheco, E. Fernandes, F. Carvalho, C.M.P. Rodrigues, C. Delerue-Matos, A.A.C. Braga, L. Moreira Gonçalves, M.B. Quinaz, Sensors Actuators B Chem. 290 (2019) 378–386.

Determinación Del Contenido De Elementos Traza En Zumos Comercializados En España Y Portugal

Max José Belo de Souza[1,2]*, María Carmen Barciela Alonso[1], Manuel Aboal Somoza[1], Pilar Bermejo Barrera[1]

[1] Universidad de Santiago de Compostela. Departamento de Química Analítica, Nutrición y Bromatología. Facultad de Química.. Avenida das Ciencias S/N, 15782, Santiago de Compostela, España

[2] Instituto Federal de Educação, Ciência e Tecnologia do Espírito Santo. Coordenadoria de Licenciatura em Química. Avenida Morobá n. 248, Bairro Morobá, 29192-733, Aracruz, Brasil

**e-mail: maxjose.belo@rai.usc.es*

En el presente trabajo se ha realizado la validación de un método para la determinación de Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, V, Sb, Mo y Zn en zumos de frutas comercializados en España y Portugal. El pretratamiento de la muestra se realizó mediante digestión acida asistida por microondas utilizando una mezcla de ácido nítrico y peróxido de hidrógeno. La determinación de los analitos en las muestras digeridas se realizó por Espectrometría de Emisión con Plasma de Acoplamiento Inductivo (ICP-OES) y/o Espectrometría de Masas con Plasma de Acoplamiento Inductivo (ICP-MS). El método presenta una buena precisión (RSDs < 10 %), sensibilidad (LODs:ICP-OES de 1,5 µg/L Ca – 0,3 µg/L Mg y para ICP-MS de 0,002 µg/L V y Co – 6 µg/L Na) y recuperación analítica (79–120 %).

Los contenidos de Al, Ca, Co, Cr, Cu, Mg, Na, Zn, Fe, Mn, Mo y Ni concuerdan en general con los valores recogidos en la bibliografía [1 2 3 4]. El As y Sb no fueron detectados en las muestras analizadas. El Pb fue detectado en una muestra de zumo de manzana, presentando una concentración de 61,7 µg/L Pb, que es superior a lo indicado por la legislación[5 6 7]. Las concentraciones de Cd encontradas en las muestras están dentro de los límites establecidos por la legislación[7]. En cuanto al vanadio, los mayores valores de concentración se encuentran en los zumos de naranja recién exprimida, presentando valores de 11,7-91,4 µg/L, superiores a los obtenidos por Tormen *et al*.[8] en análisis de 19 zumos (0,7-33,1 µg/L V). Para Ca, Na, Mg, Zn, y Fe las concentraciones se encuentran en el rango de 10,2-96,5 mg/L para el Ca, 3,1-39,9 mg/L Na, 17,5-104,7 mg/L Mg, 0,084-0,98 mg/l Zn y 0,16-3,71 mg/L Fe. Los valores obtenidos en el estudio son concordantes con los valores obtenidos en estudios publicados previamente[1].

Agradecimientos

Los autores pertenecen al Grupo de Referencia Competitivo ED431C2018/19 (Xunta de Galicia) y a la Agrupación Estratégica de Materiales-AEMAT (ED431E2018/08), de la Universidad de Santiago de Compostela) financiados por la Consellería de Eduación, Universidade e Formación Profesional de la Xunta de Galicia. Estos programas están cofinanciados por los fondos FEDER (UE).

Referencias

[1] M. Harmankaya, S. Gezgin, M. M. Özcan, Environ. Monit. Assess, 184 (2012) 5415.
[2] D. S. Velimirović, S. S Mitić, S. B. Toši, B. M. Kaličanin, A. N. Pavlović, M. N. Mitić, Tropical Journal of Pharmaceutical Research, 12 (2013) 805.
[3] I. Coelho, A. Rego , S. Gueifão, A. C. Nascimento, I. Castanheira, Journal of Chemometrics. 31 (2017) 1.
[4] A. B. Williams, O. O. Ayejuyo, A. F. Ogunyale. Environmental Monitoring and Assessment, 156 (2009) 303.
[5] CODEX ALIMENTARIUS. Roma, FAO, 2018.
[6] REGULAMENTO (CE) Nº 1881/2006. Luxembourg, Jornal Oficial da Unión Europea, 2006.
[7] RDC Nº 42. Brasília, Diário Oficial [da] República Federativa do Brasil, 2013.
[8] L. Tormen, D. P. Torres, I. M. Dittert, R. G. O. Araújo, V. L. A. Frescura, A. J. Curtius, Journal of Food Composition and Analysis, 24 (2011) 95.

Application of FTIR (Fourier Transform Infrared Spectroscopy) for determination of nutritional and antinutritional parameters in bean samples

Bruna Carbas[1,2*], Nelson Machado[1], David Oppolzer[1], Luís Ferreira[1], Carla Brites[2], Eduardo AS Rosa[1] and Ana IRNA Barros[1]

[1]Centre for the Research and Technology of Agro-Environmental and Bilogical sciences, University of Trás-os-Montes and Alto Douro (CITAB-UTAD), Vila Real, Portugal
[2]Instituto Nacional de Investigação Agrária e Veterinária, I.P. (INIAV) Oeiras, Portugal
**bruna_carbas@hotmail.com*

Common beans (*Phaseolus vulgaris* L.) represent an important and sustainable source of proteins, carbohydrates, minerals, vitamins and dietary fiber, which are essential constituents of a balanced human diet, and consequently, a vital food resource worldwide [1]. Despite presenting high nutritive value, beans contain also some anti-nutritional compounds that can influence the absorption of minerals and protein, thus displaying depletory effects concerning nutrition [2].

Therefore, the main objective of this work was to determine the nutritional (protein and amino acids) and antinutrients (tannins and phytic acid) of common bean flours by analytical methods. Additionally, the FTIR spectra were registered for all the samples analysed, in order to correlate the chemical composition of each bean flour sample with its corresponding FTIR spectrum. Both the NIR (near-infrared) and MIR (mid-infrared) intervals, were registered, and explored, taking advantage multivariate analysis to develop spectroscopy analytical approaches. Partial least squares (PLS) regression was used to build a calibration and validation model, the regression models were evaluated thought cross-validation, and further validated with an external set of samples. The regression coefficients for calibration and validation of protein, tannins and phytic acid content were higher using the NIR interval, though, for amino acids the most suitable regression models were found for the MIR interval. Even though these FTIR methodologies showed good regression results for compounds with concentrations as low as 0.01 mmol g^{-1} dw of amino acids, in both the NIR and MIR intervals the calibration models were unable to quantify amino acids with larger ranges of concentrations, such as His, Lys and Arg, in the validation procedure.

Concluding, the Infrared spectroscopy methodologies are an appropriate method to evaluate the quality of bean flours.

Acknowledgements
This work was supported by National Funds by FCT - Portuguese Foundation for Science and Technology, under the project UID/AGR/04033/2019. The first author also acknowledges the financial support provided by the FCT-Portuguese Foundation for Science and Technology (PD/BD/128277/2017), under the Doctoral Programme “Agricultural Production Chains – from fork to farm” (PD/00122/2012)”

References

[1] L. Kan, S. Nie, J. Hu, S. Wang, S.W. Cui, Y. Li, Z. Bai, M. Xie, Food and Chemical Toxicology, 108 (2017) 467–477
[2] R. Campos-Vega, G. Loarca-Piña, B.D. Oomah, Food Research International, 43 (2010) 461–482

Development of a selective electrochemical sensor based on molecularly imprinted polymers (MIPs)

Constantino C. Coelho[1,*], Rosa A.S. Couto[1], Félix Carvalho[2], Luís Moreira Gonçalves[3], Wallans T.P. Santos[4] and M. Beatriz Quinaz[1]
[1]LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[2]REQUIMTE, UCIBIO, Laboratory of Toxicology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[3]Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo (USP), SP, Brazil
[4]Departamento de Farmácia, Universidade Federal dos Vales do Jequitinhonha e Mucuri, Diamantina, MG, Brazil
**up201705249@fc.up.pt*

MIPs are 'chemical tissues' with selective recognition lacunas for analytes, somehow imitating antibodies. These chemical fabrics are obtained by polymerization, a process in which the monomers are entangled around the target analyte, which works as template [1]. Following polymerization, the template molecule is removed, and the MIP is manufactured, possessing spots complementary in shape, size, and functionality to the imprinted molecule.

Preparation of MIPs by electropolymerization directly on the working electrode surface enables a simple way of controlling the polymer features, thus electrochemical MIPs synergistically combine the MIPs' advantages - in particular their selectivity - with the inherent gains of electrochemical sensors, like simplicity, sensitivity, portability, speed of analysis and user-friendliness, important key features in forensics.

In this work we propose a sensor based on screen-printed carbon electrodes (SPCEs) modified with an electrochemical molecularly imprinted polymer (MIP) to selectively detect the novel psychoactive substance methylenedioxypyrovalerone (MDPV), a stimulant synthetic cathinone that acts as a norepinephrine–dopamine reuptake inhibitor [2]. Different parameters that influence the sensor performance were studied, namely the monomer and template concentrations, the number of cycles during polymerization, extraction conditions and incubation period, and satisfactory analytical properties were obtained.

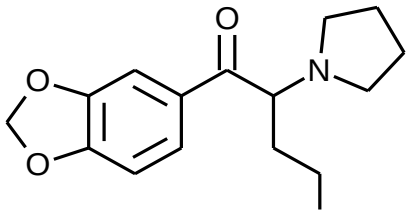


Fig.1. Chemical structure of 3,4-metilenodioxipirovalerona (MDPV)

Acknowledgements
This work was supported by UID/QUI/50006/2019 with funding from FCT/MCTES through national funds. RASC wishes to acknowledge FCT for her PhD fellowship (PD/BD/127797/2016) from the PhD Programme in Medicines and Pharmaceutical Innovation (i3DU). LMG (grant 2018/14425-7) thank the São Paulo Research Foundation (FAPESP) for financial support.

References

[1] R.A.S. Couto, S.S. Costa, B. Mounssef, J.G. Pacheco, E. Fernandes, F. Carvalho, C.M.P. Rodrigues, C. Delerue-Matos, A.A.C. Braga, L.M. Gonçalves, M.B. Quinaz, Sensors and Actuators B: Chemical 290 (2019) 378.
[2] R.A.S. Couto, L.M. Gonçalves, F. Carvalho, J.A. Rodrigues, C.M.P. Rodrigues and M.B. Quinaz, Critical Reviews in Analytical Chemistry 48 (2018) 372.

Comparative amperometric determination of mercury using ionophor chelator and enzyme inhibition approaches

Mariana Emilia Ghica[1,*], Basant Elsebai[2], Mohammed N. Abbas[2], Christopher M.A. Brett[1]
[1]Department of Chemistry, Faculty of Sciences and Technology, University of Coimbra, 3004-535 Coimbra, Portugal
[2]Applied Organic Chemistry Department, National Research Centre, Giza, Egypt
**meghica@qui.uc.pt*

Mercury compounds are widely present in air, water and soil as elemental, metallic, inorganic and organic mercury. Mercury is a very toxic pollutant because of its high volatility and the possibility to combine easily with many organic compounds [1]. It is toxic due to its deleterious effects on the central nervous system, disturbing haemin synthesis, as well as causing neuropsychiatric disorders [2]. High exposure to mercury may cause serious health troubles like kidney and respiratory failure, damage in the gastrointestinal tract and nervous system, and failure of speech, hearing, and working. Hence, the development of inexpensive, fast response, sensitive and selective methods for mercury determination is a very important need. Electrochemical approaches are particularly advantageous because of their high sensitivity, low cost and simple operation and can be made into portable sensing systems. Among them, enzyme inhibition based electrochemical biosensors exhibit high selectivity and low detection limit [3]. On the other hand, modified electrodes with polymers, clays and organic chelators have received increasing attention for enhancing selectivity and sensitivity of mercury electrochemical measurements [4].

In this work, a comparative study for mercury determination by two different electrochemical approaches was performed. One methodology deals with the direct determination of mercury by a glassy carbon electrode modified with the organic chelator ionophore, N,N di(2-hydroxy-5-[(4-nitrophenyl)diazenyl]benzaldehyde) benzene-1,2-diamine), (NDBD) without or with the addition of carbon nanotubes. The other strategy involves the development of an amperometric catalase-based biosensor for indirect mercury detection based on enzyme inhibition. The analytical performance of the two methods will be compared, as well as with other similar studies in the literature. Application to natural samples will also be discussed.

Fig.1. Schematic representation of mercury determination principle by (a) ionophore chelator and (b) enzyme inhibition approach

Acknowledgments
Financial support from the European Commission 7th Framework Programme Marie Curie Actions People IRSES Nº 294993 SMARTCANCERSENS, Fundação para a Ciência e a Tecnologia (FCT) through projects PTDC/QEQ-QAN/2201/2014, in the framework of the project 3599-PPCDT and UID/EMS/00285/2013 and postdoctoral fellowship SFRH/BPD/103103/2014 are gratefully acknowledged.

References

[1] Ciucu, Anal. Lett. 43 (2010) 1377–1386.
[2] S. Majid, M. El Rhazi, A. Amine, C.M.A. Brett, Anal. Chim. Acta 464 (2002) 123–133.
[3] Elsebai, M.E. Ghica, M.N. Abbas, C.M.A. Brett, J. Hazard. Mater. 340 (2017) 344-350.
[4] D. Martín-Yerga, M.B. González-García, A. Costa-García, Talanta 116 (2013) 1091–1104.

Nanofibers for solid phase extraction. How can we use them?

Ivana H. Šrámková[1], Burkhard Horstkotte[1], Laura Carbonell Rozas[2], Francisco J. Lara[2], Ana García-Campaña[2], Petr Solich[1], Dalibor Šatínský[1]
[1]Department of Analytical Chemistry, Faculty of Pharmacy in Hradec Králové, Charles University, Czech Republic [2]Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Av. Fuente Nueva s/n, E-18071 Granada, Spain
**sramkovai@faf.cuni.cz*

Electrospun nanofibers (NF) have gained a lot of attention during the last years due to their unique features such as a large surface-to-volume ratio, possibility of using natural materials, and the possibility of customized chemical modification. Apart from their novel implementation e.g. in medicine [1], NF are currently in the focus of analytical chemists for their great potential as a sorbent in solid phase extraction (SPE) techniques [2,3].

A Sequential Injection Analysis (SIA) system, comprising a piston pump, a switching valve, and a suitable detector, is an advantageous tool to study the potential of NF as extraction sorbent offering simple operation, flow manipulation, and fast results evaluation. We tested the extraction capacities of six different types of nanofibers with 17 model analytes with different physical-chemical properties using a simple and universal SIA method. The 3D printing technology was exploited to produce an optimal holder for the fibrous sorbent [4].

Using 3D-printing technology, we also designed a cage-like holder that incorporated a magnetic stirring bar, in which the nano-polycaprolactone/micro-polycaprolactone fibers were loosely accommodated. This way, we took advantage of the lacking stiffness but high robustness of the fibrous sorbent material and achieved reproducible filling of the device with it. This system was successfully applied to the extraction of eight bisphenols from river water samples. Procedural repeatability was below 5 % RSD and limits of detection and quantitation were between 0.1 - 2.1 µg L^{-1} and 1.1 - 7.0 µg L^{-1}, respectively. Analyte recoveries ranged between 93.6 -106.3% [5].

Online SPE-HPLC [6] offers a high level of automation, combining sample clean-up, analyte preconcentration and separation, and detection in one system. Hyphenation of the low-pressure systems with HPLC enables loading milliliter volumes of sample, often desired in environmental analysis. Such system with polyimide nanofibers was applied in the determination of neonicotinoid herbicides in environmental water samples.

The benefits and pitfalls of different nanofibers extraction systems will be discussed in detail.

Acknowledgements
The authors also acknowledge the support of the Czech Science Foundation through project No. 17-08738S. This work was supported by the STARSS project (Reg. No. CZ.02.1.01/0.0/0.0/15_003/0000465) co-funded by ERDF.

References

[1] L. Wen, J. Xie. Jouranl of Current Pharmaceutical Design 21 (2015) 1944-1959.
[2] J. Płotka-Wasylka, M. Marć, N. Szczepańska, J. Namieśnik, Current Reviews in Analytical Chemistry 47 (2017) 373-383.
[3] M. Háková, L. Chocholoušová Havlíková, P. Solich, F. Švec, D. Šatínský, Trend in Analytical Chemistry, 110 (2019) 81-96.
[4] H. Šrámková, L. Carbonell-Rozas, B. Horstkotte, M. Háková, J. Erben, J. Chvojka, F. Švec, P. Solich, A. M. García-Campaña, D. Šatínský, Talanta 197 (2019) 517-521.
[5] H. Šrámková, B. Horstkotte, D. Šatínský, P. Solich, Euroanalysis XX, Istanbul, Turkey 2019, P1-63.
[6] M. Háková, L. Chocholoušová Havlíková, J. Chvojka, P. Solich, D. Šatínský, Talanta 178 (2018) 141-146.

Biogenic amines determination by ion-pair chromatography using potentiometric detection

R.L. Gil[1*], C.G. Amorim[1], M.C.B.S.M. Montenegro[1], A.N. Araújo[1]
[1] LAQV-REQUIMTE/Departamento de Ciências Químicas,
Faculdade de Farmácia – Universidade do Porto, R. Jorge
Viterbo Ferreira, 228. 4050-313 Porto, Portugal.
*renatogil19@gmail.com

The most common analytical methods used for the determination of biogenic amines are based on liquid chromatography with spectrophotometric detection [1]. However, these compounds show little retention on conventional reversed-phase chromatographic columns and low detectability by spectrophotometric techniques, involving laborious and hazardous derivatization steps to overcome these drawbacks.

Alternatively, electroanalytical detection offers high selectivity and sensitivity with simple and inexpensive instrumentation, without the need of derivatization steps. Amperometric and coulometric detectors have been proposed for determination of biogenic amines after separation by HPLC but those based on potentiometry seems however overlooked [2].

In this work, a novel RP-HPLC method based on ion-pair chromatography combined with a potentiometric miniaturized ion-selective electrode inserted in a wall-jet flow-cell with low-dead volume is proposed for the simultaneous determination of ten different biogenic amines. The compounds of interest are the aliphatic amines – methylamine, ethylamine, cadaverine, putrescine, spermidine and spermine as well as the aromatic heterocyclic amines - histamine, tyramine, phenethylamine and tryptamine. Different experimental factors were studied such as the ion-pair agent and its concentration, the content of organic modifier and the stationary phase. The optimized method allowed the separation of the mentioned amines with a good resolution using a Luna® Omega 5µm Polar C18 150x4.6mm column by a gradient elution with butane 1-sulfonic acid as ion-pair agent and acetonitrile as organic modifier, at the flow-rate of 1.2 mL min^{-1}. The analysis time was 25 min.

The performance characteristics of the proposed detector were then evaluated and detection limits of the order of 10^{-6} mol L^{-1} (injected concentrations) were obtained for all amines. The described method is now under validation phase according to the requirements of ICH (International Conference on Harmonisation).

Potentiometry already proved its ability as a competitive detection technique in liquid chromatography [2]. Therefore, the proposed method has a great potential to be used for the determination of biogenic amines in different food matrices.

Acknowledgements
This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through grant UID/QUI/50006/2019. Renato Gil thanks FCT (Fundação para a Ciência e Tecnologia) and ESF (European Social Fund) through POCH (Programa Operacional Capital Humano) for his PhD grant SFRH/BD/131504/2017.

References
[1] M. Papageorgio, D. Lambropoulou, C. Morrison, E. Kłodzińska, J. Namieśnik, J. Płotka-Wasylka, Trends in Analytical Chemistry, 98 (2018) 128.
[2] R.L. Gil, C.G. Amorim, M.C.B.S.M.Montenegro, A.N.Araújo, Journal of Chromatography A, 1602 (2019) 326.

Estudio de los niveles de elementos críticos tecnológicos (TCEs) en muestras de algas mediante ICP-MS

J.J. López-Mayán*, E. Peña-Vázquez, M.C. Barciela-Alonso, P. Bermejo-Barrera
Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Química, Universidad de Santiago de Compostela, Av. das Ciencias, s/n, 15782, Santiago de Compostela, España.
**juanjoselopez.mayan@usc.es*

En la actualidad el uso de los Elementos Críticos Tecnológicos (TCEs) se está incrementando debido a su empleo en las nuevas tecnologías. Se trata de un grupo de elementos muy variado y heterogéneo, considerados críticos para la Unión Europea debido a su difícil obtención y reciclaje. Actualmente es necesario desarrollar métodos que permitan determinarlos en diferentes matrices medioambientales. La matriz objeto de estudio son las algas, debido fundamentalmente a su efecto bioacumulador, y a su empleo en la industria alimentaria y farmacéutica.

La finalidad principal de esta investigación es el estudio de la concentración de diversos TCEs (Ga, Ge, Y, Nb, Ru, Rh, In, Te, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ta, Pt, Tl), metales nobles (Ag, Au, Cu), y Th y U en algas gallegas. Para la determinación de los TCEs se ha desarrollado un método basado en la utilización de la Espectrometría de Masas acoplada con Plasma de Acoplamiento Inductivo (ICP-MS), previa digestión ácida asistida por microondas con HNO_3 (69% v/v) y H_2O_2 (33% v/v).

Las calibraciones se realizaron mediante el método de adiciones estándar en el rango entre 1 y 10 µg L^{-1}. Se empleó el Material de Referencia Certificado BCR®-670 correspondiente a la planta acuática *Lemna Minor* para la elección de los isótopos de medida, así como el flujo de He en la celda de colisión para eliminar las interferencias moleculares. Para la selección de los isótopos también se tuvo en cuenta la Norma UNE-EN ISO 17294-1:2007 de calidad de aguas, su abundancia relativa y los límites de detección obtenidos.

Se evaluaron las características analíticas del método, y se concluyó que el método es sensible, preciso y exacto. Los límites de detección obtenidos fueron de 0,03 ng g^{-1} para Lu hasta 86,72 ng g^{-1} para el Th. Para evaluar la precisión se hicieron estudios de repetitibilidad en los cuales los coeficientes de variación fueron para todos los elementos menores al 9%. Se estudió la exactitud del método con el BCR®-670 encontrándose una buena concordancia entre los valores certificados y los valores medidos para los elementos presentes en el material (Sc, Y, La, Pr, Nd, Eu, Sm, Tb, Gd, Dy, Ho, Er, Tm, Yb, Lu y U). Además, la recuperación analítica fue para todos los elementos cercana al 100%.

El método, se aplicó finalmente al análisis de diferentes especies de algas rojas, pardas y verdes procedentes principalmente de las costas gallegas. Se hizo además un estudio sobre la posible contaminación por tierras raras después de una normalización del contenido de lantánidos empleando los valores de la Condrita y la Lutita Europea.

Agradecimientos
Los autores pertenecen al Grupo de Investigación de Referencia Competitiva de Galicia ED431C2018 /19. Esta investigación fue parcialmente financiada por la Consellería de Educación, Programa para el Desarrollo de la Agrupación Estratégica de Materiales (AEMAT) en la USC bajo la Subvención No. ED431E2018 /08, Xunta de Galicia. Estos programas están cofinanciados por FEDER (UE).

Biomimetic magnetic particles for Sensing and Biosensors

María Isabel Pividori
1. Grup de Sensors I Biosensors, Departament de Química, Universitat Autònoma de Barcelona
2. Edifici Cn, Campus UAB
**isabel.pividori@uab.es*

Since the early reports on magnetic separation technology [1], magnetic particles (MPs) have been used as a powerful and versatile preconcentration tool in a variety of analytical and biotechnology applications. This technology has been widely incorporated for researchers in classical methods including PCR and immunoassays, and in emerging technologies such as biosensors and microfluidic devices with application ranging from biomarker detection of infectious diseases, foodborne pathogens, among others. Magnetic particles have been commercially available for many years. The use of MPs greatly improves the performance of the biological reaction by increasing the surface area, enhancing the washing steps and, importantly, minimizing the matrix effect. In addition, MPs can be easily magneto-actuated using permanent magnets. Beside the amazing properties and the huge range of applications, the main drawback of the biologically-modified MPs is their high cost and low stability at harsh conditions. Molecularly Imprinted Polymers (MIPs) are synthetic biomimetic materials mimicking biological receptors [2]. They are highly cross-linked macromolecular structures towards the template which is then extracted after polymerization, originating cavities (binding sites) complementary to the template molecule, acting as plastic antibodies. Although MIPs have in general lower affinity and selectivity compared to the biological counterparts, they show important technological features: i) they can be easily and affordably synthesized on a animal-free large scale procedures, and ii) they show high chemical and mechanical stability, allowing to work in harsh conditions (pH, temperature, solvents). This lecture addresses the synthesis of magneto-actuated molecularly imprinted polymers (magnetic-MIPs) in order to merge the outstanding properties of MIPs and MPs [3]. The characterization of the magnetic-MIP is performed by several techniques as SEM, TEM, XRD, FTIR, VSM and BET analysis. Finally, magnetic-MIP is used for preconcentration of the analyte from the complex samples allowing the quantification by the direct electrochemical detection on magneto-actuating electrodes. This novel material was evaluated, among others, in different applications including for the isolation and detection of biotin and biotinylated biomolecules [4], for food pollutants (methyl parathion) and contaminants (histamine) in fish samples as a model and it was also successfully applied for determination of diseases related to hormone (L-thyroxine) giving promising results [5]. This proves the ability of this material to preconcentrate analyte from complex samples and opens the way to incorporate this material in magneto-actuating devices which could be used easily in the field of environmental control, food safety, and medical applications.

Agradecimientos
Financial support from Ministry of Economy and Competitiveness, Madrid (Grants BIO2016-75751-R) and from Generalitat de Catalunya (2014SGR837)]

Referencias

1. A. Rembaum, R.C.K. Yen, D.H. Kempner, J. Ugelstad, 1982. J. Immunol. Methods 52, 341-351.
2. G. Vlatakis, L.I. Andersson, R. Müller, K. Mosbach, 1993. Nature 361, 645-647.
3. Pividori,M.I. , Sotomayor,M.D.P.T. , European Patent EP15169505.3.(2016).
4. AB Aissa, A Herrera-Chacon, RR Pupin, MDPT Sotomayor, MI Pividori, 2017. Biosensors and Bioelectronics 88, 101-108.
5. S. Lima Moura, L. Martinez Fajardo, L. dos Anjos Cunha, MDPT Sotomayor, F.B. Bolivar Correto Machado, L.F. Araújo Ferrão, MI Pividori, 2018. Biosensors and Bioelectronics 107, 203-210.

Estudo do perfil de aminas biogénicas em amostras biológicas recolhidas de vacas leiteiras

Inês M. Valente[1,2*], Margarida R. G. Maia[2], António J. M. Fonseca[2], Ana Rita J. B. Cabrita[2], José António Rodrigues[1]
[1]REQUIMTE/LAQV - Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre n. 687, 4169-007 Porto, Portugal.
[2]REQUIMTE/LAQV – Departamento de Clínicas Veterinárias, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Rua de Jorge Viterbo Ferreira n. 228, 4050-313 Porto, Portugal.
**ines.valente@fc.up.pt*

Nos ruminantes as aminas biogénicas podem ser provenientes da dieta, em particular dietas ricas em proteínas, ou da descarboxilação de aminoácidos no rúmen por ação de microorganismos [1]. As aminas desempenham funções fisiológicas importantes, mas acima de determinados níveis de concentração podem ter diversas consequências negativas na eficiência e saúde dos animais ruminantes, tais como a redução da ingestão de matéria seca, a diminuição da degradabilidade do azoto no rúmen, e efeitos tóxicos em diversos órgãos [1]. Vários estudos demonstram a relação de elevados teores de algumas aminas biogénicas com doenças metabólicas e digestivas, o que justifica o estudo destes compostos com vista à sua utilização como marcadores desses problemas de saúde.

Neste trabalho estudou-se o perfil de aminas biogénicas em amostras biológicas de uma vaca leiteira com o objetivo de avaliar as variações intra- e inter-dia do teor destes compostos. As amostras (leite, fezes, urina e conteúdo ruminal) foram recolhidas em 3 períodos por dia (antes da refeição da manhã, 3 h após refeição e 9 h após refeição), 2 vezes por semana, durante 4 semanas de uma vaca Holstein adulta, fistulada e em lactação, alimentada com uma dieta composta por farinha de milho, silagem de milho, palha e concentrado. As aminas foram extraídas das amostras com HCl 0,4 mol L^{-1} e os extratos foram posteriormente derivatizados com cloreto de dansilo para análise por cromatografia líquida de alta eficiência com deteção fluorimétrica (HPLC-FLD) [2]. A identificação dos compostos foi realizada por espetrometria de massa (HPLC-MS/MS).

As amostras de fezes e de conteúdo ruminal apresentaram um perfil em aminas biogénicas semelhante, composto por putrescina, cadaverina, tiramina, espermidina e espermina. No leite foram identificadas etilamina, tiramina, espermidina e espermina. Nas amostras de urina recolhidas foram identificadas etilamina, *iso*-pentilamina e tiramina. Em geral, os teores de aminas biogénicas variaram significativamente (ANOVA, $P < 0,05$) ao longo dos dias e com a hora de recolha das amostras. No entanto, verificaram-se alguns casos em que os teores de algumas aminas não variaram estatisticamente ($P = 0,05$) com a hora de colheita: *iso*-pentilamina e tiramina nas amostras de urina; cadaverina e espermidina nas fezes. Os resultados deste estudo permitiram avaliar a evolução no teor de aminas biogénicas em amostras biológicas de uma vaca leiteira, associadas às variações intra- e inter-dia. A identificação de compostos em que não se verificou variação estatisticamente significativa com a hora de colheita permitirá avançar com a hipótese de que essas aminas poderão ser usadas como potenciais marcadores de distúrbios digestivos e/ou metabólicos em ruminantes.

Agradecimentos
Agradece-se o apoio financeiro de fundos nacionais (FCT/MEC, Fundação para a Ciência e Tecnologia e Ministério da Educação e Ciência) no âmbito do financiamento UID/QUI/50006/2019. I. M. Valente e M. R. Maia agradecem à FCT (Fundação para a Ciência e Tecnologia) o financiamento através do programa DL 57/2016 – Norma transitória.

Referencias
[1] Fusi, E.; Rossi, L.; Rebucci, R.; Cheli, F.; Di Giancamillo, A.; Domeneghini, C.; Pinotti, L.; Dell'Orto, V.; Baldi, A. Small Ruminant Research 53 (2004) 1.
[2] Saarinen, M. T. Chromatographia 55 (2002) 297.

Identificación de compuestos volátiles y semivolátiles en mieles mediante microextracción en fase sólida miniaturizada (SPME) seguida de GC-MS

Lúa Vázquez[1]*, Meruyert Sergazina[1,3], María Celeiro[1], Thierry Dagnac[2], María Llompart[1]
[1]Laboratorio de Investigación y Desarrollo de Soluciones Analíticas (LIDSA), Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Química, E-15782, Santiago de Compostela, España
[2]Agencia Galega da Calidade Alimentaria, Centro de Investigaciones Agrarias de Mabegondo (AGACAL-CIAM), Unidad de Contaminantes Orgánicos, Apartado 10, 15080, A Coruña, España
[3]Departamento de Química, Instituto de CIencias Naturales y Geografía, Universidad Pedagógica Nacional Abai Kazakh, Almaty, Kazajistán
* lua.vazquez.ferreiro@usc.es

La miel es un producto natural compuesto principalmente por azúcares, agua y otros compuestos como minerales, granos de polen, enzimas, cera, aminoácidos, proteínas, ácidos orgánicos y compuestos fitoquímicos [1]. Su composición depende de las especies de planta de las que proceden, y otros factores como las condiciones ambientales y climáticas [2]. Por esta razón, es importante identificar marcadores específicos para garantizar la calidad y la autenticidad de la miel, en este caso, de Galicia.

Se ha desarrollado un método miniaturizado basado en microextracción en fase sólida (SPME) seguido por cromatografía de gases acoplada a espectrometría de masas (GC-MS) para la determinación de los principales compuestos volátiles y semivolátiles en mieles. Se han llevado a cabo estudios preliminares (cantidad de muestra, volumen de dilución, temperatura de extracción, ...) utilizando para ello una muestra de miel multifloral. Posteriormente, el procedimiento fue optimizado mediante un diseño experimental fraccionado $3 \times 2^{3-1}$ y 2 puntos centrales, con un total de 14 experimentos.

Asimismo, parámetros de calidad del método fueron evaluados obteniendo resultados satisfactorios para su posterior aplicación sobre muestras reales.

Agradecimientos
Este trabajo ha sido apoyado por el Proyecto UNST10-1E-491 (Programa de Infraestructuras, MINECO, España), FEADER 2018/054B, RED2018-102522-T (Ministerio de Ciencia, Innovación y Universidades, España) y el Proyecto CTQ2013-46545-P (Ministerio de Economía y Competitividad, España).
Los autores pertenecen al Grupo de Investigación Competitivo de Galicia GPC 2017/04, GPC 2019/13 y a la Asociación Estratégica de CRETUS (ED431E 2018/01). Estos programas se encuentran cofinanciados por FEDER (UE).
Los autores querrían agradecer al Consello Regulador de Mieles Gallegas (IXP Mel de Galicia) por recolectar y suministrar las muestras de mieles.

Referencias
[1] P. De Lima Morais da Silva, L.S. de Lima, I. Kaminski, Y. Reyes Torres, *Food Research International*, 102 (2017) 536-543.
[2] J.N. Bianchin, G. Nardini, J. Merib, A. Neves Días, E. Martendal, E. Carasek, *Food Chemistry*, 145 (2014) 1061–1065.

Method validation for quantification of metals in natural waters by ICP-OES

Nicole Ferreira[1,*], Cláudia Batista Lopes[1], Lina Carvalho[3], Bruno Henriques[2], Thainara Viana[2], Eduarda Pereira[2]

[1]Departament of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
[2] Departament of Chemistry, LAQV-REQUIMTE & CESAM, University of Aveiro, 3810-193 Aveiro, Portugal
[3]Central Laboratory of Analysis, University of Aveiro, 3810-193 Aveiro, Portugal
*nicoleviana@ua.pt

Over the years, quality has become crucial in technical and scientific fields. Quality assurance is very important when it comes to validate a method, in order to perform valid analysis and to achieve reliable results [1]. Validation main goal is to, not only provide reliable results, but also to promote an assurance of equal results within an estimated measurement uncertainty when performing different analytical techniques [2].

The objective of this work was to validate a method for multi-elemental analysis in natural water samples, which is more and more relevant given the growing release of different metals into this matrix due to industrialization processes. Moreover laboratories had to improve their analysis method due to changes on quality parameters established by the new directive on the quality of water (Directive 2015/1787 of the European Commission of October 6, 2015).The work was conducted at an accredited laboratory, in the Central Laboratory of Analyses (LCA) of the University of Aveiro. Several performance parameters were considered to validate the studied method characteristics (Table 1). Quality control was ensured through the analysis of blanks, certified reference material, duplicates, and fortification samples.

The Environment Protection Agency (EPA) 3015A method: microwave assisted acid digestion of aqueous samples and extracts is applicable to a microwave-assisted acid extraction of available metals in aqueous samples that contain suspended solids for extraction and quantification of 26 elements. For the acid extraction, HNO_3 and HCl were used, followed by a microwave digestion. An increase of temperature and pressure boosts both the rate of samples decomposition and the elements solubility.

In this work a method was validated for natural waters using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) for the quantification of Ca, Cu, Fe, Mg, Mn, Na, and Zn after microwave assisted acid digestion, The blank (with values lower than the LOD), fortification samples (percentages of recuperation always between 80-120%), certified reference material (to evaluate the trueness), and natural water samples analysis results met the performance requirements defined in ISO/IEC 17025 [3]. This validation allowed the LCA to guarantee the accreditation for multi-elemental quantification in natural waters by ICP-OES.

Table 1: Summary of analytical quality control parameters evaluated during a validation method

Execution Characteristics		
Working range	**Analytical Sensitivity**	**Precision:**
Selectivity	**Measurement uncertainty**	**Reproducibility, repeatability**
Limit of detection	**Trueness:**	• **Robustness**
Limit of quantification	• **Bias, recovery**	

Agradecimientos

Bruno Henriques and Cláudia Batista Lopes benefited from a Research position funded by national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. Thanks are also due for the financial support to CESAM (UID/AMB/50017), to FCT/MEC through national funds, and the co-funding by the FEDER, within the PT2020 Partnership Agreement and Compete 2020.

Referencias

[1] R. J. N. Bettencourt, M. F. G. F. C. Camões, and J. Seabra e Barros, Analytica Chimica Acta, 393 (1999). 167–175.
[2] S. M. R. Wille, F. T. Peters, V. Di Fazio, and N. Samyn, Accreditation Quality Assurance, 16(6) (2011) 279–292.
[3] International Organization for Standardization - NP ISO/IEC 17025:2018, 3rd ed. Caparica, Portugal, 2018.

QUÍMICA-FÍSICA

The Solubility Of Amino Acids In Aqueous Electrolyte Solutions

Mehriban Aliyeva[1-3], José R. B. Gomes[1], João A.P. Coutinho[1], Olga Ferreira[2,3], Simão P. Pinho[2,3*]
[1]CICECO, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
[2]CIMO, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5301-857 Bragança Portugal
[3]LSRE-LCM, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5301-857 Bragança Portugal
*spinho@ipb.pt

The presence of water, ions and biomolecules such as proteins in biochemical processes is indisputable. The complexity of these systems leads scientists to study aqueous electrolyte solutions containing model compounds, namely amino acids (AA) and peptides. Additionally, the importance of amino acid or peptide solubility for food, pharmaceutical and cosmetic applications has been widely reported [1-3]. In particular, the ability to understand the interactions between ions and biomolecules in aqueous media will open new ways to explore solutions for diseases induced by biochemical disorders [4].

This work starts by presenting an extended bibliographic review on the solubility of AA in water and how it is affected by the presence of different electrolytes. The inconsistency between different experimental results is explored focusing also on the importance to perform solid phase studies, not only because AA c an be present in many different solid structures, but also can present significant changes due to the presence of the salts. This review showed that most of the amino acids studied so far are glycine, valine and alanine, while the most studied salts contain Na^+ or K^+ cations; and Cl^- and NO_3^- anions.

The new experimental data here presented contain salts combining some of these ions, not only to validate the experimental methodology by direct comparison with the results for glycine, but also to perform a more extensive comparative analysis on the effect of each salt, as the L-form of AA like aspartic acid, leucine or phenylalanine are now also included, presenting different polarities and distinct functional groups. To perform the measurements (at 298.2 k) the isothermal shake-flask method was applied, combined with gravimetry or UV spectroscopy. Due to its enormous relevance in biochemical systems, the pH of each saturated solution was also measured.

Both salting-in and salting-out effects were observed in this study. The results showed that while the relative solubility of glycine in NaCl, KCl, $NaNO_3$ and KNO_3 solutions increased slightly, for L-aspartic acid a much more significant increase was observed. For both amino acids the relative solubility was higher for the nitrate salts. On the other hand, in solutions with nitrate anions the relative solubility of L-leucine and L-phenylalanine increased, while in solutions containing chloride anions their relative solubility notably decreased. The data inconsistencies between different authors show the impact of mixing time, drying temperature, compounds source and solid phase structure on the solubility results. Finally, the anion effects on the solubility are in good qualitative agreement with the results from classical molecular dynamics simulations reported in the literature [5] in which the salting-in/salting-out mechanisms were based on the interactions between the anions and the nonpolar moieties of the AAs.

Acknowledgments
The authors acknowledge the support of: Foundation for Science and Technology (FCT, Portugal) and FEDER under Programme PT2020 for financial support to CIMO (UID/AGR/00690/2019); UID/CTM/50011/2019 (CICECO), financed by national funds through the FCT/MCTES; Associate Laboratory LSRE-LCM - UID/EQU/50020/2019 - funded by national funds through FCT/MCTES (PIDDAC). Mehriban Aliyeva also thanks the PhD grant from FCT (SFRH/BD/139355/2018).

References
[1] K. Drauz, I. Gayson, A. Kleemann, H.-P. Krimmer, W. Leuchtenberger, C. Weckbecker in Ullmann's Encyclopedia of Industrial Chemistry, Weinheim, Wiley-VCH, (2012) 3.
[2] C.-H. Bang, H.-K. Choi, B.-S. Lee, Journal of Molecular Liquids, 9 (2016) 223.
[3] R. Carta, Journal of Chemical Thermodynamics, 9 (1998) 30.
[4] H. Zhao, Journal of Molecular Catalysis B: Enzymatyc, 16 (2005) 37.
[5] L.I.N. Tomé, M. Jorge, J.R.B. Gomes, J.A.P. Coutinho, The Journal of Physical Chemistry B, 114 (2010) 16450.

Multicomponent Diffusion in Hydrocarbon Mixtures

Cecília I.A.V Santos [1], **Marisa C.F. Barros**[1], **Valentina Shevtsova**[2] **and Ana C.F. Ribeiro**[1]
[1]Department of Chemistry, University of Coimbra, 3004 - 535 Coimbra, Portugal,
[2]MRC, CP-165/62, Université Libre de Bruxelles, 50, Av. F.D. Roosevelt, B-1050 Brussels, Belgium
**ceciliasantos@qui.uc.pt*

Accurate knowledge on thermophysical properties of working fluids in energy and process engineering is necessary for the design of efficient processes and the corresponding apparatus. Diffusive mass transport in liquids is a fundamental process, which plays an important role in chemical engineering as well as in biological systems. Progress in this research area relies on the availability of high-quality mass transport property data. Taylor dispersion technique has become a fast and reliable method for the measurement of mutual diffusion coefficients (D_{ik}), with the advantage of relative simplicity of the equipment used. The latter has been extensively tested for electrolytes and diluted solutions [1, 2] and, more recently, for the case of binary mixtures of organic compounds [3]. Ternary mutual diffusion coefficients for mixtures of cyclohexane-toluene-methanol, a mixture of exceptional interest due to the fact that it exhibits a very complex behaviour as well as a miscibility gap at ambient conditions [4] have been experimentally measured with the Taylor dispersion technique.

To a better understanding of the system isothermal molecular diffusion in conjunction with the coupled flows of solutes occurring in such fluid systems, twenty ternary systems with different composition of cyclohexane-toluene-methanol were investigated in order to accurately obtain the mass diffusion coefficients (see Fig. 1). The good agreement with the results already obtained with other teams for some compositions of this system is discussed together with the behaviour of the diffusion coefficients along three concentration paths for different mass fraction of each solute.

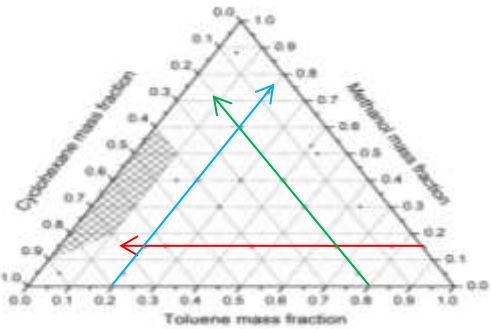


Figure 1**:** Map of Toluene-Methanol-Cyclohexane in mass fractions (Dots show measured points; Shaded region outlines demixing zone; arrows show concentration paths)

Acknowledgements
The authors are grateful for the funding granted by FEDER –European Regional Development Fund through the COMPETE Programme and FCT -Fundação para a Ciencia e a Tecnologia, for the KIDIMIX project POCI-01-0145-FEDER-030271.

References
[1] Santos C. I.A.V., Esteso M.A., Lobo V.M.M., Cabral A.M.T.D.P.V., Ribeiro A.C.F., J. Chem. Thermodyn., 84, (2015) 76.
[2] Ribeiro A.C.F., Gomes J.C.S., Santos C.I.A.V., Lobo V.M.M., Esteso M.A., Leaist D.G., J. Chem. Eng. Data, 56, (2011) 4696.
[3] Mialdun A., Sechenyh V., Legros J. C., Ortiz de Zárate J. M., Shevtsova V., J. Chem. Phys. 139, (2013) 104903.
[4] Nagata, I., Fluid Phase Equilib. 18 (1984) 83.

Caracterización fotofísica del 6-amino-1,3-benzotiazol-2-carbonitrilo para su uso como sonda fluorescente

Ana Arias Rodríguez*, **Flor Rodríguez Prieto, Carmen Ríos Rodríguez, Manuel Mosquera González**

Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS) y Dpto. de Química Física, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, España
**ana.arias.rodriguez@rai.usc.es y flor.rodriguez.prieto@usc.es*

El gran interés en la cuantificación de parámetros como la acidez o la polaridad en microentornos reactivos químicos y biológicos ha impulsado de manera notable el desarrollo de técnicas de análisis que emplean sondas moleculares fluorescentes [1,2]. Estas sondas aprovechan la elevada sensibilidad de su fluorescencia al medio en el que se encuentran. En este trabajo investigamos las propiedades de una nueva sonda fluorescente, el 6-amino-1,3-benzotiazol-2-carbonitrilo (ABTC). El objetivo de este trabajo ha sido la caracterización de su comportamiento fotofísico por medio de espectroscopía de absorción UV-Vis y de fluorescencia y el análisis de la influencia del entorno sobre su fluorescencia. Los estudios realizados tanto en medio acuoso como en otros disolventes y en distintas condiciones de pH evidencian su elevada sensibilidad tanto a la acidez como a la polaridad del medio. El análisis de la fluorescencia de la forma neutra (la única emisora) ha demostrado la existencia de especies protonadas diferentes en los estados fundamental y excitado, y ha puesto de manifiesto la existencia de procesos de transferencia intramolecular de carga fotoinducida y de desactivación por protones. El modelo de comportamiento propuesto (Figura 1) justifica la evolución temporal del decaimiento de la señal de fluorescencia. Se ha demostrado también que el proceso de solvatación tiene dos etapas, y se ha corroborado la alta sensibilidad de la fluorescencia de esta molécula a las condiciones del medio, lo que respalda su validez como sonda fluorescente.

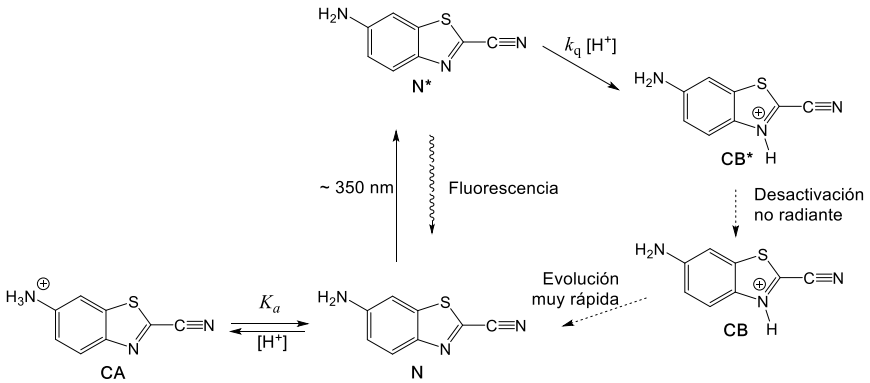


Figura 1. Procesos que experimenta el ABTC en agua, en el estado fundamental y primer singlete excitado

Agradecimientos
Agradecemos la financiación de este trabajo al Gobierno de España (Proyecto CTQ2014-59020-R), a la Xunta de Galicia (Proyecto ED431B 2019/18 y Acreditación de Centro Singular de Investigación de Galicia 2016-2019, ED431G/09), y a la Unión Europea (FEDER).

Referencias
[1] Principles of Fluorescence Spectroscopy, J. R. Lakowicz, (3ª ed.), New York, Springer, 2006.
[2] S. Klymchenko, Acc. Chem. Res. 50 (2017) 366.

Polymorphism of cocrystals: A case study

João A. Baptista[1], Ricardo A.E. Castro[1,2], Teresa M.R. Maria[1], Manuela R. Silva[3], João Canotilho[1,2], M. Ermelinda S. Esébio[1]
[1]CQC, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
[2] Faculty of Pharmacy, University of Coimbra, 3000-548 Coimbra, Portugal
[3] Department of Physics, University of Coimbra, Coimbra, Portugal

Pharmaceutical cocrystals have emerged in recent years as alternative solid forms of active pharmaceutical ingredients, APIs, for enhancement of desirable physicochemical properties and/or biopharmaceutical performance [1, 2]. They are multicomponent solids made up of an API and of one or more coformers, all solid when pure at ambient conditions, joined together in a stoichiometric ratio in a new crystalline structure [1-3]. The supramolecular synthons responsible for supramolecular association involve, in most of the cases, hydrogen bond interactions, although other kind of (weaker) interactions may also play a role [1-3]. For the same multicomponent system (API + coformer) several supramolecular synthons are often possible.

Polymorphism, the ability of a substance to give rise to different crystalline structures, is quite prevalent in active pharmaceuticals ingredients [4]. Concerning the polymorphism of multicomponent solids, in particular cocrystals, fewer studies have been reported and an open discussion about the prevalence of cocrystals polymorphism is still on-going [5, 6]. The ability to associate through different supramolecular heterosynthons and molecular conformational flexibility may play a role on the propensity to originate different cocrystal structures [6].

As part of an ongoing project aiming to get insight on these effects, in this work results are presented and discussed for the investigation of cocrystallization of pyrimethamine, a dihydrofolate reductase inhibitor, with two closely related coformers, theophylline and caffeine, Figure 1. As an highlight, thermal analysis was crucial in discovering polymorphs of both (1:1) pyrimethamine:caffeine and pyrimethamine:theophylline cocrystals.

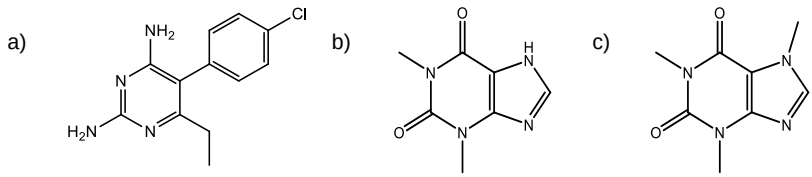


Figure 1. Molecular structures: a) pyrimethamine, b) theophylline, c) caffeine

[1] N.Duggirala, M.L. Perry, O Almarsson, M. J. Zaworotko, Chem. Commun., 52 (2016) 640.
[2] A.O.L. Évora, R.A.E. Castro, T.M.R. Maria, M.R. Silva, J.H. ter Horst, J. Canotilho, M.E.S. Eusébio, Int. J. Pharm., 466 (2014) 68.
[3] E. Grothe, H. Meekes, E. Vlieg, J.H. ter Horst, R.X. de Gelder, Cryst. Growth Des., 16 (2016) 3237.
[4] R. Hilfiker, M. Raumer, Eds, Polymorphism in the Pharmaceutical Industry, Wiley-VCH, Weinheim, 2019.
[5] K. Kersten, R. Kaur, A. Matzger, IUCrJ, 5 (2018) 124.
[6] S. Aitipamula, P. S. Chow, R. B. H. Tan, CrystEngComm, 16 (2014) 3451.

Comportamiento de sistemas ternarios de sal sodica con surfactantes en función de la temperatura

A. Gayol[1,2,*], D. Gómez-Díaz[3], J.M. Navaza[3]

[1]Departamento de Física Aplicada, Universidad de Vigo, Lagoas-Marcosende s/n, 36310 Vigo. España.
[2]Xunta de Galicia, CIFP Compostela, Departamento Artes Gráficas, Lamas de Abade s/n, 15702 Santiago de Compostela.
[3]Universidade de Santiago de Compostela, ETSE, Lope Gomez de Marzoa s/n, 15705 Santiago de Compostela.

**e-mail:anagayol@uvigo.es*

Palabras clave: propiedades fisicas, Tween-20, Triton X-101, sal sódica.

En los últimos años se desarrollaron de manera importante el estudio de sistemas de dos fases acuosas, ya que tienen aplicaciones importantes en diversidad de campos, desde la alimentación, procesos de separación del etanol, industria cosmética, entre otros.

En este trabajo se estudia el comportamiento de los sistemas binarios obtenidos a partir de polímeros (Tween 20, Triton X-101) + agua + sal en función de la temperatura, en el rango 288.15 K a 308.15 K y a presión atmosférica.

Se realizan medidas de propiedades físicas [1,2], que son la densidad [1,2,3,5], el índice de refracción [1-4] y la velocidad del sonido en el laboratorio, en las condiciones anteriormente mencionadas. Finalmente, a partir de ellas se procede al cálculo, para la obtención de las propiedades derivadas que en este caso son: el volumen molar de exceso y la compresibilidad isentrópica también a presión atmosférica y en rango de temperatura 288.15-308.15 K.

La densidad y la velocidad del sonido fueron medidas en un densímetro tubo vibrante Anton Paar DMA 5000.

Se han estudiado los sistemas (Tween 20, Triton X-102) + Na_2SO_4 + agua. Se trata de una combinación de sistemas binarios ya que los sistemas polímero agua son completamente miscibles, mientras que sal + agua es parcialmente miscible. En el caso particular del la concentración de saturación esta en torno al 25%.

Referencias

[1] A. Blanco. A.Gayol. D. Gómez-Díaz, J.M. Navaza, J. Molec. Liquids.. 195 (2014) 1.
[2] E. Alvarez, A. Blanco. A.Gayol. D. Gómez-Díaz, J.M. Navaza, J. Chem. Eng. Data. 59 (2014) 926.
[3] M.E. Taboada, H.R. Galleguillos, T.A. Graber, J.Alvarez-Benedí, Fluid Phase Equilibr. 235 (2005) 104.
[4] S.C. Silverio, A. Wegrzyn. E. Lladosa, E.A. Macedo, J. Chem. Eng. Data. 57 (2012) 1203.
[5] F.J. Deive, A. Rodriguez, A.B. Pereiro, J.M.M. Araujo, M.A. Longo. M.A.Z. Coelho, J.N. Canongia Lopes, J.M.S.S. Esperanca, L.P.N. Rebelo, I.M. Marrucho, Green Chem. 54 (2011) 385.

Estudo da dinámica da transferencia protónica no 2-ciano-6-hidroxibenzotiazol

Sara Illodo Brea*, **Flor Rodríguez Prieto, Manuel Mosquera González***

Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) e Dpto. de Química Física, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, España
**sara.illodo@rai.usc.es e manuel.mosquera@usc.es*

Unha parte importante das reaccións químicas transcorren en disolventes próticos, estando implicado en gran medida o movemento do protón e a interacción das moléculas de reactivos co disolvente. Ademais, a transferencia protónica xoga un papel fundamental en numerosos procesos biolóxicos e en sistemas tecnolóxicos relevantes, como as pilas de combustible [1]. Para a mellor comprensión destes importantes procesos é fundamental coñecer a súa dinámica, moi complexa polas especiais características do protón [2,3]. Neste traballo investigamos a dinámica da transferencia protónica ao disolvente dunha especie non estudada ata o momento, o 2-ciano-6-hidroxibenzotiazol (6HCBZ).

A caracterización fotofísica do 6HCBZ en diferentes condicións de pH e disolvente levouse a cabo mediante técnicas de espectroscopía electrónica de absorción UV-Vis e fluorescencia. Os datos espectrais mostraron un grande incremento de acidez no grupo OH trala excitación electrónica, pasando o pK_a de 7.5 no estado fundamental a −1.1 no primeiro estado excitado singlete (método do ciclo de Förster), o que determina a tendencia á disociación desta especie trala absorción de luz. Esta disociación observouse experimentalmente en disolventes como o etanol e a auga. O estudo da dinámica do proceso de disociación levouse a cabo con medidas de decaemento da fluorescencia na escala de picosegundos. A análise cinética permitiu postular o mecanismo mostrado na Figura 1 para explicar a dinámica da disociación protónica do 6HCBZ en etanol trala excitación electrónica e achar o valor das constantes de velocidade implicadas.

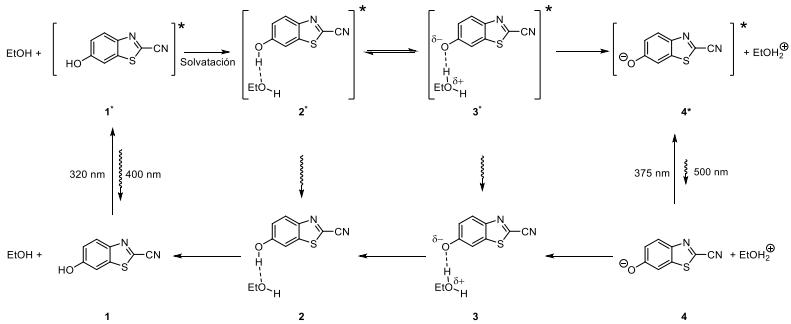


Fig.1. Mecanismo proposto para a disociación do 6HCBZ excitado en etanol mediante transferencia protónica ao disolvente

Agradecementos
Agradecemos a financiación deste traballo ao Goberno de España (Proxecto CTQ2014-59020-R), á Xunta de Galicia (Proxecto ED431B 2019/18 e Acreditación de Centro Singular de Investigación de Galicia 2016-2019, ED431G/09), e á Unión Europea (FEDER).

Referencias

[1] Hydrogen-Transfer Reactions. J. T. Hynes, J. P. Klinman, H. H. Limbach, R. L. Schowen, (Eds.), Vol. 1-4, Berlin, Wiley-VCH, 2007.

[2] T. Kumpulainen, B. Lang, A. Rosspeintner, E. Vauthey, Chem. Rev, 117 (2017) 10871.

[3] A. Brenlla, M. Veiga Gutiérrez, M. C. Ríos Rodríguez, F. Rodríguez-Prieto, M. Mosquera, J. L. Pérez Lustres, J. Phys. Chem. Lett., 5 (2014) 989.

Exploring the role of surface chemistry of carbon xerogels in the oxygen reduction reaction

Katarzyna Morawa Eblagon*, Natalia Rey-Raap, M. Fernando R. Pereira, José L. Figueiredo

Laboratory of Separation and Reaction Engineering—Laboratory of Catalysis and Materials (LSRE-LCM), Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto
*keblagon@fe.up.pt

The broader expansion of renewable-energy technologies such as proton exchange membrane fuel cells (PEMFCS) or metal air batteries is hindered by the low efficiency of the oxygen reduction reaction (ORR). The benchmark electrocatalyst for this important reaction is Pt/C; however, its future is shadowed with its high cost, scarcity, and insufficient durability [1,2]. Thus, it is imperative to find a cheaper, metal –free electrocatalyst able to enhance the kinetics of ORR and to replace Pt in these devices. Among other materials, heteroatom-doped carbons, mainly those with nitrogen functionalities [2], showed very promising results as electrocatalysts for the ORR.

The surface chemistry of carbon materials, in addition to their texture, is a key factor determining the activity and selectivity of the electrocatalyst. In this regard, our work highlights the importance of the surface chemistry in ORR, through an electrochemical and physicochemical study of N- and O-doped carbon xerogels (CXs).

In the present work, CXs were synthesized by carbonization of organic gels prepared according to Pekala's method [3]. The prepared CXs were subsequently functionalised with N via treatment in gaseous NH_3 at different temperatures (650-950 °C). For comparison, oxygen groups with different acidity were introduced into CXs by functionalisation using citric or nitric acids, as well as by thermal treatment in the flow of diluted oxygen. The characterisation of the samples demonstrated that the type of nitrogen groups as well as the texture of the N-doped CXs could be tuned by changing the ammonia treatment temperature. In addition, it was found that ball-milling of the materials prior to the preparation of the electrodes resulted in the introduction of oxygen functionalities to N-doped CXs. Regarding functionalisation with oxygen, the treatment of CXs with nitric acid introduced carboxylic functionalities, whereas functionalisation in gaseous oxygen resulted mainly in carbonyl groups. Interestingly, as shown by EA, the aforementioned O-doped CXs contained similar total amounts of oxygen. On the other hand, the treatment with citric acid resulted in a much lower total amount of oxygen that was mainly in the form of carboxylic anhydrides, according to TPD results.

The electrocatalytic activity of the doped CXs was compared in electrochemical measurements adopting a typical three-electrode cell setup in alkaline solution. In general, it was found that the limiting current density and the onset potential were determined by the surface chemistry of the samples, and did not depend solely on their microporosity. Considering the N-doped materials, the number of electrons involved in the reaction mechanism increased with the temperature of the ammonia treatment; however, it was always lower than that observed in the case of O-enriched samples. A considerable onset potential was obtained for CX treated in ammonia at 950 °C, and the number of transferred electrons was stable in case of this sample. A general correlation was established between the type of active centres and the electrochemical activity of heteroatom-doped CXs in ORR.

Acknowledgements
Financed by projects: Project UNIRCELL – POCI-01-0145-FEDER-016422 – funded by European Structural and Investment Funds (FEEI) through - Programa Operacional Competitividade e Internacionalização - COMPETE2020, NORTE-01-0145-FEDER-000006 - funded by NORTE2020 through PT2020 and ERDF, and Associate Laboratory LSRE-LCM - UID/EQU/50020/2019 - funded by national funds through FCT/MCTES (PIDDAC).Dr A. Malaika is thanked for assistance in the preparation of N-doped CXs.

References
[1] X. Ge et al, ACS Catalysis, 5 (2015) 4643.
[2] R. Gomes Morais, N. Rey-Raap, J. L. Figueiredo, M.F.R Pereira, Journal of Nanotechnology,10 (2019) 1089.
[3] R.W. Pekala, Journal of Material Science, 24 (1989) 3221.

Investigation of Orientationally Disordered Solid Phases

Joana F.C. Silva[1,*], Mário T.S. Rosado[1], M. Ermelinda S. Eusébio[1]
[1]CQC; Departamento de Química, Universidade de Coimbra, Rua Larga, 3004-535 Coimbra, Portugal
**joana.silva@student.uc.pt*

Disordered solid phases include amorphous solids and mesophases like liquid and plastic crystals. They have some attractive properties due to their higher energy, lower thermodynamical stability, than the corresponding ordered phases, namely higher solubility.

The major difference between amorphous and crystalline materials lies in the long-range structural order. Plastic crystals retain long-range positional order, while amorphous solids do not. The orientational disorder in plastic crystals increases their relative enthalpy and entropy, making them closer to liquids. Thus, they are characterized by small enthalpies and entropies of fusion.

The occurrence of orientationally disordered crystal phases was investigated in the polymorphism of hydrogen bonded molecules. Aiming to find correlations between the ability to form this type of phases, the molecular shape and intermolecular interactions existing in solid phases, pinanediol, a globular vicinal diol, was chosen.

A preliminary conformational search and optimization with DFT calculations was followed by experimental investigation of the thermal behavior using DSC and polarized light thermomicroscopy. FTIR-ATR and powder and single crystal X-ray diffraction were used for the analysis of the observed phases.

The formation of plastic crystal phases was observed, in addition to the identification of several ordered polymorphic forms. The crystal structure of the most stable ordered polymorph was resolved by single-crystal X-ray diffraction.

The Hirshfeld surfaces and their fingerprints were generated from the structures of the ordered crystals. Parameters calculated from these surfaces related to the shape of the molecules were found to be related to the plastic crystal forming ability. It was concluded that the globular form of the molecules has an essential contribution to the plastic phase forming capacity, despite the existence of intermolecular hydrogen bonding.

The thermal analysis of the chiral compound was focused not only on the pure enantiomers but also on their binary mixtures of various compositions. The binary phase diagram revealed that the equimolar mixture of pinanediol enantiomers produces a racemic compound. Mixtures of different composition also formed plastic crystals, being identified as solid solutions melting at a lower temperature than the pure enantiomers.

Acknowlegement
Coimbra Chemistry Center, CQC, is supported by national funds through FCT - Fundação para a Ciência e Tecnologia, under the project UID/QUI/00313/2019. This work was also supported by the FCT Programme for Cooperation in Science between Portugal and Poland under the project: Polymorphism – from molecular crystals to mesomorphic phases – structure and dynamics. JFCS acknowledges the support of a PhD grant awarded by FCT (SFRH/BD/146809/2019).

Investigation on the solubility and other thermophysical properties of quaternary ammonium salts aqueous solutions

Sérgio M. Vilas-Boas[1-3], Emanuel A. Crespo[2], Dinis O. Abranches[2], Olga Ferreira[1,3], João A. P. Coutinho[2] and Simão P. Pinho[1,3]
[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]CICECO − Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[3]LSRE-LCM, Instituto Politécnico de Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal
sergiovboas@ipb.pt

Quaternary ammonium salts (QAS) are a large class of cationic compounds with a wide range of applications, such as ingredients in the manufacturing of clothing softeners, asphalt emulsions and several personal care products [1]. Some QAS have also been used in the design of alternative solvents, such as eutectic solvents, or ionic liquids, due to their particular physical chemical properties, such as low melting temperatures, low viscosity, negligible vapor pressure and high ionic conductivities [2]. Once selected as a separation agent thermodynamic data, such as solubility and density, are key information in process design and development. In addition, the use of predictive and semi-predictive thermodynamic models in the correlation and prediction of thermophysical properties, and phase equilibria, is also important to reduce the time-consuming experimental work.

In this context, the solubility of choline chloride [Ch]Cl, choline bromide [Ch]Br and a series of eight tetraalkylammonium halides ($N_{1111}X$, $N_{2222}X$, $N_{3333}X$, $N_{4444}X$, where X is the chloride or bromide anion) were measured by the isothermal shake-flask method coupled with refractometry analysis in the temperature range between 298.2 K and 343.2 K. The experimental data were then compared with the scarce data available in literature. To the best of our knowledge, solubility data of the studied QAS in aqueous systems are reported for the first time for temperatures higher than 298.2 K. Also, the phase behavior of the pure salts was investigated by differential scanning calorimetry, even though the inherent thermal instability of these salts considerably limits the interpretation of the results. The solid-solid and melting transitions provide insights to understand the solubility deviations from ideality, providing a closer picture of the solid-liquid equilibrium behavior of those systems.

Densities of the aqueous solutions of the selected QAS (salt mole fractions from 0.05 up to saturation at 298.2 K) were also experimentally determined by a vibrating densimeter coupled to a U-shaped tube in a wide temperature range. Whenever possible, the densities were critically compared to literature data. In addition, the experimental density data as well as water activity coefficients reported in literature [3] were correlated by the PC-SAFT equation of state. One advantage of the SAFT type EoS is the transferability of the fitted parameters to compounds where only small structural changes are present. Thus, the parameters obtained here could be used to predict the PC-SAFT parameters for similar salts with different chain length. The prediction of the solubility of the QAS in water were in very good agreement with the experimental data for $[N_{2222}]Br$, [Ch]Br, $[N_{1111}]Cl$ and $[N_{2222}]Cl$. Aiming to extend the satisfactory results to all the studied systems, the SAFT parameters were successfully refitted by including the solubility data. Finally, the PC-SAFT model was used to calculate the activity coefficients of the salt as well as to estimate the melting temperatures of the pure compounds.

Acknowledgments
This work was developed within the scope of the project CICECO – Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES; and project AllNat - POCI-01- 0145-FEDER-030463 (PTDC/EQU-EPQ/30463/2017), financed by FEDER funds through COMPETE and Portugal2020 and national funds through FCT - Fundação para a Ciência e a Tecnologia. The authors also thank FCT for financial support to Sérgio. M. Vilas-Boas grant (SFRH/BD/138149/2018) and Emanuel. A. Crespo grant (SFRH/BD/130870/2017).

References

[1] C.W. Weston, J.R. Papcun, M. Dery, Ammonium compounds, Kirk-Othmer. 2 (2007) 711–761.
[2] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep Eutectic Solvents (DESs) and Their Applications, Chem. Rev. 114 (2014) 11060–11082.
[3] S. Lindenbaum, G.E. Boyd, Osmotic and Activity Coefficients for the Symmetrical Tetraalkyl Ammonium Halides in Aqueous Solution at 25°, J. Phys. Chem. 68 (1964) 911–917.

Assessment of the actual light dose in phototherapies and photoreactions

Fabio A. Schaberle
Centro de Química da Universidade de Coimbra, Rua Larga, Coimbra, Portugal
**e-mail: fschaberle@qui.uc.pt*

All photoreactions or phototherapies initiate when a chromophore absorbs light. Absorption of light depends on the spectral overlap between the light source emission and the chromophore spectral absorption, resulting in the number of photons absorbed that is a key parameter starting photoprocesses [1]. Most papers on phototherapy field report light doses regardless if the light is only partially absorbed or shifted relatively to the absorption peak, misleading the actual light dose value and not allowing quantitative comparisons between photosensitizers and light sources. In addition, in photoreactions, the overlap between chromophore absorption spectrum and emission of a light source allows for the correct assessment of the light dose needed for inducing a reaction.

As an example, in the figure 1 are depicted the absorption spectrum of Tetraphenylporphyrin (TPP) and the solar emission spectrum. If a hypothetical photoreaction or phototherapy was intended to be initiated using the sun as light source, the Light Dose Correction (LCD) would indicate that, in this particular case, the light power measured with a power meter should be multiplied by a factor of 0.084; meaning that only 8.4% of the sun light is actually absorbed by TPP initiating the photoprocesses. Thus, if the irradiance of sun light was measured as 100mW/cm^2 the actual light power initiating the processes would be 8.4 mW/cm^2 (grey curve in fig. 1). This value of 8.4 mW/cm^2 is the actual irradiance that should be considered in the calculation of light dose (J/cm^2) needed for initiating photoreaction, and the irradiance value that should be reported.

This correction for the actual light dose absorbed is calculated using the Beer-Lambert equation for the intensity of light absorbed. From this equation, the number of photons absorbed can be calculated using the emission and absorption spectra from the light source and chromophore, respectively. In order to normalize the possible maximum absorption, an ideal light source is considered (monochromatic light source at the peak of absorption) having the same irradiance as that of the light source employed. In this way the LCD factor can be obtained as the ratio of number of photons absorbed between the light source employed and the ideal light source. This method allows comparing light doses delivered for any combination of light source (broad or narrow band or daylight) and photosensitizers and for the correct assessment of light doses in photoreactions.

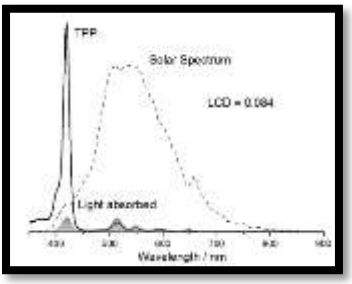


Fig.1. Tetraphenylporphyrin (TPP) absorption spectrum and solar emission spectrum showing the actual light absorbed by TPP and the correction factor (LCD) for the measured irradiance.

Acknowledgements
The author thank FCT and QREN/FEDER for funding (UID/QUI/00313/2019, POCI-01-0145-FEDER-027996).

References
[1] Schaberle, F. A., Photodiagnosis and Photodynamic Therapy, 23 (2018), 75.

Activity coefficients at infinite dilution of water and organic compounds in methylimidazolium based ionic liquids

Sérgio M. Vilas-Boas[1-3], Mónia A. R. Martins[2], Sabrina Rosini[1,3,4], Priscila G. Leite[4], Urszula Domańska[5], João A. P. Coutinho[2], Olga Ferreira[1,3] and Simão P. Pinho[1,3]
[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]CICECO − Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[3]LSRE-LCM, Polytechnic Institute of Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal
[4]UTFPR-Departamento de Engenharia Química, Universidade Tecnológica Federal do Paraná, 84016-210 Ponta Grossa, Brazil
[5]Physical Chemistry Department, Warsaw University of Technology, 00-661 Warsaw, Poland
sergiovboas@ipb.pt

Ionic liquids (ILs) are well-recognized as potential designer solvents in several extraction and separation processes due to their exceptional solvation capability, low vapor-pressure, nonflammability among other [1]. In addition, ionic liquids ability to selectively interact with different solutes makes them suitable candidates to compose stationary phases in gas-chromatography [2]. Solute activity coefficients at infinite dilution can so be measured by gas chromatography being a very useful property in the design of separation processes [3].

In this work, activity coefficients at infinite dilution (γ_{13}^{∞}) of water, and several organic compounds (including alkanes, aromatics, ketones, esters, ethers, alcohols, terpenes and others) were measured in methylimidazolium based ILs, namely [C_{12}mim][BF_4], [C_{14}mim][BF_4] and [C_4mim][OAc] at six different temperatures. Excess partial molar properties at infinite dilution, such as enthalpy, entropy and Gibbs energy were derived from the experimental data, providing further information regarding the interactions between the solutes and the ILs. In general, the entropic effects are dominant over the enthalpic ones for less polar solvents, while for alcohols and polar solvents is the opposite. For [C_{12}mim][BF_4] and [C_{14}mim][BF_4], calorimetric studies showed the formation of liquid crystals before melting. The thermodynamic analysis was then evaluated in both liquid crystal and liquid phases.

Density data were either experimentally measured or estimated for the selected ILs, and used in the calculation of gas-liquid partition coefficients. This coefficient gives information on the distribution of the solutes between liquid and gas phases, providing a more complete picture for the role of each ionic liquid in extraction and separation processes. In general, the gas/liquid partition coefficients increase as the temperature increases as well as the alkyl-chain increases for hydrocarbons, ketones, esters, or alcohols.

Lastly, selectivity and capacity were calculated for industrially relevant separations, namely octane/benzene and cyclohexane/benzene, and compared with literature data for other methylimidazolium based ionic liquids. The selectivity increases as the alkyl-chain of the ILs decreases, whereas higher capacity requires longer alkyl-chains. Once a suitable solvent is one that presents both high selectivity and capacity, a fair compromise between these two attributes should be accomplished.

Acknowledgments
This work was developed with the scope of project AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by NORTE 2020. Sérgio M. Vilas-Boas thanks the support given by Fundação de Ciência e Tecnologia -FCT for the grant SFRH/BD/138149/2018.

References

[1] S.P.M. Ventura, F.A. E Silva, M. V. Quental, D. Mondal, M.G. Freire, J.A.P. Coutinho, Ionic-Liquid-Mediated Extraction and Separation Processes for Bioactive Compounds: Past, Present, and Future Trends, Chem. Rev. 117 (2017) 6984–7052.
[2] H. Zhao, S. Xia, P. Ma, Use of ionic liquids as "green" solvents for extractions, J. Chem. Technol. Biotechnol. 80 (2005) 1089–1096.
[3] M.A.R. Martins, J.A.P. Coutinho, S.P. Pinho, U. Domańska, Measurements of activity coefficients at infinite dilution of organic solutes and water on polar imidazolium-based ionic liquids, J. Chem. Thermodyn. 91 (2015) 194–203.

QUÍMICA INORGÁNICA

Influence of UiO-66(Zr) preparation strategies in its catalytic efficiency for desulfurization processes

Alexandre Viana*, **Susana Ribeiro, Baltazar de Castro, Salete S. Balula and Luís Cunha-Silva**
REQUIMTE-LAQV & DQB, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal.
**up201405091@fc.up.pt*

Oxidative desulfurization (ODS) is one of the most promising cost-effective methods for the deep desulfurization of diesel fuel, corresponding to the need for lower emission of sulfur which results from its combustion.[1] ODS process allows the efficient removal of the most refractory sulfur-containing compounds leading to near zero sulfur fuels under mild conditions (low temperature and pressure). Following our research activity, we have been developing novel catalytic systems for efficient ODS processes resorting on Metal-Organic Frameworks (MOFs) as active heterogeneous catalysts. MOFs are highly organized coordination polymers that are often crystalline and porous. UiO-66(Zr) is a highly stable and, due to its high surface area and exceptional chemical, thermal and mechanical stability, was applied as heterogeneous catalyst in ODS processes.[2]

UiO-66(Zr) samples obtained by solvothermal and microwave assisted synthesis (MWAS) procedures were characterized, and their catalytic efficiency was investigated for ODS processes using a multicomponent model diesel containing benzothiophene and dibenzothiophene derivatives. Several preparation parameters seemed to play an important role in the catalytic performance of the UiO-66(Zr) material, as well as in its recycle capacity. The material prepared by the solvothermal procedure with a fast cooling time showed the best catalytic performance (desulfurization efficiency of 99.5% after 3 h). However, the application of the UiO-66(Zr) material prepared by the MWAS method (desulfurization efficiency of 96% after 3 h) conciliated a higher number of advantages, such as shorter reaction time preparation (15 min) and high catalytic activity for a higher number of reaction cycles. The UiO-66(Zr) prepared by the MWAS method was used for the first time in an oxidative desulfurization process, and according to the catalytic results obtained (high recycle capacity and stability) and shorter reaction time preparation, seems to be a promising material for industrial application. We are following these investigations by developing procedures for the activation and reactivation of the UiO-66(Zr) catalysts.

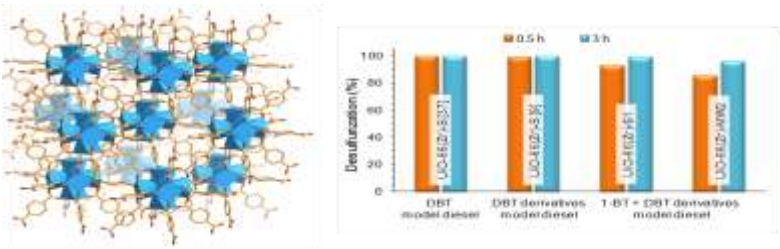


Fig.1. 3D framework of UiO-66(Zr) (left) and desulfurization performances of several samples (right).

Acknowledgements
This work was partly funded through the project REQUIMTE-LAQV (Ref. UID/QUI/50006/2019) and the project GlyGold, PTDC/CTM-CTM/31983/2017, financed by national funds through the FCT/MCTES and when appropriate co-financed by FEDER (Fundo Europeu de Desenvolvimento Regional) under the PT2020 Partnership Agreement.

References

[1] Granadeiro, C. M.; Ribeiro, S. O.; Karmaoui, M.; Valença, R.; Ribeiro, J. C.; Castro, B.; Cunha-Silva, L.; Balula, S. S. Chemical Communications 51 (2015) 13818.
[2] Viana, A. M.; Ribeiro, S. O.; Castro, B.; Balula, S. S.; Cunha-Silva, L. Materials 12 (2019) 3009.

Copper and cobalt complexes as a structural model for the galactose oxidase active site

L. Rodríguez-Silva[1*], L. Rouco[1], E. Gómez-Fórneas[1], S. Fernández-Fariña[2] , L. M. González-Barcia[2]
[1]Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela,
27002, Lugo, Spain
[2]Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, Campus Vida, 15782, Santiago de Compostela, Spain.
**laura.rodriguez@usc.es*

Some metalloenzymes have coordinated phenolate or proximal phenol moieties of tyrosine residues at the active site, which are essential for the enzymatic activities. Galactose oxidase (GOase) is a single-copper oxidase, and the active form has a Cu(II)–phenoxyl radical bond performs the two-electron oxidations of primary alcohols to aldehydes, respectively, coupled with the reduction of O_2 to H_2O_2.[1]
From the standpoint of coordination chemistry, one-electron oxidation of transition-metal may be either a metal- or a ligand-centered reaction. [2] The proposed mechanism of catalysis has a multielectron redox reactions by using multinuclear active sites (i.e., 1 e^- per Cu, shuttling between Cu^I and Cu^{II}).[3]
On the other hand, the coordination chemistry of transition metal complexes containing catechols and o-benzoquinone ligands has been developed with interesting and surprising results.[4] Initial interest in these complexes was associated with the redox activity of quinone ligands. In this sense studies using M(II)-phenoxyl radical complexes (M= Cu and Co) have provided profound insight into the structure and physicochemical properties of the active form of GOase.

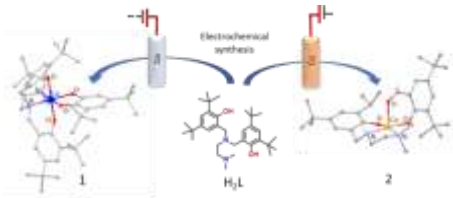


Fig.1. Reaction scheme for cobalt (1) and copper (2) complexes

Herein, we report the electrochemical synthesis and characterization of M-phenoxyl complexes (M=Co and Cu) derived from 'non-innocent o-aminophenol N_2O_2 based ligand H_2L. With the $L^{(2-)}$ form of a tetradentate ligand, with a redox-active (o-aminophenol) and a redox-inactive part, the complexes $[Co^{III}L(semiquinone)]$ (1) and Cu(II)-phenoxyl (2), have been synthesized and structurally characterized. These complexes complete a series of N_2O_2-donors ligands with bulky substituents on the phenolate moiety. This type of system has allowed isolating complexes with ligands in different redox levels.

Acknowledgment
Xunta de Galicia (GRC ED431C 2018/13 y Red de Investigación MetalBIO ED431D 2017/01).

References

[1] J. W. Whittaker, Met. Ions Biol. Syst. 30, (1994), 315.
[2] P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller, K. J. Wieghardt. J Am. Chem. Soc. 123, (2001) 2213
[3] Y. Shimazaki, S. Huth, A. Odani, O. Yamauchi, Angew. Chem., Int. Ed. 39, (2000) 1666.
[4] Y. Shimazaki, R. Kabe, S. Huth, F. Tani, Y. Naruta, O. Yamauchi, Inorg Chem. 46,15 (2007) 6083

Mn(III) biomimetic models: catalase activity and kinetic studies of their reaction with H_2O_2 and TBHP

Marcelino Maneiro[1,*], Lara Rouco[1], Andrea Liberato[2], M. Jesús Fernández-Trujillo[2], Manuel G. Basallote[2]
[1]Universidade de Santiago de Compostela, Facultade de Ciencias, Avda. Alfonso X, Lugo, Spain
[2]Universidad de Cádiz, Facultad de Ciencias, Puerto Real, Cádiz, Spain
**marcelino.maneiro@usc.es*

Catalases enzymes are part of the defence mechanisms against the reactive oxygen species generated by oxidative stress [1], catalysing the decomposition of hydrogen peroxide to water and oxygen. It is well established that some manganese(III)-salen complexes may protect cells from oxidative damage in animal models. However, the mechanism of action of these biomimetic models remain exiguously understood [2]. In this communication, we report the catalase studies on three novel manganese(III)-salen complexes (**1**-**3**) and the commercially available EUK-134. We have also performed kinetic studies of the reaction of the four systems versus H_2O_2 and tertbutyl hydroperoxide (TBHP) in different conditions (varying the solvent, temperature and illumination).

During studies aimed to getting a better understanding of the kinetics of the processes involved in this antioxidant behavior, an important effect on the solvent in the kinetics of reaction of the complexes with H_2O_2 was revealed that suggests a change in the mechanism of reaction of the complexes. The kinetic data in methanol and buffered aqueous solutions correlate well with the results of the test of catalase activity, thus showing that the rate determining step in the catalytic cycle corresponds to the initial reaction of the complexes with H_2O_2 (Fig. 1).

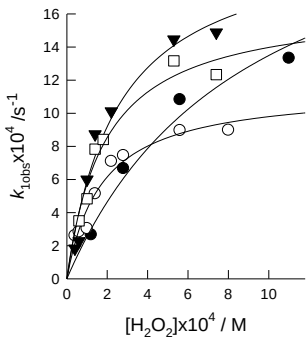


Fig.1. Plot of the [H_2O_2] dependence of the observed rate constant in the reaction of the Mn complexes with H_2O_2 in water solution at 37ºC and pH= 7.25: **1** (empty circles), **2** (triangles), **3** (filled circles) and **EUK-134** (squares).

Acknowledgements
Xunta de Galicia (GRC ED431C 2018/13), and Red de Investigación MetalBIO (ED431D 2017/01).

References

[1] M.T. Lin, M.F. Beal, Nature, 443 (2006) 787.
[2] Liberato, M.J. Fernández-Trujillo, Á. Máñez, M. Maneiro, L. Rodríguez-Silva, M.G. Basallote, Inorg. Chem. 57 (2018) 14471.

NMR study of the interaction of Ga(III) complexes with liposomes

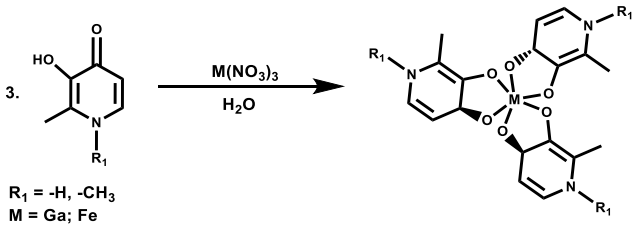
S. Vinhas[1,*], G. Ivanova[1], A. Leite[1], B. Castro[1] and M. Rangel[2]
[1]REQUIMTE-LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4069-007 Porto, Portugal
[2]REQUIMTE-LAQV, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, 4050-313 Porto, Portugal
**Silvia_vinhas@hotmail.com*

We found that *tris*(3-hydroxy-4-pyridinonate)Fe(III) complexes are potential novel iron fertilizers [1]. Studies performed with soybean plants, in which two Fe-chelates were compared, [Fe(mpp)$_3$] and [Fe(dmpp)$_3$], were indicative that the first chelate presents a superior ability to be translocated from the roots to the shoots. The complexes exhibit variable lipophilicity and for that reason are expected to interact differently with biological membranes.

To get insight on the permeation properties of the Fe(III)-chelates we performed EPR studies using liposomes prepared from a soybean lipid extract and enriched with spin probes 5-DSA and 16-DSA. NMR studies with the parent diamagnetic/isostructural Ga(III)-chelates were also performed. The complexes were synthesized in our group as described in literature and characterized by HRMS, elemental analysis and NMR (^{1}H; ^{13}C and ^{135}DEPT) for Gallium complexes (synthesis and formulae in Fig. 1).

The EPR results obtained for both the Fe and Ga-chelates are consitent with influence of the ligand on the chelates permeation properties.
The alterations observed on a number of NMR parameters, such as chemical shifts, line shape, spin−lattice relaxation time (T1), and translational diffusion coefficient of thecomplexes and the liposomes allowed to obtain information on the affinity of the Ga-chelates for the phospholipid bilayer.

Fig.1. Scheme of the used method to synthesise Ga(III) and Fe(III) complexes.



Agradecimientos
This work received financial support from FCT/MEC through national funds and co-financed by FEDER, under the Partnership Agreement PT2020, through the projects UID/QUI/50006/2013-POCI/01/0145/FEDER/007265 (LAQV/REQUIMTE) and project PTDC/AGRPRO/3515/2014-POCI-01-0145-FEDER-016599.

Referencias
[1] Santos, C.S., Carvalho, S.M.P., Leite, A., Moniz, T., Roriz, M., Rangel, A.O.S.S., Rangel, M., Vasconcelos, M.W., Plant Physiology and Biochemistry, 2016, 106, 91-100.

QUÍMICA ORGÁNICA

Understanding the Mechanism of Action of LpxK - a Key Therapeutic Target for Antibiotic Drug Discovery

Tania Gerpe Amor,[1] Emilio Lence,[1] Concepción González-Bello[1*]

Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Departamento de Química Orgánica, Universidade de Santiago de Compostela, Jenaro de la Fuente s/n, 15782 Santiago de Compostela, Spain.
**Contact e-mail: concepcion.gonzalez.bello@usc.es*

As recently reported by the World Health Organization, *Acinetobacter baumannii* is one of the most dangerous Gram-negative pathogens since it has developed the biggest antibiotic resistance in the last decades, including to carbapenems, which are often considered as antibiotics of last resort. It is a healthcare-associated human pathogen that has been linked with a broad spectrum of infectious diseases, including pneumonia and blood-stream infections and a major concern on patients with a weak immune system undergoing surgery, cancer chemotherapy and dialysis, amongst others, for whom our ability to deal with secondary infections is crucial. It is therefore not surprising that the development of new antibiotics for the effective treatment of infections caused by this pathogen is nowadays a priority worldwide.[1]

Our research group is interested in studying the therapeutic potential of an unexplored enzyme, the tetraacyldisaccharide 4'-kinase (LpxK), which role in the viability of *A. baumannii* and its capacity to produce infection has been recently identified by us to be crucial. LpxK is involved in the biosynthesis of Lipid A, which is an essential component of the outer membrane of Gram-negative bacteria.[2] The enzyme catalyzes the stereospecific phosphorylation of the 4-hydroxyl group in the 1P-dissacharide (DSMP) to provide lipid IV_A by using ATP. As part of a project aimed at the development of inhibitors of the LpxK enzyme, we report herein the study in atomic detail of the keys of the substrate recognition for catalysis and turnover, for the subsequent rational design of inhibitors. To this end, we have taken the advantage of the structural information available for *A. aeolicus* LpxK (Aa-LpxK) to create reliable models of the *A. baumannii* LpxK (*Aa*-LpxK) Michaelis complex, as well as the corresponding product complex. [3,4]. Our recent progress in this project will be presented.

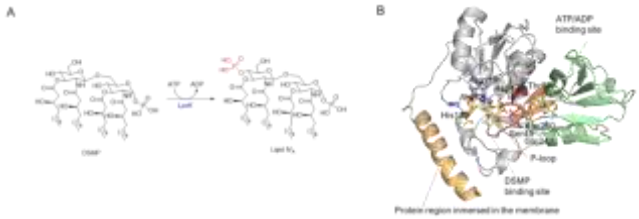


Fig 1. A) Reaction catalysed by the LpxK enzyme. B) Relevant structural features of *Aa*-LpxK enzyme. The *N*-terminal domain (grey), the *C*-terminal domain (green) and the protein region that is inmersed in the membrane (orange) are higlighted.

Acknowledgements
Financial support from the Spanish Ministry of Economy and Competiveness (SAF2016-75638-R), the Xunta de Galicia [Centro singular de investigación de Galicia accreditation 2016-2019 (ED431G/09) and ED431B 2018/04] and the European Regional Development Fund is gratefully acknowledged.

References
[1] V. M. D`Costa, C. E. King, L. Kalan, M. Morar, W. W. L. Sung, C. Schwarz, D. Froese, G. Zazula, F. Calmels, R. Debruyne, G. B. Golding, H. N. Poinar, G. D. Wright, Nature 477 (2011) 461.
[2] C. González-Bello, Adv. Ther. 2 (2018) 180011.
[3] R. P. Emptage, K. D. Daughtry, C. W. Pemble, C. R. H. Raetz, PNAS 109 (2012) 12961.
[4] R. P. Emptage, C. W. Pemble, J. D. York, C. R. H. Raetz, P. Zhou, Biochemistry 52 (2013) 2290.

Novas pirano-3-desoxiantocianinas e estudo das suas propriedades cromáticas

Vânia Gomes, Nuno Mateus, Victor de Freitas, Luís Cruz*

Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre s/n, 4169-007Porto, Portugal
**luis.cruz@fc.up.pt*

As pirano-3-desoxiantocianinas são pigmentos que derivam das antocianinas, apresentam uma ampla gama de cores que vão desde o amarelo ao laranja, vermelho até ao roxo e azul, e podem ser encontrados em alimentos processados como em sumos de fruta e vinhos.[1] Comparativamente aos seus percursores, as pirano-3-desoxiantocianinas possuem um anel pirânico adicional (anel D) que lhes confere uma maior estabilidade cromática em solução. A presença deste anel previne a ocorrência de determinadas reações características das antocianinas (hidratação, tautomerização e isomerização) que levam à perda de cor com o aumento do pH. Assim, as espécies em equilíbrio das pirano-3-desoxiantocianinas dependem essencialmente de reações de transferência de protão (reações ácido-base) com a variação de pH.[2][3] A mudança de cor dos pigmentos em solução é determinada pelos seus valores de pK_a, os quais são dependentes dos grupos substituintes suscetíveis à protonação/desprotonação (-OH, -NH_2, etc).
As pirano-3-desoxiantocianinas descritas até ao momento possuem geralmente substituição no carbono 7 (ver figura 1) por um grupo hidroxilo, o qual se sabe que tem um papel importante nos equilíbrios de reação. Neste trabalho, pretendeu-se estudar o efeito da ausência deste grupo hidroxilo nos valores de pK_a deste tipo de pigmentos. Diferentes pigmentos com a estrutura geral apresentada na figura 1 foram sintetizados, caracterizados estruturalmente e as suas propriedades cromáticas foram estudadas em solução. De forma geral, a ausência do grupo hidroxilo na posição 7 levou a um aumento dos valores de pK_{a1} relativamente aos valores dos pigmentos com o grupo hidroxilo nessa posição. Os valores de pK_{a1} obtidos variam ente 5,8 ± 0,1 e 6,8 ± 0,1. Estes valores encontram-se no intervalo de pH de deterioração de muitos alimentos, o que faz com estes pigmentos se apresentem como potenciais candidatos para o desenvolvimento de sensores de pH para embalagens alimentares com o objetivo de monitorizar a qualidade dos alimentos em tempo real.

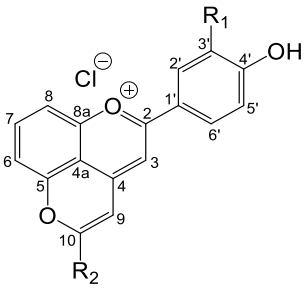


Fig.1. Estrutura geral dos pigmentos sintetizados e estudados neste trabalho.

Agradecimentos
Este trabalho de investigação foi apoiado pelo projeto PTDC/OCE-ETA/31250/2017 financiado pela FCT/MEC através de fundos nacionais e cofinanciado pela FEDER, no âmbito do Acordo de Parceria PT2020 (UID/QUI/50006/2013-POCI/01/0145/FEDER/007265). Luís Cruz agradece à FCT pelo seu contrato de investigador. Vânia Gomes agradece à FCT pela sua bolsa de doutoramento (SFRH/BD /136556/2018).

Referencias
[1] J. L. C. Sousa, V. Gomes, N. Mateus, F. Pina, V. de Freitas, L. Cruz, *Tetrahedron* 2017, 73 (41), 6021-6030
[2] L. Cruz, J.L.C. Sousa, A. Marinho, N. Mateus, V. de Freitas, *Tetrahedron Lett* 2017, 58, 159–62
[3] V. Gomes, N. Mateus, V. Freitas, L. Cruz, *Dyes and Pigments* 2019, 167, 60-67

Chlorophyll derivatives bearing uracil-alditols: synthesis and antibacterial and antitumor properties

Cristina J. Dias[1,*], Nuno M. M. Moura[1], Maria G. P. M. S. Neves[1], Margarida Fardilha[2], Adelaide Almeida[3], Maria A. F. Faustino[1]

[1]QOPNA & LAVQV REQUIMTE and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2]Laboratory of Signal Transduction, IBIMED, Medical Sciences Department, University of Aveiro, 3810-193 Aveiro, Portugal
[3]Microbiology Group, CESAM and Department of Biology, University of Aveiro, 3810-193 Aveiro, Portugal
*cristina.jesus.dias@ua.pt

Photodynamic therapy (PDT) has been used with success in the treatment of various oncological and non-oncological diseases such as bacterial infections [1-4]. This therapy involves the use of visible light, oxygen and the administration of a photosensitizer (PS), leading to the formation of reactive oxygen species (ROS) which will induce tissue damage leading to cell death [1,2]. The chlorophylls derivatives, such as chlorin e_6 or pheophorbide *a* due to the good absorption in the red region of the electromagnetic spectrum has been investigated as PSs in PDT of tumors, however, their solubility in physiological medium and selectivity to neoplastic tissues is low [2]. In order to overcome this drawback, the conjugation of potential photosensitizers with some biomolecules such as carbohydrates has been attracting the attention of the scientific community [2]. The presence of these molecules linked to the porphyrinic core bring a positive impact on their selectivity, solubility and photosensitizing properties, making them potential therapeutic agents for PDT of cancer or even on the photoinactivation of microorganisms [2]. However, the introduction of other bioactive moieties, such as uracil derivatives, known by their biological activities can allows a synergic effect that can bring an improvement of PDT efficiency [5].

In this communication it will be reported an efficient access to new chlorophylls derivatives extracted from *Spirulina maxima*, functionalized with different uracil-alditols moieties (Fig. 1) and will be discussed their photodynamic efficiency against a prostate cancer cell line (PC3) and to *Staphylococcus aureus* a gram-positive bacterium.

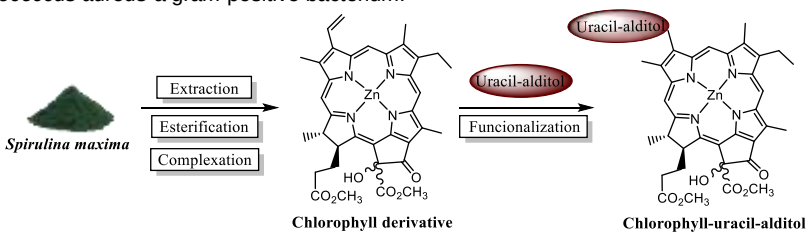


Fig.1. Key steps for the preparation of the chlorophyll derivatives bearing uracil-alditols.

Acknowledgements
Thanks are due to the University of Aveiro and FCT/MCT for the financial support for the QOPNA (FCT UID/QUI/00062/2019), CESAM (FCT UID/AMB/50017/2019), and Institute for Biomedicine – iBiMED (UID/BIM/04501/2013 and to project PREVINE (FCT-PTDC/ASP-PES/29576/2017) through national funds (OE) and where applicable co-financed by the FEDER-Operational Thematic Program for Competitiveness and Internationalization-COMPETE 2020, within the PT2020 Partnership Agreement. Thanks are also due to the Portuguese NMR and Mass Networks. C. J. Dias also thanks FCT for her research grant (BI/UI51/8448/2018). and N.M.M. Moura his research contract respectively (REF.-048-88-ARH/2018) supported by national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia.

References

[1] Alves E., Faustino M.A.F., Neves M.G., Cunha Â., Nadais H., Almeida A., J Photochem Photobiol C Photochem Rev, 22 (2015) 34. [2] Abrahamse, H., Hamblin M., Biochem J, 473 (2016) 347. [3] Mesquita, M.Q., Dias C.J., Gamelas S., Fardilha M., Neves M.G.P.M.S., Faustino M.A.F., Ann Brazilian Acad Sci, 90 (2018) 1101. [4] Mesquita M.Q., Dias C.J., Neves M.G.P.M.S., Almeida A., Faustino M.A.F., Molecules, 23 (2018) 2424. [5] Pałasz, A., Ciez, D., Eur. J. Med. Chem., 97 (2015), 582.

Synthesis of new tetrasubstituted imidazoles with potential biological activity

Fábio Conceição[1,2*], Fernanda Proença[1], Concepción Gonzalez-Bello[2]

[1]Universidade do Minho, Largo do Paço, 4704-553, Braga, Portugal
[2]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, Jenaro dela Fuente s/n, 15782 Santiago de Compostela, Spain

*id6970@uminho.pt

Azoles (in particular imidazoles) are a very important pharmacophore widely present in natural products, such as biotin, amino acids, histidine, histamine and others, as well as in synthetic drugs already commercialized such as metronidazole (antibiotic and antiprotozoal agent), ketoconazole and clotrimazole (antifungal agents). Azole derivatives are also relevant motifs for drug discovery since they are incorporated in a variety of studies for the search of new anticancer[1–4], antibacterial[4], antinflamatory[4], antiglaucoma[4], antimicrobial[4] and antiviral agents[4,5].

In the present study, we report a new synthetic route for preparing novel tetrasubstituted imidazole derivatives, starting from diaminomaleonitrile and a selection of aldehydes, for the discovery of new potential anticancer drugs (**Fig.1**).

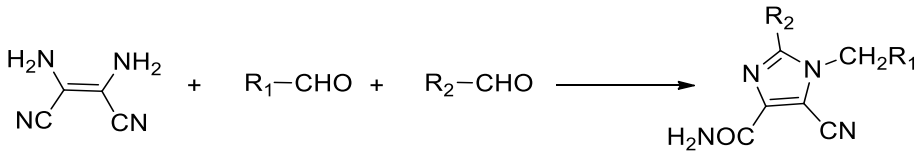


Fig.1. Tetrasubstituted imidazoles synthesized by the proposed method

Aknowledgments

We acknowledge the financial support from the Doctoral Programme in Chemistry funding at University of Minho and University of Santiago de Compostela. The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network (RNRMN) was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT

References

[1] James, D. A., Koya, K., Li, H., Chen, S. & Xia, Z. Conjugated indole-imidazole derivatives displaying cytotoxicity against multidrug resistant cancer cell lines. **16**, 5164–5168 (2006)
[2] Li, L. *et al.* Design, synthesis, and biological evaluation of 1-substituted -2-aryl imidazoles targeting tubulin polymerization as potential anticancer agents. *Eur. J. Med. Chem.* 111732 (2019)
[3] Bellina, F., Guazzelli, N., Lessi, M. & Manzini, C. Imidazole analogues of resveratrol: synthesis and cancer cell growth evaluation. *Tetrahedron* (2015).
[4] Ali, I. *et al,* Imidazoles as potential anticancer agents. *MedChemComm*, **8**, 1742–1773 (2017).
[5] Sharma, D. *et al.* Synthesis, antimicrobial and antiviral evaluation of substituted imidazole derivatives. *Eur. J. Med. Chem.,* **44**, 2347–2353 (2009).

Combined ammonium and pyridinium phthalocyanines for bacteria photoinactivation

Leandro M. O. Lourenço[1,*]
[1]QOPNA and LAQV-REQUIMTE, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal
*e-mail: leandrolourenco@ua.pt

Phthalocyanines (Pcs) are photoactive molecules that can absorb and emit light in a wide range of the UV-Vis spectrum with recognized potential for public health applications [1-4]. Several Pc molecules have been used as photosensitizers (PSs) in photodynamic inactivation (PDI) of pathogenic microorganisms [1,5,6]. Novel water soluble Zn(II)phthalocyanines (ZnPcs) peripherally substituted with 4-dimethylaminopyridine (DMAP) units (ZnPc **1** and **2**), and the corresponding quaternized derivatives (ZnPc **1a** and **2a**) were synthesized and characterized (**Scheme 1**). The presence of multi-positive charges on their periphery prevent their aggregation and enhance the solubility in aqueous medium. ZnPc **1a** and **2a** exhibited good photostability and high singlet oxygen ($^1O_2$) quantum yields. The biological assessment toward bioluminescent *E. coli* strain of the pyridinium ZnPc **1** and **2** and quaternized ZnPc **1a** and **2a** will be discussed.

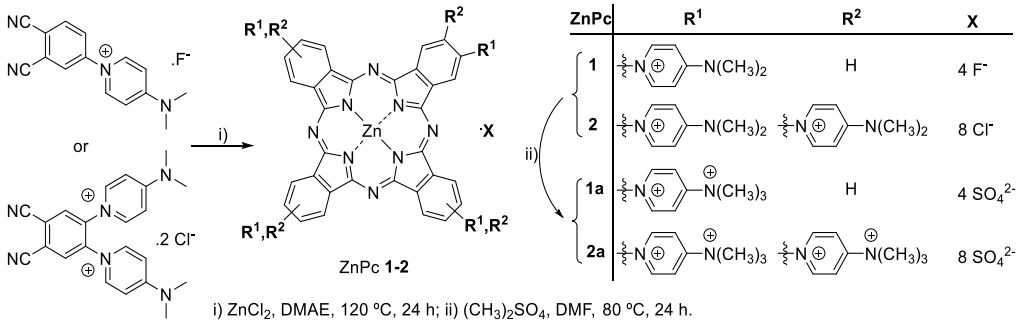


Fig. 1. Structures of pyridinium and ammonium zinc(II)phthalocyanines.

Acknowledgements:
Thanks are due to FCT/MEC for the financial support to QOPNA (FCT UID/QUI/00062/2019), CESAM (FCT UID/AMB/50017/2019), CICECO (FCT UID/CTM/50011/2019) and CQE (UID/QUI/0100/2019) research units, to the FCT projects (PTDC/QUI-QOR/31770/2017 and P2020-PTDC/QEQ-SUP/5355/2014), through national founds (PIDDAC) and where applicable co-financed by the FEDER-Operational Thematic Program for Competitiveness and Internationalization-COMPETE 2020, within the PT2020 Partnership Agreement. Thanks are also due to the Portuguese NMR and Mass Networks. I also thank all the co-authors of this work.

References:

[1] L. M. O. Lourenço, D. M. G. C. Rocha, C. I. V. Ramos, M. C. Gomes, A. Almeida, M. A. F. Faustino, F. A. A. Paz, M. G. P. M. S. Neves, Â. Cunha, J. P. C. Tomé, ChemPhotoChem, 3 (2019) 1.
[2] L. Marciel, L. Teles, B. Moreira, M. Pacheco, L. M. O. Lourenço, M. G. P. M. S. Neves, J. P. C. Tomé, A. Faustino, A. Almeida, Future Med. Chem., 9 (2017) 365.
[3] L. M. O. Lourenço, P. M. R. Pereira, E. Maciel, Válega, F. M. J. Domingues, M. R. M. Domingues, M. G. P. M. S. Neves, J. A. S. Cavaleiro, R. Fernandes, J. P. C. Tomé, Chem. Commun., 50 (2014) 8363.
[4] L. M. O. Lourenço, M. G. P. M. S. Neves, J. A. S. Cavaleiro, J. P. C. Tomé, Tetrahedron, 70 (2014) 2681.
[5] L. M. O. Lourenço, A. Sousa, M. C. Gomes, M. A. F. Faustino, A. Almeida, A. M.S. Silva, M. G. P. M. S. Neves, J. A. S. Cavaleiro, Â. Cunha, J. P. C. Tomé, Photochem. Photobiol. Sci., 14 (2015) 1853.
[6] M. Li, B. Mai, A. Wang, Y. Gao, X. Wang, X. Liu, S. Song, Q. Liu, S. Wei, P. Wang, RSC Adv., 7 (2017) 40734.

Síntesis de un Inhibidor de la Enzima 3β-HSD por Conversión Directa del Grupo Metilcetona de la 16-DPA en Amida Secundaria

Jhoan H. Piermattey[1,*], Ricardo Gaitan[1], Marisa CabezaSegundo[2]
[1]Universidad de Cartagena, Campus de Zaragocilla, Área de la Salud, Cartagena, Colombia
[2]Universidad Autónoma Metropolitana de México-Xochimilco. Calzada del Hueso #1100. Col. Villa Quietud. CP04960, Ciudad de México, México

**jpiermatteyditta@gmail.com*

La 3-β-Hidroxiesteroide deshidrogenasa (3β-HSD), enzima importante en los procesos de esteroidogénesis y metabolismo de hormonas esteroideas, se ha propuesto como diana en el tratamiento del cáncer de próstata avanzado resistente a la castración (CRPC) [1]. En el presente trabajo se realizó el diseño de un compuesto antiandrogénico modificando la funcionalidad en C17 del acetato de 16-dehidropregnenolona (16-DPA), convirtiendo el grupo metilcetona a una amida secundaria unida a la 5-hidroxi-1,4- naftoquinona (Fig. 1) y se le determinó la IC_{50} frente a 3β-HSD. Tradicionalmente las rutas de síntesis para llevar a cabo este proceso involucran múltiples pasos y condiciones especiales de reacción convirtiéndolo en un proceso engorroso y que demanda muchas horas de trabajo [2]. Nuestro grupo de investigación utilizó una ruta de aminación directa (en un solo paso) donde una aminonaftoquinona es usada como nucleófilo en una reacción de Lieben-Haller-Bauer en tándem, con el fin de simplificar el proceso de síntesis [3]. La reacción fue monitoriada por cromatografía de capa fina y la elucidación estructural se llevó a cabo por análisis de los espectros ^{1}H y ^{13}C RMN y los experimentos bidimensionales HSQC y HMBC (Fig. 2).
El producto de reacción fue purificado por cromatografía de capa fina preparativa y subsecuente recristalización en metanol, dando cristales en forma de aguja de color ámbar con punto de fusión de 164-168 ºC, m/z = 529.
La actividad inhibitoria sobre la enzima 3β-HSD fue medida utilizando homogenizado de próstata humana como fuente de la proteína, testosterona marcada con tritio como sustrato de la reacción, una solución de DTT 1 mM, buffer de fosfato de sodio 20 mM, NADPH 200 μM como medio de reacción y el compuesto de síntesis como inhibidor [4]. La IC_{50} obtenida fue de $6{,}5X10^{-7}$ M.

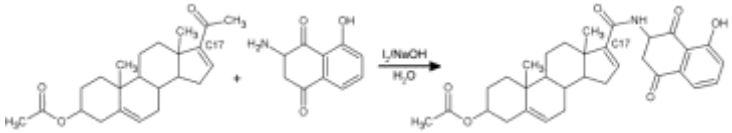


Fig. 1. Conversión directa de la metilcetona de la 16-DPA en una amida primaria por reacción de Lieben-Haller-Bauer en tándem.

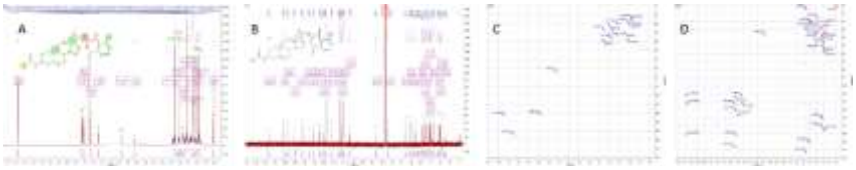


Fig. 2. Espectros de RMN 1D y 2D del compuesto de síntesis. A) Espectro de ^{1}H RMN. B) Espectro de ^{13}C RMN. C) HSQC. D) HMBC

Agradecimientos
A Colciencias por el apoyo financiero otorgado para la realización del Doctorado en Ciencias Biomédicas de la Universidad de Cartagena a través de un crédito condonable establecido en la convocatoria 647 de becas para doctorados nacionales.

Referencias

[1] K. Evaul, R. Li, M. Papari-Zareei, R. Auchus, & N. Sharifi, *Endocrinology*, *151(8)* (2010) 3514.
[2] L. Cao, J. Ding, M. Gao, Z. Wang, J. Li, & A. Wu, *Organic letters*, *11*(17) (2009) 3810.
[3] J. Ding, L. Cao, J. Wang, W. Xue, Y. Zhu, & A. Wu, *Journal of Chemical Research*, *35*(5) (2011) 298.
[4] E. Bratoeff, I. Moreno, F. Cortés-Benítez, Y. Heuze, M. Bravo, & M. Cabeza, *Current Enzyme Inhibition*, *14*(1) (2018) 36.

Estudo Mecanístico para a Transproteção de Aminas Terciárias usando Boc_2O: Acesso a Ambos os Enantiómeros do Ácido 2-Azanorbornano-3-*exo*-carboxílico

Ivo E. Sampaio-Dias[1,*], Sara C- Silva-Reis[1], Xerardo García-Mera[2], José E. Rodríguez-Borges[1]

[1]LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal.

[2]Departamento de Química Orgánica, Facultad de Farmacia, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, España.

**idias@fc.up.pt*

Este trabalho aborda uma metodología de síntese para a transproteção de aminas terciárias sob condições de hidrogenólise N-C exocíclica catalisada por Pd/C.

Aminas terciárias estericamente impedidas contendo o grupo 1-feniletilo são convertidas em aminas secundárias protegidas com o grupo *terc*-butiloxicarbonilo (Boc) através do uso do anidrido de *terc*-butiloxicarbonilo (Boc_2O) como aditivo para promover efetivamente a hidrogenólise e, consequentemente, a *N*-proteção após hidrogenólise exocíclica, originando aminas secundárias *N*-Boc protegidas. Estudos de RMN e experiências *in silico* sugerem a formação transiente de um carbamato carregado como possível intermediário que, em condições de hidrogenólise, sofre *N*-desalquilação com a remoção do grupo 1-feniletilo.[1]

Estas reações de transproteção permitiram o desenvolvimento de uma metodologia estereosseletiva robusta para a preparação de ambos os enantiómeros do ácido 2-azanorbornano-3-*exo*-carboxílico (**Fig. 1**) partindo de reações assimétricas de aza-Diels-Alder usando dois importantes auxiliares quirais: (−)-8-fenilmentol (**8PM**) e o (+)-8-fenilneomentol (**8PnM**).[1]

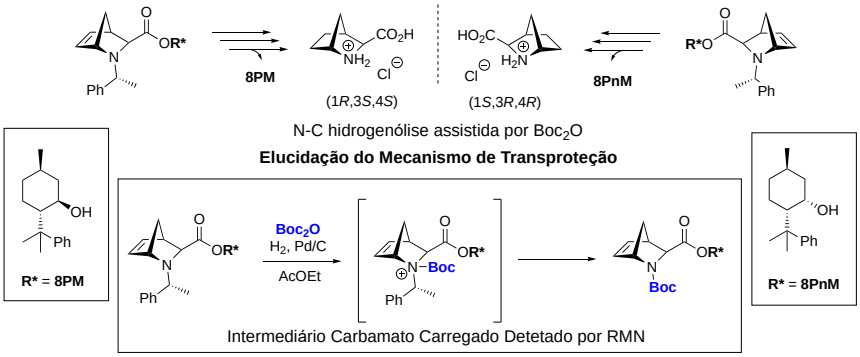


Fig.1. Preparação de ambos os enantiómeros do ácido 2-azanorbornano-3-*exo*-carboxílico.

Agradecimentos

Este trabalho foi financiado pela Fundação para a Ciência e Tecnologia (FCT/MCTES) através de fundos nacionais e pelo projeto PTDC/BIA-MIB/29059/2017. IESD agradece à FCT a bolsa de doutoramento com referencia SFRH/BD/93632/2013.

Referências

1. Sampaio-Dias, I. E., Silva-Reis, S. C., da Silva, L. P., García-Mera, X., Maestro, M. A., Rodríguez-Borges, J. E., Org. Chem. Front., 6 (2019) 3540.

Análogos Gémini de vitamina D: Síntesis total de UVB1

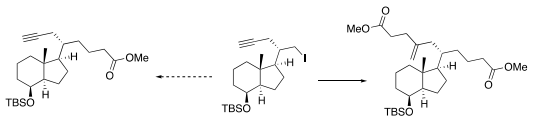
Hugo Santalla[1*], Generosa Gómez[1], Yagamare Fall[1]

[1]Departamento de Química Orgánica (Universidade de Vigo) e Instituto de investigación Sanitaria Galicia Sur (IISGS), Campus Lagoas-Marcosende, 36310 Vigo, Spain

**hsantalla@uvigo*

El calcitriol, forma activa de la vitamina D_3, cuenta con propiedades antiproliferativas y podría ser usado como agente terapéutico. Sin embargo, la dosis terapéutica necesaria conlleva riesgo de hipercalcemia. Actualmente las investigaciones se centran en el diseño de nuevos análogos del calcitirol con mayor selectividad, aumentando sus propiedades antiproliferativas y reduciendo el efecto calcémico.[1] Entre los numerosos análogos del calcitriol cobran especial relevancia aquellos que poseen una doble cadena lateral, conocidos como análogos de tipo Gémini, los cuales mejoran significativamente tanto la selectividad como la actividad antiproliferativa.

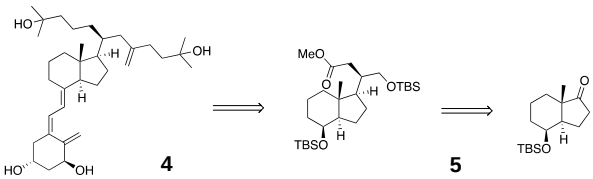
UVB1 es un análogo de tipo Gémini recientemente sintetizado en nuestro grupo. Se ha conseguido demostrar que este análogo inhibe la progresión del cáncer colorrectal con una mínima toxicidad en ensayos *in vivo*.[2] La estructura de este análogo se obtuvo como un producto no esperado de la adición conjugada de acrilato de etilo catalizada por Ni(II) sobre el yoduro **1** (**Figura 1**) y no ha podido ser reproducida.



3 **1** **2**

Fig.2. Producto deseado de la adición conjugada **3** y obtenido **2**

A la vista de lo mencionado anteriormente, nos propusimos el diseño racional de una ruta sintética para la obtención del análogo Gémini UVB1 **4**, utilizando como intermedio clave el éster **5** como se muestra en el **figura 2**. [4]



4 **5** **6**

Fig.2. Esquema retrosintético para la obtención del análogo Gemini UVB1

Referencias

[1] G. Jones, S. A. Strugnell, H. F. DeLuca, *Physiol. Rev.*, **1998**, *78*, 1193.
[2] M. J. Ferronato, et. al., *Arch. Pharm. Chem. Life Sci.*, **2015**, *348*, 1-15.
[3] G. Pazos, M. Pérez, Z. Gándara, G. Gómez, Y. Fall, *RSC Adv.*, **2016**, *6*, 61073-61076.
[4] H. Santalla, F. Garrido, G. Gómez, Y. Fall, *Org. Chem. Front.* **2018**. 5. 2016-2019.

Micro y nanopartículas de celulosa para su uso en productos industriales estratégicos

J. L. Francisco-Fuentes[1,*], M.M. Castro-López[2]

[1] ENCE Energía y Celulosa c/ Lourizán, s/n. 36153 – Pontevedra. España.
[2] CETIM, Parque empresarial de Alvedro, c/ H 20, 15180- Culleredo (Coruña). España
* *jlfrancisco@ence.es*

El mercado y la sociedad actuales están experimentando un cambio de paradigma en términos tecnológicos y medioambientales. Se postula que la sexta gran onda de prosperidad o ciclo económico Kondratieff estará movido por la economía circular y la tecnología ambiental [1].

Los nanomateriales derivados de la celulosa, el producto químico orgánico más abundante en la tierra, tienen el potencial de mejorar el comportamiento de muchos productos y de desplazar materiales no renovables [2, 3].

En este contexto surge el proyecto NOVACELL, financiado por el CDTI (CIEN 2017) y promovido por un consorcio de empresas de sectores como el papelero, la automoción, recubrimientos y adhesivos, cosmética, tratamiento de aguas y polimérico/construcción. El proyecto abarca desde la obtención de las micro y nanopartículas de celulosa a partir de la pasta Kraft, posterior funcionalización para mejorar su adaptabilidad a distintas aplicaciones y ensayos de aplicación.

En la obtención de las micro y nanopartículas de celulosa se estudian pretratamientos de las fibras para facilitar la posterior etapa de desestructuración mecánica, reduciendo el consumo de energía y el desgaste excesivo en los equipos; las etapas de obtención mediante tratamiento mecánico o químico para obtener nanofibras o nanocristales respectivamente; etapas de post-tratamiento de la nanocelulosa a fin de obtener la nanocelulosa en el estado deseado (suspensión/solución, polvo) en función de la aplicación a que se dirija.

Entre los retos a superar están el alto consumo energético, la agregación irreversible que se produce en el secado y la redispersión, la definición y medida de la calidad, la hidrofilicidad y su compatibilidad con ciertos materiales [4].

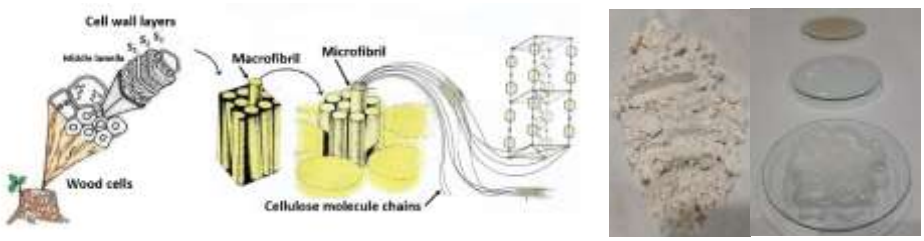


Fig.1. Ultraestructura de la celulosa [5] (izquierda) y Micro/nanopartículas de celulosa (derecha)

Agradecimientos
Agradecemos al CDTI la ayuda concedida para este proyecto (IDI-20171074)

Referencias

[1] P. Morone. Making the transition towards a biobased economy. Proc. Biocomp, Concepción, Chile (2016).
[2] J.A. Shatkin et al. Market projections of cellulose nanomaterial-enabled products- Part 1: Applications. Tappi J. 10, 5 (2014) 9
[3] D. Klemm et al. Nanocelluloses: A New Family of Nature-Based Materials. Angewandte Chem. Int. Ed. 50 (2011) 5438
[4] J. Miller. Cellulose Nanomaterials: State of the Industry. The Road to Commercialization. (2017) Paper Days. U. Maine (2017).
[5] V. Sajaniemi. Proof of concept for manufacturing microfibrillated cellulose. MsC. Thesis, Aalto University (2018)

Coumarin derivatives as versatile scaffolds towards potential GSK-3β inhibitors

Carla S. Francisco[1,*], Clara L. Javarini[1], Pedro A. B. Morais[2], Heberth de Paula[2], Warley de S. Borges[1], Álvaro Cunha Neto[1] and Valdemar Lacerda Jr.[1]
[1]Centro de Ciências Exatas, Universidade Federal do Espírito Santo, 29075-910 Vitória - ES, Brazil
[2]Ciências Exatas, Naturais e da Saúde, Universidade Federal do Espírito Santo, 29500-000 Alegre - ES, Brazil
**carla.iq@gmail.com*

The coumarin (2*H*-cromen-2-one) class of compounds is highly relevant for therapeutic applications, such as anti-tumor, anti-inflammatory, and antioxidant activities [1], and has been associated with a variety of biological activities against neurological and neurodegenerative diseases, such as Alzheimer´s disease (AD) [2] and Parkinson´s disease (PD). Glycogen synthase kinase-3 (GSK-3) is relationed as many protein kinases with phosphorylation and inactivation of glycogen synthase and this finding allowed to this protein the deserved attention of researches, as well as pharmaceutical companies, who were looking for therapeutic targets for Alzheimer's disease [3,4]. GSK-3 inhibitors have been associated with a variety of diseases, including diabetes type II, neurologic disorders, and cancer. In this work is described *in silico* experiments and enzymatic activity evaluation against the GSK-3β enzyme with 11 coumarin derivatives (Figure 1). Different synthetic methods were used to prepare coumarin derivatives. GSK-3β activity was measured via the ADP-Glo™ Kinase Assay, which quantifies the kinase-dependent enzymatic production of ADP from ATP, using a coupled-luminescence-based reaction. All reagents were purchased from Promega, LLC. A docking study was performed, using the program Gold Suite 5.1 (CCDC Software Limited), to determine the crystallographic structure of the staurosporine/GSK-3β complex [Protein Data Bank (PDB) code: 1Q3D].

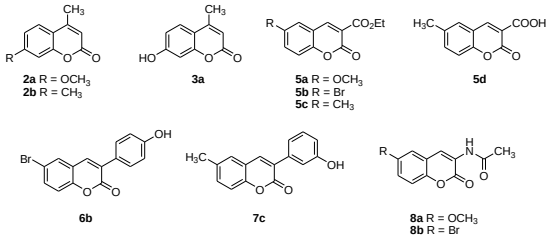


Figure 1. Structures of the coumarin derivatives prepared.

Our results revealed that three compounds inhibited more than 50% of the GSK-3β enzymatic activity at 1mM: **5c** (49.62%), **5d** (38.97%), and **6b** (47.34%). The other coumarin derivatives were tested at 1 mM, 1 µM, and 1 nM concentrations and were shown to be inhibitor candidates, with significant IC_{50} (1.224–6.875 µM) values, except for compound **7c** (IC_{50} = 10.809 µM). Docking simulations showed polar interactions between compound **5b** and Lys^{85} and Ser^{203}, clarifying the mechanism of the most potent activity. A total of 11 coumarin derivatives were successfully synthesized and characterized. The coumarin derivatives **3a** and **5b** showed remarkable activity as GSK-3β inhibitors. The molecular docking study revealed that compound **5b** showed an interesting placement near the glycine-rich loop and C-helix in the ATP-binding site and was moored by two important hydrogen bonds.

Acknowledgements
The authors thank the National Council for Scientific and Technological Development (CNPq), the Coordination for the Improvement of Higher Education Personnel (CAPES), and the Espírito Santo Research Foundation (FAPES) for the financial support and fellowships.

References

[1] (1)S.K. Gadakh, S. Dey, A. Sudalai, Journal of Organic Chemistry, 80 (2015) 11544.
[2] S. Hamulakova, M. Kozurkova, K.X. Kuca, Current Organic Chemistry, 21 (2017) 602.
[3] 3.E. Beurel, S.F. Grieco, R.S. Jope, Pharmacology & Therapeutics, 148 (2015) 114.
[4] 4. J. Bertrand et al., Journal of Molecular Biology, 333 (2003) 393.

QUÍMICA Y SALUD

Flor de *Aloe vera*: composición fenólica y propiedades bioactivas

Mikel Añibarro-Ortega[1], José Pinela[1,*], Ana Ćirić[2], Andrei Mocan[3,4], Marina Soković[2], Lillian Barros[1], Isabel C.F.R. Ferreira[1]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]University of Belgrade, Department of Plant Physiology, Institute for Biological Research "Siniša Stanković", Bulevar despota Stefana 142, Belgrade, Serbia
[3]Department of Pharmaceutical Botany, "Iuliu Hațieganu" University of Medicine and Pharmacy, Gheorghe Marinescu Street 23, 400337 Cluj-Napoca, Cluj, Romania
[4]Laboratory of Chromatography, Institute of Advanced Horticulture Research of Transylvania, University of Agricultural Sciences and Veterinary Medicine, 400372 Cluj-Napoca, Romania
**jpinela@ipb.pt*

En las últimas décadas, el *Aloe vera* ha sido sujeto de varios estudios científicos con el objetivo de caracterizar sus propiedades químicas y biológicas [1,2]. A pesar de ello, la flor es una parte poco explorada de la planta, por lo que este trabajo se centró en la evaluación de la composición en compuestos fenólicos y las propiedades bioactivas de esta matriz vegetal. Para este estudio, las flores de *Aloe vera* producidas en Elvas, Portugal, fueron liofilizadas, pulverizadas y sometidas a una extracción solido-líquido con una mezcla de etanol:agua (80:20, *v/v*). El perfil fenólico del extracto seco obtenido se caracterizó mediante HPLC-DAD-ESI/MS^n. En cuanto a las bioactividades, se evaluó la actividad antioxidante mediante los ensayos celulares OxHLIA y TBARS utilizando eritrocitos y células cerebrales como sustratos biológicos, respectivamente, y el ensayo de inhibición de la decoloración del β-caroteno; la actividad antimicrobiana contra diferentes bacterias y hongos asociados con problemas de la piel; y la capacidad de inhibir la enzima tirosinasa utilizando L-DOPA como sustrato [3].

El perfil fenólico de la flor está constituido principalmente por los flavonoides apigenina-6,8-*C*-diglucósido, apigeniana-2''-*O*-pentóxido-*C*-hexósido, apigenina-6-*C*-glucósido y trazas de derivados de luteolina (los que representan un 93,4% del extracto), y por el ácido fenólico ácido 5-*O*-cafeoilquínico. Hasta donde sabemos, es la primera vez que algunos de estos compuestos se describen en la flor de *Aloe vera*. No se detectaron glicósidos de antraquinonas en esta parte de la planta. La flor mostró una elevada capacidad de proteger eritrocitos de origen ovino ante la hemolisis causada por radicales libres generados por el AAPH, así como de inhibir la decoloración del β-caroteno producida por radicales linoleato. También se observó una capacidad tanto de inhibir el crecimiento como de eliminar bacterias multirresistentes como *Pseudomonas aeruginosa* o *Escherichia coli*, y actividad antifúngica contra varias especies de hongos, entre ellas *Candida albicans*. Asimismo, mostró capacidad de inhibir la actividad de la enzima tirosinasa [3]. Se concluyó que la flor de *Aloe vera* presenta capacidad antioxidante, antimicrobiana y de inhibir la actividad de la enzima tirosinasa. Todas estas propiedades convierten a esta parte menos explorada de la planta en una potencial fuente de compuestos naturales de valor añadido, la cual podría ser empleada para la formulación de cosméticos o aditivos alimentarios.

Agradecimientos
Los autores agradecen a la Fundación para la Ciencia y la Tecnología (FCT, Portugal) y al FEDER (Fondo Europeo de Desarrollo Regional) en el marco del Programa PT2020 por el apoyo financiero a CIMO (UID/AGR/00690/2019) y los contratos de investigación de J. Pinela y L. Barros (financiación nacional de FCT, a través del contrato-programa de empleo científico institucional); al Proyecto AllNat - POCI-01-0145-FEDER-030463 (PTDC/EQU-EPQ/30463/2017), financiado por fondos del FEDER a través de COMPETE2020 - Programa Operacional de Competitividad e Internacionalización (POCI) - y por fondos nacionales a través de FCT/MCTES; al programa FEDER-Interreg España-Portugal por el apoyo financiero a través del proyecto 0377_Iberphenol_6_E; al Proyecto TRANSCoLAB (0612_TRANS_CO_LAB_2_P); y a la empresa "aCourela do Alentejo" por haber suministrado el material vegetal.

Referencias
[1] S. Keyhanian, E. Stahl-Biskup, Planta Medica, 73 (2007) 599.
[2] J.H. Hamman, Molecules, 13 (2008) 1599.
[3] M. Añibarro-Ortega, J. Pinela, L. Barros, et al., Antioxidants, 8 (2019) 444.

Hypoxia-activated triazene prodrugs for tumor-selective delivery

C. Braga[1,*], R. Moreira[1], G. Bernardes[2], Maria J. Perry[1]
[1]Research Institute for Medicines (iMed.ULisboa), Faculdade de Farmácia, Universidade de Lisboa, Av. Professor Gama Pinto, 1649-003 Lisboa, Portugal;
[2]Instituto de Medicina Molecular, Faculdade de Medicina da Universidade de Lisboa, Av. Prof Egas Moniz 1649-028 Lisboa, Portugal
**cbraga@ff.ulisboa.pt*

Displaying a broad-spectrum chemistry, triazenes are best known for their cytotoxic properties, as exemplified by dacarbazine and temozolomide, well-known anticancer agents. Triazenes exert their chemotherapeutic activity through a unique mechanism of action that involves formation of a reactive alkyl diazonium intermediate capable of alkylating DNA and promoting cell death [1]. Herein, we have developed a triazene-based platform that can be selectively activated by nitroreductases (NTRs) [2], specifically overexpressed in hypoxic solid tumours, to undergo a self-immolative process that culminates with the release of the cytotoxic triazene.

A series of nitro(hetero)aromatic prodrugs **1a-k** (Fig. 1) of cytotoxic triazenes was synthesized and NTR-triggered activation was investigated by HPLC and LC-MS. Corroboration of the reduction reaction was attained through chemical reduction using zinc/acetic acid and by means of the synthetic des-nitro analogues. Triazene prodrugs **1a-k** cell viability was evaluated in A549 and U-87 MG human cancer NTR-overexpressing cell lines. Human glioblastoma cells U-87 MG were treated with 4-nitrobenzyl derivatives and cytotoxicity was low under either hypoxic (5% O_2) or normoxic (20% O_2) conditions. In contrast, bioreductive experiments employing 5-nitrofurfuryl derivatives, disclosed a substantial decrease on cell viability, with compound **1h** presenting significant hypoxia-selective cytotoxicity at 100 µM. After a 48h incubation, **1h** cell viability mean relative to control was 0,36±0,061 under normoxia and 0,19±0,013 under hypoxia environment. U-87 MG cells exposed to temozolomide, used as a reference compound, currently applied in glioblastoma chemotherapy, did not result in any change of cell viability.

Overall, this approach unveils a novel triazene release system, suggesting that 5-nitrofurfuryl derivatives may act as hypoxia-activated prodrugs, enhancing selective delivery into solid tumours.

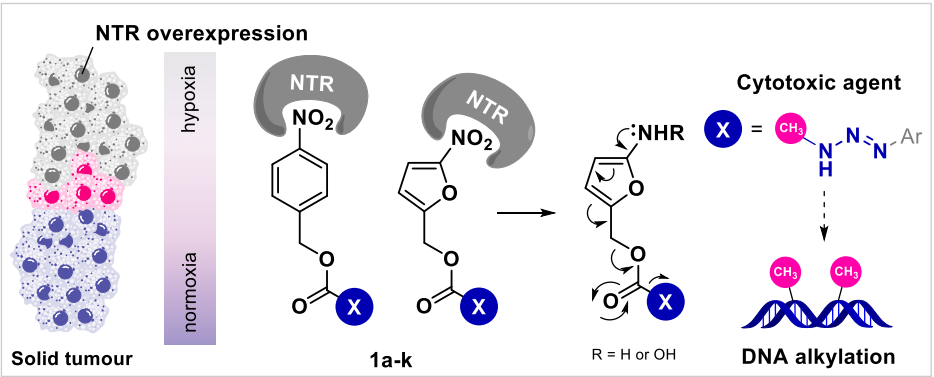


Fig.1. Schematic representation of triazene prodrugs 1 activation by NTR selective targeting.

Agradecimientos
We thank the Fundação para a Ciência e Tecnologia for financial support through the PhD fellowship awarded (PD/BD/135286/2017) through MedChemTrain PhD Programme and through iMed.ULisboa grant, UID/DTP/04138/2019 from FCT, Portugal.

Referencias

[1] F. Marchesi, M. Turriziani, G. Tortorello, G. Avvisati, F. Torino, L. De Vecchis, Pharmacol Res, 56, (2007), 275.
[2] A. Chevalier, Y. Zhang, O.M. Khdour, J.B. Kaye, S.M. Hecht, J Am Chem Soc, 138, (2016), 12009.

QS03

Bioactive compounds in haemodialysis polysulfone membrane to reduce oxidative stress and inflammation in patients on dialysis

Kohlová Michaela[1,*], Amorim G. Célia [2], Rocha Susana[2], Santos-Silva Alice[3], Solich Petr, Montenegro Conceição

[1] Department of Analytical Chemistry, Faculty of Pharmacy in Hradec Králové, Charles University, Hradec Králové, Czech Republic
[2] LAQV\REQUIMTE, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[3] UCIBIO\REQUIMTE, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
*kohlm5aa@faf.cuni.cz

Oxidative stress and chronic inflammation are commonly present in haemodialysis patients, due to long term contact of patient´s blood with dialysis membrane. To reduce oxidative stress, vitamin E-coated polysulfone (PSF) membranes are used to scavenge the free reactive oxygen species, in site-specific manner, formed during the haemodialysis process. Although the use of this type of membrane showed improvement in inflammation, oxidative stress, anaemia and response to erythropoietin therapy [1], the overall beneficial effect on the risk for cardiovascular events that are the major cause of death in dialysis patients, is still uncertain.

For this reason, the aim of our work was to evaluate if the enrichment of PSF membranes with other bioactive substances, such as lipoic acid or synthetic inhibitors of human neutrophil elastase, are able to reduce oxidative stress and/or inhibit elastase. Membranes under study were incubated with human blood samples Lipoic acid possesses antioxidant activity and can therefore potentiate vitamin E scavenging of free radicals, while inhibitors of neutrophil elastase can diminish inflammation by inactivation of neutrophil elastase, whichmay contribute to perpetuate the cycle of inflammation by promoting the generation of chemoattractants and further activation of neutrophils [2].

Lipoic acid was incorporated in PSF membranes alone or together with vitamin E. These modified membranes were evaluated *in vitro* to study their antioxidant activity and biocompatibility. The PSF membranes enriched with lipoic acid didn't induce platelet activation and decreased haemolysis, when compared with PSF membranes, without modification. The PSF membranes enriched with lipoic acid and vitamin E showed an improvement in total antioxidant status. Overall antioxidants incorporation showed beneficial effects concerning to the membrane biocompatibility.

Three different synthetic inhibitors with β-lactam structure were immobilized on the membranes through adsorption phenomena and by direct incorporation during polymer preparation. Those were tested *in vitro* and the former showed better inactivation activity. We found that elastase inhibition was dependent on the concentration of the inhibitors and on their lipophilicity properties.

Both types of bioactive compounds immobilized on polysulfone membrane showed promising effect on oxidative stress/inflammation and therefore, should be considered for further studies, considering its potential value for commercial production.

Acknowledgement
This work was financially supported by the Charles University Grant Agency, project GAUK no. 860216 and by project of specific research of Charles University, project no. SVV 260 412. The project was also supported by the project EFSA-CDN (No. CZ.02.1.01/0.0/0.0/16_019/0000841) co-funded by ERDF; and had financial support from the European Union (FEDER funds POCI/01/0145/FEDER/007265) and National Funds (FCT/MEC,) under the Partnership Agreement PT2020 UID/QUI/50006/2019; UID/QUI/50006/2019 with funding from FCT/MCTES through national funds and project (CCDR-N)/NORTE2020/Portugal 2020 (Norte-01-0145-FEDER-000024); and PTDC/MEC-CAR/31322/2017.

References

[1] G. D'Arrigo, et al., Blood Purification, 2017. 43(1-3): p. 101-122.
[2] K. Kessenbrock, T. Dau, D.E. Jenne, Journal of Molecular Medicine, 2011. 89(1): p. 23-28.

Photodynamic inactivation of antibiotic resistant bacteria using cationic porphyrins

Joana M. D. Calmeiro[1,*], Sara Gamelas[1] , Ana T. P. C. Gomes[2], Maria A. F. Faustino[1], Maria G. P. M. S. Neves[1], Adelaide Almeida[2], João P. C. Tomé[3], Leandro M. O. Lourenço[1]

[1]QOPNA and LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2]CESAM and Department of Biology, University of Aveiro, 3810-193 Aveiro, Portugal

[3]CQE, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

*e-mail: jcalmeiro@ua.pt

Porphyrins and analogues are considered to have unique photochemical and photophysical properties to be used as photosensitizers in the photodynamic inactivation of microorganisms, namely those resistant to conventional antimicrobials (e.g. bacteria) [1,2]. This therapeutic process requires the activation of the photosensitizer by light in the presence of oxygen leading to the formation of cytotoxic reactive oxygen species (ROS) that cause lethal oxidative damage in microbial targets [2,3].

In this communication, it will be reported and discussed the synthesis and characterization of the neutral and cationic free-base and zinc(II) porphyrin derivatives presented in **Figure 1**. The photodynamic efficiencies of these dyes against the Gram-negative bioluminescent *E. coli* bacterium will be also analysed.

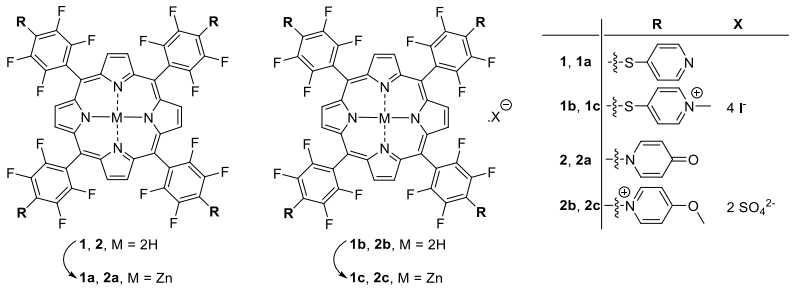


Fig.1. Structure of porphyrin derivatives.

Acknowledgements:
Thanks are due to FCT/MCTES for the financial support to QOPNA (UID/QUI/00062/2019), CESAM (FCT UID/AMB/50017/2019) and CQE (FCT UID/QUI/0100/2019) research units, and FCT projects P2020-PTDC/QEQ-SUP/5355/2014 and P2020-PTDC/QUI-QOR/31770/2017, through national founds (PIDDAC) and where applicable co-financed by the FEDER-Operational Thematic Program for Competitiveness and Internationalization-COMPETE 2020, within the PT2020 Partnership Agreement. J. C. and S. G. thank FCT for the research fellow BI/UI51/7955/2019 and SFRH/BD/143549/2019, respectively.

References

[1] a) D. C. S. Costa, M. C. Gomes, M. A. F. Faustino, M. G. P. M. S. Neves, A. Cunha, J. A. S. Cavaleiro, A. Almeida, J. P. C. Tomé Photochemical & Photobiological Sciences, 11 (2012) 1905. b) D. C. S. Costa, V. F. Pais, A. M. S. Silva, J. A. S. Cavaleiro, U. Pischel, J. P. C. Tomé Tetrahedron Letters, 55 (2014) 4156. c) L. M. O. Lourenço, A. Sousa, M. C. Gomes, M. A. F. Faustino, A. Almeida, A. Almeida, A. M. S. Silva, M. G. P. M. S. Neves, J. A. S. Cavaleiro, Â. Cunha, J. P. C. ToméPhotochemical & Phtobiological Sciences, 10 (2015) 1853.

[2] a) M. C. Gomes, S. M. Woranovicz-Barreira, M. A. F. Faustino, R. Fernandes, M. G. P. M. S. Neves, A. C. Tomé, N. C. M. Gomes, A. Almeida, J. A. S. Cavaleiro, Â. Cunha, J. P. C. Tomé Photochemical & Photobiological Sciences, 10 (2011) 1735. b) E. Alves, M. A. F. Faustino, M. G. P. M. S. Neves, Â. Cunha, H. Nadais, A. Almeida Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 22 (2015) 34.

[3] E. Alves, J. M. M. Rodrigues, M. A. F. Faustino, M. G. P. M. S. Neves, J. A. S. Cavaleiro, Z. Lin, Â. Cunha, M. H. Nadais, J. P. C. Tomé, A. Almeida Dyes and Pigments, 110 (2014) 80.

Phlorotannins from *Fucus vesiculosus* and their potential to prevent diseases of the modern civilization

Marcelo D. Catarino[1,*], Maria Teresa Cruz[2], Nuno Mateus[3], Artur M.S. Silva[1], Susana M. Cardoso[1]

[1]QOPNA & LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

[2]CNC.IBILI, Faculty of Pharmacy, University of Coimbra, Health Sciences Campus, 3000-548, Coimbra, Portugal

[3]REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto

**mcatarino@ua.pt*

Marine macroalgae have been well recognized for centuries by their importance in the diet of many Far Eastern countries, such as Japan and Korea. Nevertheless, during the recent years, consumption of these food ingredients is becoming more and more popular worldwide. Indeed, these marine food sources are holders of an exceptional nutritional value containing several bioactive compounds capable of acting on a large spectrum of disorders and/or diseases [1]. In this context, phlorotannin-rich extracts from *Fucus vesiculosus* were evaluated *in vitro* for their potential inhibitory activity towards key enzymes from lipid or carbohydrate metabolism, namely α-glucosidase, α-amylase and pancreatic lipase, showing good inhibitory capacity against the three enzymes, particularly against α-glucosidase. Moreover, when tested for their NO• scavenging activity, an effect comparable to that of ascorbic acid was observed, suggesting not only a good antioxidant activity but also a potential anti-inflammatory capacity. In parallel, HPLC-DAD-ESI-MS^n analysis of the extracts revealed a very complex profile with great variability of phlorotannins in terms of degree of polymerization (DP). To separate the compounds according to their molecular weights, further purification was carried out by preparative chromatography in a Sephadex LH-20 column, yielding several fractions that were evaluated for their anti-inflammatory potential in lipopolysaccharide (LPS)-stimulated RAW 264.7 macrophages to understand if they interact with key pro-inflammatory signaling pathways. The results, revealed that the crude extract and some of its fractions markedly inhibited the LPS-induced NO• production as well as the expression of inducible NO synthase (iNOS) and other pro-inflammatory mediators such as cyclooxygenase (COX)-2 and Interleukin (IL)-1β. Interestingly, these effects seem to be related with molecular weight of phlorotannins, since those with lower DPs exhibited much stronger effects than those with high DPs.

Overall, this study provides evidence that *F. vesiculosus* phlorotannin-rich extracts and subsequent purified fractions, not only hold potential for weight and glycemia management, but may also have a protective role on inflammatory-related conditions, suggesting that phlorotannin might be suitable for applications with nutraceutical and even pharmaceutical purposes.

Aknowledgements: Authors acknowledge the financial support of the project AlgaPhlor (PTDC/BAA-AGR/31015/2017), financed by National funds thought FCT. We also thank University of Aveiro, FCT/MEC for financial supporting QOPNA research Unit (FCT UID/QUI/00062/2019), through national funds and where applicable co-financed by the FEDER, within the PT2020 Partnership Agreement. Susana Cardoso thanks the research contract under the project AgroForWealth (CENTRO-01-0145-FEDER-000001), funded by Centro2020, through FEDER and PT2020. Marcelo D. Catarino acknowledges FCT for financial support (fellowship PD/BD/114577/2016).

References

[1] S. Cardoso, L. Carvalho, P. Silva, M. Rodrigues, O. Pereira, L. Pereira, *Current Organic Chemistry*, 18 (2004) 896-917

Sin Comunicación

Ésteres alquílicos de homarina: uma nova classe de inibidores da acetilcolinesterase

Karen G. João[1*], Romeu A. Videira[1], Patrícia Valentão[1], David M. Pereira[1], Fátima Paiva-Martins[2], Paula B. Andrade[1]

[1]REQUIMTE/LAQV, Laboratório de Farmacognosia, Departamento de Química, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, no. 228, 4050-313 Porto, Portugal
[2]REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 1021/1055, 4169-007 Porto, Portugal
**karenjoao23@gmail.com*

A acetilcolinesterase é considerada um alvo terapêutico importante para o tratamento de doenças neurodegenerativas, dado que um défice de atividade nas redes neuronais colinérgicas é sistematicamente detetado nas doenças de Alzheimer e Parkinson desde as suas etapas iniciais [1]. Assim, o desenvolvimento de novos compostos com capacidade de inibir a acetilcolinesterase continua a ser uma área de investigação ativa. O ácido 1-metil-2-piridinocarboxílico (conhecido como homarina) é um alcaloide metilpiridínico sintetizado por vários organismos invertebrados marinhos (*e.g.* filos Mollusca, Porifera, Arthropoda) [2,3], com inúmeras funções biológicas, inclusive a nível de defesa contra predadores [2,4,5,6], sugerindo ter potencial para modular a atividade de redes neuronais colinérgicas. No presente trabalho avalia-se o efeito da homarina, e dos seus ésteres alquílicos, sobre a atividade da acetilcolinesterase de cérebro de rato, com o objetivo de desenvolver novos compostos para o tratamento das doenças neurodegenerativas. Foram sintetizados seis ésteres alquílicos de homarina, através de uma reação de esterificação entre o ácido picolínico (PA) e álcoois com cadeias de diferentes tamanhos, seguida de uma reação de metilação com iodometano. Os compostos obtidos na primeira etapa (derivados do ácido picolínico: PA-C1, PA-C2, PA-C4, PA-C8, PA-C16) e os compostos finais (derivados da homarina: HO-C1, HO-C2, HO-C4, HO-C8, HO-C16) foram caracterizados por RMN (^{1}H e ^{13}C), assegurando o seu elevado grau de pureza. Os ensaios de cinética enzimática mostraram que a homarina é um inibidor competitivo da acetilcolinesterase, apresentando um valor de Ki (54,9±8,3 µM) semelhante ao valor de Km da enzima (Km = 46,2 ± 3,5 µM). No geral, os ésteres alquílicos de homarina preservam a capacidade de inibição da enzima, sendo o HO-C16 o mais eficaz (Ki= 37,4±10,2 µM) dos compostos testados. A atividade da butirilcolinesterase foi também avaliada para averiguar a seletividade dos compostos face às duas colinesterases. Foi usado um painel de linhas celulares humanas (AGS, A549 e SH-SY5Y) para avaliar os efeitos dos compostos sintetizados sobre a viabilidade celular. Os dados obtidos indicam que os compostos não apresentam citotoxicidade na gama de concentrações em que inibem a acetilcolinesterase. Portanto, é possível concluir que a homarina e os seus ésteres alquílicos têm potencial para serem considerados no desenvolvimento de abordagens terapêuticas para o tratamento de doenças neurodegenerativas caracterizadas por défice de atividade colinérgica.

Agradecimentos
Este trabalho foi apoiado pela UID / QUI / 50006/2019 com financiamento de FCT / MCTES através de fundos nacionais. Karen G. João agradece à Fundação para a Ciência e a Tecnologia pela sua bolsa de doutoramento (PD / BD / 135084/2017).

Referências

[1] M. Taveira, C. Sousa, P. Valentão, F. Ferreres, J. P. Teixeira, P. B. Andrade, The Journal of Steroid Biochemistry and Molecular Biology 140 (2014), 106-115.
[2] P. Polychronopoulos, P.Magiatis, A. L. Skaltsounis, F. Tillequin, E. Vardala-theodorou, A. Tsarbopoulos, Natural Product Letters 15 (6) (2001), 411-418.
[3] T. C. Silva, P. Andrade, F. Paiva-Martins, P. Valentão, D. Pereira, International Journal of Molecular Sciences 18 (2017), 653.
[4] R. X. Poulin, S. Lavoie, K. Siegel, D. A. Gaul, M. J. Weissburg, J. Kubanek, Proceedings of the National Academy of Sciences USA 115 (4) (2018), 662-667.
[5] J. B. McClintock, B. J. Baker, M. T. Hamann, W. Yoshida, M. Slattery, J. N. Heine, P. J. Bryan, G. S. Jayatilake, B. H. Moon, Journal of Chemical Ecology 20 (10) (1994), 2539-2549.
[6] N. M. Targett, S. S. Bishop, O. J. McConnell, J. A. Yoder, Journal of Chemical Ecology 9 (7) (1983), 817-829.

QS08

Bioactive compounds in haemodialysis polysulfone membrane to reduce oxidative stress and inflammation in patients on dialysis

Kohlová Michaela[1, *], Amorim G. Célia [2], Rocha Susana[2], Santos-Silva Alice[3], Solich Petr, Montenegro Conceição

[1] Department of Analytical Chemistry, Faculty of Pharmacy in Hradec Králové, Charles University, Hradec Králové, Czech Republic
[2] LAQV\REQUIMTE, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[3] UCIBIO\REQUIMTE, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
**kohlm5aa@faf.cuni.cz*

Oxidative stress and chronic inflammation are commonly present in haemodialysis patients, due to long term contact of patient´s blood with dialysis membrane. To reduce oxidative stress, vitamin E-coated polysulfone (PSF) membranes are used to scavenge the free reactive oxygen species, in site-specific manner, formed during the haemodialysis process. Although the use of this type of membrane showed improvement in inflammation, oxidative stress, anaemia and response to erythropoietin therapy [1], the overall beneficial effect on the risk for cardiovascular events that are the major cause of death in dialysis patients, is still uncertain.

For this reason, the aim of our work was to evaluate if the enrichment of PSF membranes with other bioactive substances, such as lipoic acid or synthetic inhibitors of human neutrophil elastase, are able to reduce oxidative stress and/or inhibit elastase. Membranes under study were incubated with human blood samples Lipoic acid possesses antioxidant activity and can therefore potentiate vitamin E scavenging of free radicals, while inhibitors of neutrophil elastase can diminish inflammation by inactivation of neutrophil elastase, whichmay contribute to perpetuate the cycle of inflammation by promoting the generation of chemoattractants and further activation of neutrophils [2].

Lipoic acid was incorporated in PSF membranes alone or together with vitamin E. These modified membranes were evaluated *in vitro* to study their antioxidant activity and biocompatibility. The PSF membranes enriched with lipoic acid didn't induce platelet activation and decreased haemolysis, when compared with PSF membranes, without modification. The PSF membranes enriched with lipoic acid and vitamin E showed an improvement in total antioxidant status. Overall antioxidants incorporation showed beneficial effects concerning to the membrane biocompatibility.

Three different synthetic inhibitors with β-lactam structure were immobilized on the membranes through adsorption phenomena and by direct incorporation during polymer preparation. Those were tested *in vitro* and the former showed better inactivation activity. We found that elastase inhibition was dependent on the concentration of the inhibitors and on their lipophilicity properties.

Both types of bioactive compounds immobilized on polysulfone membrane showed promising effect on oxidative stress/inflammation and therefore, should be considered for further studies, considering its potential value for commercial production.

Acknowledgement
This work was financially supported by the Charles University Grant Agency, project GAUK no. 860216 and by project of specific research of Charles University, project no. SVV 260 412. The project was also supported by the project EFSA-CDN (No. CZ.02.1.01/0.0/0.0/16_019/0000841) co-funded by ERDF; and had financial support from the European Union (FEDER funds POCI/01/0145/FEDER/007265) and National Funds (FCT/MEC,) under the Partnership Agreement PT2020 UID/QUI/50006/2019; UID/QUI/50006/2019 with funding from FCT/MCTES through national funds and project (CCDR-N)/NORTE2020/Portugal 2020 (Norte-01-0145-FEDER-000024); and PTDC/MEC-CAR/31322/2017.

References
[3] G. D'Arrigo, et al., Blood Purification, 2017. 43(1-3): p. 101-122.
K. Kessenbrock, T. Dau, D.E. Jenne, Journal of Molecular Medicine, 2011. 89(1): p. 23-28..

The photobiological role of the sulfur atoms introduction into squaric ring in indolenine-based squaraine cyanine dyes

Eurico Lima[1,*], Octávio Ferreira[2], Adriana O. Santos[2], Renato E. Boto[2], José R. Fernandes[1], Paulo Almeida[2], Samuel M. Silvestre[2], Lucinda V. Reis[1]

[1] Chemistry Centre of Vila Real (CQ-VR), University of Trás-os-Montes and Alto Douro, Vila Real, Portugal
[2] Health Sciences Research Centre (CICS-UBI), University of Beira Interior, Covilhã, Portugal

*eurico_lima@icloud.com

Squaraine cyanine dyes, also commonly known as squaraines, are 1,3-disubstituted derivatives of 3,4-dihydroxycyclobut-3-ene-1,2-dione. Since these dyes usually present good photochemical stability, narrow and intense absorption bands in the visible and near infrared regions, and high molar absorption coefficient, they have relevant potential application as fluorescent probes for biomolecules detection, as well as photosensitizers for cancer photodynamic therapy [1].

The aim of this study was to prepare novel indolenine-based squaraine dyes bearing one and two sulfur atoms in the four-membered central ring by procedures adapted from the literature [2], as well as to evaluate their singlet oxygen ability production, photodegradation and their *in vitro* photodynamic activity against several tumor (Caco-2, PC-3 and MCF-7) and normal (NHDF) cell lines. To evaluate its singlet oxygen formation ability, 1,3-diphenylisobenzofuran assay was performed. The cytotoxicity assessment was performed by the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium assay, a colorimetric method that allows to evaluate the mitochondrial metabolic activity.

Thiosquaraine dyes have been successfully synthesized and fully characterized. Both dyes displayed intense absorption within the tissue transparency spectral region (650-850 nm). The synthesized dyes have been shown to have moderate light stability and high singlet oxygen production ability. The monothiosquaraine dye exhibited strong phototherapeutic activity against the PC-3 cell line and a slight tumor selectivity effect were observed.

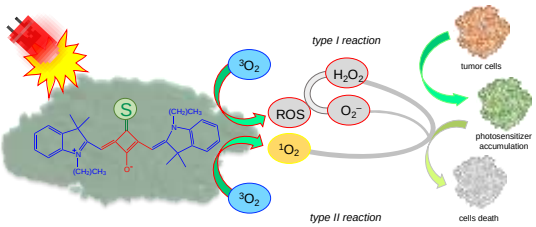


Fig.1. Graphical representation of the squaraine photodynamic activity mechanism.

Acknowledgments

We acknowledge the European Investment Funds by FEDER/COMPETE/POCI under projects and POCI-01-0145-FEDER-007491 (CICS-UBI) and Funds by FCT, under the project UID/QUI/UI0616/2019 (CQ-VR). This work was also supported by funds from the CICS-UBI through National Funds by FCT (UID/Multi/00709/2019).

References

[1] S. Friães, A. M. Silva, R. E. Boto, D. Ferreira, J. R. Fernandes, E. B. Souto, P. Almeida, L. F. V. Ferreira, L. V. Reis, Bioorganic & Medicinal Chemistry, 25 (2017) 3803-3814.
[2] E. Lima, O. Ferreira, V. S. D. Gomes, A. O. Santos, R. E. Boto, J. R. Fernandes, P. Almeida, S. M. Silvestre, L. V. Reis, Dyes and Pigments, 167 (2019) 98-108.

Influência da viabilidade das sementes na composição química e propriedades bioativas de *Cynara cardunculus* L.

Filipa Mandim[1,2], Maria Inês Dias[1], José Pinela[1], Paulo Barracosa[3], Marija Ivanov[4], Dejan Stojkovic[4], Marina Sokovic[4], Lillian Barros[1], Celestino Santos-Buelga[2], Isabel C.F.R. Ferreira[1,*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Bragança, Portugal
[2]GIP-USAL, Faculdad de Farmacia, Universidad de Salamanca, Salamanca, Espanha
[3]Escola Superior Agrária de Viseu, Instituto Politécnico de Viseu, Viseu, Portugal
[4]Institute for Biological Research "Siniša Stanković", University of Belgrade, Belgrade, Serbia
*iferreira@ipb.pt

Cynara cardunculus L., vulgarmente conhecida por Cardo, é uma planta herbácea nativa da bacia Mediterrânica e pertencente à família *Asteraceae*. É uma cultura adaptada à tendência das alterações climáticas, devido à capacidade de resistir a diferentes tipos de stresse. Esta planta é parte integrante da dieta mediterrânica e utilizada na medicina popular desde tempos remotos. A sua composição nutricional e a presença de compostos com propriedades bioativas (antimicrobianas, diuréticas, coleréticas e antioxidantes) desempenham um papel fulcral na alimentação humana [1,2]. O seu potencial comercial e económico tem vindo a ser reconhecido devido ao valor nutricional e potencial bioativo, bem como às suas diversificadas aplicações (produção de biodiesel, pasta de papel, bioenergia, biomassa e queijo) [2,3]. A valorização dos seus constituintes é extremamente importante, podendo contribuir para a redução de desperdícios e para um eficiente aproveitamento dos recursos.

Neste estudo, sementes de cardo (var. *altilis*) cultivadas em Viseu, Portugal (projeto CARDOP), foram separadas segundo a sua viabilidade e caracterizadas quanto à sua composição química e propriedades bioativas. A composição fenólica de extratos hidrometanólicos foi analisada por HPLC-DAD-ESI/MS. Foram ainda determinados os perfis individuais de tocoferóis, ácidos orgânicos, açúcares e ácidos gordos através de métodos cromatográficos. A atividade citotóxica foi avaliada pelo método colorimétrico da sulforrodamina B. A atividade anti-inflamatória foi determinada pela inibição da produção de NO em macrófagos de rato. As atividades antibacteriana e antifúngica foram avaliadas através do método de microdiluições sucessivas e a atividade antioxidante através dos ensaios TBARS e OxHLIA. Os extratos revelam a presença dos ácidos 5-*O*-cafeoilquínico e 3,5-*O*-dicafeoilquínico, ambos em maior quantidade nas sementes viáveis. Estas apresentaram igualmente os teores mais elevados de α-tocoferol. Relativamente aos ácidos orgânicos, foram identificados os ácidos oxálico, quínico, cítrico e fumárico; no entanto, os ácidos oxálico e fumárico foram detetados unicamente nas sementes viáveis. Os açúcares frutose, glucose e sacarose foram encontrados em ambos os lotes. Apesar de ter sido detetado óleo nas sementes inviáveis, a fração lipídica é 61,6% inferior à das sementes viáveis. Dos vinte ácidos gordos identificados, os ácidos oleico, palmítico e caproico foram os mais abundantes. As sementes viáveis apresentaram uma maior abundância em ácidos gordos monoinsaturados, enquanto as inviáveis tiveram um maior teor em ácidos gordos saturados. Nenhum dos extratos apresentou citotoxicidade em células tumorais humanas, nem em células normais, mas apresentaram atividade antibacteriana e antifúngica; as sementes inviáveis destacam-se contra algumas estirpes bacterianas (*Staphylococcus aureus*, *Bacillus cereus*, *Escherichia coli* e *Salmonella typhimurium*). Os extratos das sementes viáveis revelaram uma atividade antioxidante claramente superior. Em conclusão, as sementes viáveis destacaram-se pelos teores de ácidos gordos monoinsaturados, α-tocoferol e ácidos fenólicos e ainda pela atividade antioxidante, enquanto que as sementes inviáveis revelaram uma maior abundância em ácidos gordos saturados e uma maior atividade antibacteriana.

Agradecimentos

Os autores agradecem à Fundação para a Ciência e Tecnologia (FCT, Portugal) e FEDER, no âmbito do Programa PT2020 pelo apoio financeiro ao CIMO (UID/AGR/00690/2019), aos contrato-programa de emprego científico institucional de M. I. Dias, J. Pinela e L. Barros. Os autores agradecem também ao programa FEDER-Interreg Espanha-Portugal pelo apoio financeiro através do projeto 0377_Iberphenol_6_E.

Referencias

[1] S. Petropoulos, Â. Fernandes, C. Pereira, et al., Food Chemistry, 289 (2019) 404.
[2] J. Gominho, M. D. Curt, A. Lourenço, J. Fernández, H. Pereira, Biomass and Bioenergy, 109 (2018) 257.
[3] B. de Falco, G. Incerti, M. Amato, V. Lanzotti, Phytochemistry Reviews, (2015) 993.

Can the elderberry anthocyanins overcome the mitochondrial dysfunction associated with degenerative brain diseases?

Dina Neves*, Patrícia Valentão, João Bernardo, Paula B. Andrade, Rui F. Gonçalves, Romeu A. Videira

REQUIMTE/LAQV, Laboratory of Pharmacognosy, Department of Chemistry, Faculty of Pharmacy, University of Porto, R. Jorge Viterbo Ferreira, nº 228, 4050-313 Porto, Portugal.
**dinaneves4@gmail.com*

The progressive loss of mitochondrial functionality is a key player of normal aging process, as well of the pathophysiological cascade underlying many age-related diseases (*e.g.* neurodegenerative pathologies) without cure [1, 2]. Thus, the development of effective medicines to overcome the mitochondrial dysfunction is a challenge to keep our ageing society healthy. Here we investigate the potential beneficial effects of an anthocyanin-enriched extract obtained from elderberry (*Sambucus nigra* L.) fruit on mitochondrial dysfunction and cell redox balance underlying neurodegenerative processes. Phenolic profile was achieved by HPLC-DAD, antioxidant properties by radical-scavenging assays, and redox behaviour by cyclic voltammetry. Mitochondrial effects were assessed on Wistar rat brain mitochondria and SH-SY5Y neuron-like cells under different metabolic conditions, using standard procedures [3]. Anthocyanin-enriched extract exhibited a high content of anthocyanins (348.0±30.0 µg/mg of dry weight), scavenging capacity against $DPPH^{\bullet}$, $^{\bullet}NO$ and $O_2^{\bullet-}$ radicals, and one electron-reversible redox behaviour in the range of redox potentials where the mitochondrial redox chain operates. On rat brain mitochondria, the elderberry anthocyanins i) showed affinity for the lipid bilayer of mitochondrial membranes, ii) did not affect the respiratory parameters of healthy mitochondria, and iii) were able to overcome the mitochondrial dysfunction promoted by rotenone (complex I inhibitor), creating an alternative pathway for electron delivery in the inner-mitochondrial membrane. Indeed, the anthocyanin-enriched extract, at non-toxic concentrations, protected SH-SY5Y cells against rotenone-induced toxicity, reduced ROS generation and increased the GSH/GSSG ratio. Moreover, anthocyanin-enriched extract triggers, in healthy neuron-like cells, an improvement of the antioxidant enzyme defence system and an increase of the mitochondrial respiratory complexes' activity. In conclusion, elderberry extract can overcome the mitochondrial dysfunction and modulate the cell redox status of cells, highlighting its putative role on the age-dependent process. Thus, we reckon that these properties render the elderberry anthocyanins as an attractive tool for the development of new mitochondria-targeted approaches with high relevance for neurodegenerative diseases.

Acknowledgements
The work was supported by UID/QUI/50006/2019 with funding from FCT/MCTES through national funds, and by Programa de Cooperación Interreg V-A España-Portugal 2014–2020 (project 0377_IBERPHENOL_6_E). João Bernardo thanks FCT/MEC for his grant (SFRH/129499/2017).

References
[1] N. Lane, Bioessays, 33 (2011) 860.
[2] V.F. Monteiro-Cardoso, M.M. Oliveira, T. Melo et al, Journal of Alzheimer's Disease, 43 (2015) 1375.
[3] D. Neves, P. Valentão, J. Bernardo et al, Journal of Functional Foods, 56 (2019) 145.

Antiproliferative and cytostatic combined effects of simvastatin and 5-fluorouracil in an *in vitro* cancer model

José Miguel P. Ferreira de Oliveira[1,*], Cláudia Vilaça[2], Diana Pádua[3,4], Patrícia Mesquita[3,4], Eduarda Fernandes[1], Conceição Santos[2,5], Raquel Almeida[2,3,4]

[1]LAQV,REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[2]Department of Biology, Faculty of Sciences, University of Porto, Porto, Portugal
[3] Institute of Molecular Pathology and Immunology, University of Porto (IPATIMUP), Porto, Portugal
[4]I3S-Instituto de Investigação e Inovação em Saúde, University of Porto, Porto, Portugal
[5] LAQV,REQUIMTE, Faculty of Sciences, University of Porto, Porto, Portugal

**jmoliveira@ff.up.pt*

Cancer is the second leading cause of death worldwide, with estimated 9.6 million associated deaths in 2018 [1]. The majority of cancer deaths are caused by lung, breast, colorectal, gastric and liver cancers [2]. Regarding gastric cancer, chemotherapy includes the administration of agents as epirubicin, cisplatin, 5-fluorouracil (5-FU) or capecitabine, as isolated drugs or in combination [3]. Despite their anticancer role, these agents can show relevant adverse effects, as cardio- and neurotoxicity by 5-FU, which limit their application [3]. In the past decades, conventional drugs have been tested in combination with non-cancer prescribed drugs to increase the therapeutic options. In this respect, statins, a class of 3-hydroxy-3-methyglutaryl CoA reductase inhibitors, have shown promising activities in combination with chemotherapeutic drugs [4].

Since 5-FU interferes with DNA replication and simvastatin previously showed antiproliferative action in combination with other agents [5], it was hypothesized that simvastatin would show antiproliferative effects with 5-FU. To investigate this, MKN-45 gastric cancer cells were exposed to simvastatin (2-20 µM) and 5-FU (5-400 µM), isolated or in combination, for 24 and 48h. Cell proliferation was determined by sulforhodamine B assay and cell cycle distribution by flow cytometry.

Simvastatin as single agent significantly decreased cell proliferation for all concentrations and exposure times tested. Combination index (CI) analysis revealed highest synergism when 20 µM simvastatin was combined with 50-400 µM 5-FU, for 24 h (CI<0.003) and 48h (CI<0.03). For fixed simvastatin concentrations, drug reduction index (DRI) was the largest for 50 µM 5-FU *vs.* higher concentrations. For fixed 5-FU concentrations, DRI was largest for 20 µM simvastatin *vs.* lower concentrations. In addition, simvastatin (10 and 20 µM, 48h) caused cell-cycle arrest in G1 phase. However, compared to cells exposed to combinations with 5-FU (50 and 100 µM, 48h), no significant difference was found in cell accumulation in G1 phase. These results highlight the anticancer potential of simvastatin in combination therapies with 5-FU, and demonstrate the cytostatic nature of simvastatin in this model.

Acknowledgments
This work was supported by European Regional Development Funds and National Funds (Fundação para a Ciência e Tecnologia and Ministério da Educação e Ciência) under the Partnership Agreement PT2020 POCI-01-0145-FEDER-007265-UID/QUI/50006/2019, and "Programa Operacional Competitividade e Internacionalização" (COMPETE) (POCI-01-0145-FEDER-029243) and in the framework of the project "Institute for Research and Innovation in Health Sciences" (POCI-01-0145-FEDER-007274). This work was also financed by the project NORTE-01-0145-FEDER-000003 (DOCnet). FCT/MCT supported J.M.P. Ferreira de Oliveira (grant number SFRH/BPD/74868/2010) as defined by Decree-Law No. 57/2016, of 29 August, amended by Law No. 57/2017, of 19 July.

References

[1] J. Ferlay, M. Colombet, I. Soerjomataram, C. Mathers, D.M. Parkin, M. Piñeros, A. Znaor, F. Bray, Int J Cancer, 144 (2019) 1941.
[2] F. Bray, J. Ferlay, I. Soerjomataram, R.L. Siegel, L.A. Torre, A. Jemal, Cancer Cytopathol, 68 (2018) 394.
[3] C.A. Bradley, M. Salto-Tellez, P. Laurent-Puig, A Bardelli, C. Rolfo, J. Tabernero, H.A. Khawaja, M. Lawler, P.G. Johnston, S. Van Schaeybroeck, Nat Rev Clin Oncol, 14 (2017) 562.
[4] MF Demierre, PD Higgins, SB Gruber, E Hawk, SM Lippman. Nat Rev Cancer, 5 (2005) 930
[5] K.A. Manu, M.K Shanmugam, F. Li, L. Chen, K.S. Siveen, K.S. Ahn, A.P. Kumar, G. Sethi, J Mol Med (Berl), 92(2014):267.

Curcumin Analogs: synthesis and study of therapeutic potential in retinal degeneration

Maria J. Perry[1,*], Ana S. Falcão [2], Marta Clariano[1]
[1] Research Institute for Medicines (iMed. Ulisboa), Faculdade de Farmácia da Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal
[2]I CEDOC, Nova Medical School (UNL), Rua Câmara Pestana, nº 6, 1150-082 Lisboa, Portugal
**e-mail mjprocha@ff.ulisboa.pt*

Curcumin is a natural polyphenolic compound, derived from the rhizomes of turmeric (*Curcuma longa* L.), with recognized ample range of biological properties, such as antioxidant, antitumoral, neuroprotective, anti-inflammatory and wound healing activities [1]. Curcumin is also capable of improve retinal function in retinal degeneration [2] and enhances autophagy [1,3].

Despite the plethora of properties of curcumin and low toxicity, its clinical use is limited by pharmacokinetic defects such as poor absorption, low bioavailability, rapid metabolism and poor chemical stability. In order to achieve better pharmacological and pharmacokinetic profiles, curcumin analogs have been developed by chemical modification on the curcumin molecular scaffold [4].

We present at this congress the synthesis of a small library of monocarbonyl analogs of curcumin, its structural characterization and evaluation of properties such as lipophilia, stability and activity-structure relationships. To assess their therapeutic interest the compounds were studied in retinal pigment epithelial cells and colorectal cancer stem cells. Because these analogues have potential activity as Michael acceptors, we have also evaluated their electrophilic nature, as this may determine the appearance of adverse effects (Figure 1).

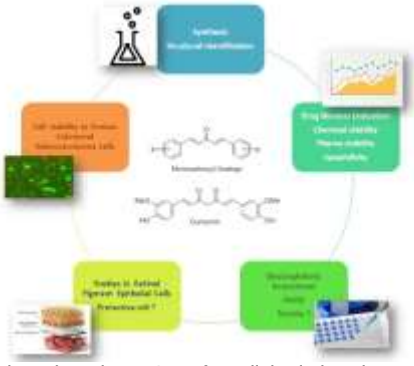


Fig.1. Curcumin and developed analogs. Set of medicinal chemistry studies performed to evaluate therapeutic interest.

Acknowledgements
Supported in part by UID/DTP/04138/2019 from FCT, Portugal.

References

[1] Pan, Z.; Chen, C.; Zhou, Y.; Xu, F.; Xu, Y., Drug Development Research, 77 (2016) 43-49.
[2] Peddada, K. V.; Brown, A.; Verma, V.; Nebbioso, M., International Ophthalmology, 39 (2019) 725-734.
[3] Shakeri, A.; Cicero, A. F. G.; Panahi, Y.; Mohajeri, M.; Sahebkar, A., Journal of Cellular Physiology, 234 (2019) 5643-5654.
[4] Song, J. X.; Sun, Y. R.; Peluso, I.; Zeng, Y.; Yu, X; Lu, J. H.; Xu, Z.; Wang, M. Z.; Liu, L. F.; Huang, Y. Y.; Chen, L. L.; Durairajan, S. S. K.; Zhang, H. J.; Zhou, B.; Zhang, H. Q.; Lu, A.; Ballabio, A.; Medina, D. L.; Guo, Z.; Li, M., Autophagy, 12 (2016), 1372-1389.

Phthalocyanine loaded nanodroplets for Photoacoustic Tomography

Maria Inês P. Mendes[1], Fábio A. Schaberle[1], Mário J.F. Calvete[1], Mariette M Pereira[1], Luis G. Arnaut[1,*]
[1]Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal
**lgarnaut@ci.uc.pt*

Photoacoustic tomography (PAT) is an emerging imaging technique with significant potential. It uses pulsed laser excitation with a wavelength which is absorbed by a contrast agent in order to produce an ultrasound wave referred to as photoacoustic wave. The contrast agent that absorbs light rapidly decay through non-radiative processes leading to a fast release of heat that generates a thermoelastic expansion and launches a photoacoustic wave. PAT was introduced in preclinical research to visualize vascular structures using hemoglobin as an endogenous contrast agent. Its translation to a clinical setting requires the development of contrast agents that allow for deeper image resolution and enhanced contrast [1].

Nanodroplets are composed of a perfluorocarbon liquid core surrounded by a lipid, protein, or polymer shell material. These particles are metastable due to the presence of a liquid perfluorocarbon core that has a boiling point near body temperature and may lead to the formation of a microbubble upon small temperature or pressure changes. Nanodroplets have been investigated in ultrasound and PAT. In this work they will be used to carry a contrast agent and increase sensitivity, as the photothermal expansion may change the nanodroplet into a microbubble [2]. Phthalocyanines have intense absorptions in the phototherapeutic window and can be used in PAT. To increase the non-radiative decay, it is possible to coordinate metals within the phthalocyanine core and increase the photoacoustic efficiency of these molecules.

In this study, the nanodroplets are composed of a perfluoropentane core and an albumin shell. Several phthalocyanines were synthetized to solubilize in the core of the nanodroplets. To increase the solubility of these molecules, different length fluorinated chains were added to them. A variety of paramagnetic metals can be used to increase the non-radiative decay of the phthalocyanines and in this study copper and manganese were used.

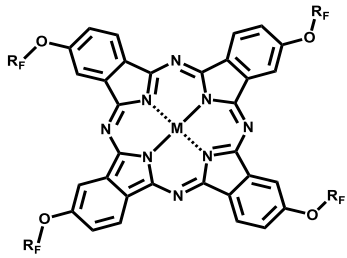


Fig. 1. Schematic representation of the phthalocyanines synthetized.

Photochemical and photoacoustic characterization of these molecules in different solvents and in nanodroplet formulation was performed. The absorption peaks are between 600 and 800 nm, which fall in the phototherapeutic window. The photoacoustic signal detected after the excitation of the phthalocyanines is higher in the nanodroplets compared to albumin solutions, suggesting that the contrast in PAT can increase using nanodroplets.

Acknowledgments
This work was financially supported by the Portuguese Science Foundation (Pest-OE/QUI/UI0313/ 2014 and PTDC/QEQ-MED/3521/2014). Maria Inês P. Mendes was financially supported by the Portuguese Science Foundation (PD/BI/135339/2017).

References
[1] Wang, L., Hu, S. Science. 335 (2012) 1458–1462.
[2] Hannah, A., Luke, G., Wilson, K., Homan, K., Emelianov, S. ACS Nano, 8 (2014) 250-259.

The potential antidiabetic effect of flavonoids through inhibition of fructose 1,6-bisphosphatase

Carina Proença[1,*], Marisa Freitas[1], Daniela Ribeiro[1], Artur M. S. Silva[2], Pedro A. Fernandes[3], Eduarda Fernandes[1]

[1] LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal
[2] QOPNA and LAQV, REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[3] UCIBIO, REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal

**up201302568@ff.up.pt*

Liver fructose 1,6-bisphosphatase (FBPase) is a well-known enzyme that regulates the gluconeogenesis, a process of special relevance in situations of long periods of fasting and starvation. In type 2 diabetes (T2D) patients, the increased endogenous glucose production (EGP) occurs mostly through the gluconeogenesis pathway. Among the different enzymes that act on this pathway, FBPase remains as one of the most promising key targets for the management of T2D. As such, the blood glucose control in T2D with FBPase inhibitors represents a potential alternative for the currently used antidiabetic agents that fulfils an unmet medical need, and major efforts have been done on the search for new compounds with the capacity to inhibit FBPase activity [1,2].

Flavonoids, a class of phenolic and heterocyclic compounds with the C6-C3-C6 basic structure, are among the most attractive plant-derived natural products due to their well-recognized biological activities, including antidiabetic activity [3,4]. However, studies concerning the flavonoids' ability to inhibit FBPase are scarce.

The aim of the present work was to evaluate the inhibitory activity of a panel of flavonoids against human FBPase and establish a structure-activity relationship. For this purpose, a fluorescent based FBPase inhibitor screening kit was used.

From the obtained results, it was possible to verify that the most active flavonoid was herbacetin, suggesting that the presence of -OH groups at 3-position of C ring, at 4'- position of B ring, and at 5-, 7- and 8- positions of A ring, as well as the C2=C3 double bond and the 4-oxo function at the pyrone ring, is favourable for the intended effect.

To the best of our knowledge, this is the first time that *in vitro* FBPase inhibition by flavonoids was performed, certainly contributing to an important first step on the understanding of the role of these compounds in the activity of the enzyme under study. In the light of these preliminary results, it can be concluded that flavonoids possess promising capacity to decrease FBPase activity, and therefore to elicit an antidiabetic effect.

Acknowledgments
The work was supported by UID/QUI/50006/2019 with funding from FCT/MCTES through national funds and "Programa Operacional Competitividade e Internacionalização" (COMPETE) (POCI-01-0145-FEDER-029241). Carina Proença acknowledges the financial support by FCT for the PhD grant (SFRH/BD/116005/2016), in the ambit of "QREN - POPH - Tipologia 4.1 - Formação Avançada", co-sponsored by Fundo Social Europeu (FSE) and by national funds of Ministério da Ciência, Tecnologia e Ensino Superior (MCTES).

References

[1] R. Kaur, L. Dahiya, M. Kumar, Eur. J. Med. Chem., 141 (2017), 473-505.
[2] P. D. van Poelje, S. C. Potter, M. D. Erion, in Diabetes - Perspectives in Drug Therapy, M. Schwanstecher (Ed.), Berlin, Springer Berlin Heidelberg, 2011, 279-301.
[3] C. Proença, M. Freitas, D. Ribeiro, J. L. C. Sousa, F. Carvalho, A. M. S. Silva, P. A. Fernandes, E. Fernandes, Food Chem. Toxicol., 111 (2018), 474-481.
[4] C. Proença, M. Freitas, D. Ribeiro, S. M. Tomé, E. F. T. Oliveira, M. F. Viegas, A. N. Araújo, M. J. Ramos, A. M. S. Silva, P. A. Fernandes, E. Fernandes, J. Enzyme Inhib. Med. Chem., 34(1) (2019), 577-588.

Photoinactivation of *Escherichia coli* through water-soluble ammonium-phthalocyanines

Sara R. D. Gamelas[1,*], Ana T. P. C. Gomes[2], Maria A. F. Faustino[1], João P. C. Tomé[3], Adelaide Almeida[2], Leandro M. O. Lourenço[1]

[1]QOPNA and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[2]CESAM and Department of Biology, University of Aveiro, 3810-193 Aveiro, Portugal.
[3]CQE and Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal.
*e-mail: sara.gamelas@ua.pt

Photodynamic inactivation (PDI) of microorganisms is gaining special attention as an effective approach against multidrug-resistant bacteria. Some molecules, usually named photosensitizers (PSs), when combined with appropriate visible light in the presence of molecular oxygen produce reactive oxygen species (ROS) that are toxic to pathogenic microorganisms. Phthalocyanine (Pc) derivatives are included in the class of promising PS molecules for biomedical applications, since they strongly absorb red light, which allow a deeper penetration/treatments [1-4]. Recently it was recognized that the addition of non-toxic salts, such as potassium iodide (KI) increases the photoinactivation efficiency of some PSs [1].

In this communication, it will be reported and discussed the synthesis, structural and photophysical characterizations of novel cationic Pcs (**1**, **2**) decorated with multi-trimethylammonium groups. The results of the photoinactivation assays towards a Gram-negative bioluminescent bacterium *E. coli* with and without the addition of KI will be also examined.

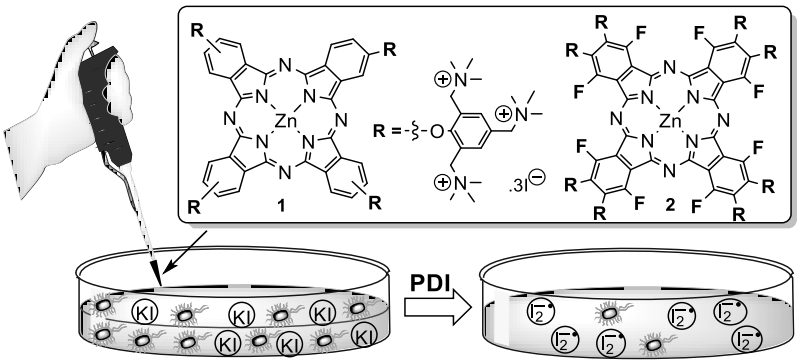


Fig.1. Structures of phthalocyanines (**1**, **2**) bearing multi-trimethylammonium groups.

Acknowledgements:
Thanks are due to FCT/MEC for the financial support to QOPNA (UID/QUI/00062/2019), CESAM (FCT UID/AMB/50017/2019) and CQE (UID/QUI/0100/2019) research units, to the FCT projects (PTDC/QUI-QOR/31770/2017 and P2020-PTDC/QEQ-SUP/5355/2014), through national founds (PIDDAC) and where applicable co-financed by the FEDER-Operational Thematic Program for Competitiveness and Internationalization-COMPETE 2020, within the PT2020 Partnership Agreement. Thanks are also due to the Portuguese NMR and Mass Networks. S. G. thanks FCT for her doctoral grant (SFRH/BD/143549/2019).

References

[1] M. R. Hamblin, Expert Review of Anti-infective Therapy, 15 (2017) 1059.
[2] C. Vieira, A. T. P. C. Gomes, M. Q. Mesquita, N. M. M. Moura, M. G. P. M. S. Neves, M. A. F. Faustino, A. Almeida, Frontiers in Microbiology, 9 (2018) 2665.
[3] L. Marciel, L. Teles, B. Moreira, M. Pacheco, L. M. O. Lourenço, M. G. P. M. S. Neves, J. P. C. Tomé, M. A. F. Faustino, A. Almeida, Future Medicinal Chemistry, 9 (2017) 365.
[4] L. M. O. Lourenço, A. Sousa, M. C. Gomes, M. A. F. Faustino, A. Almeida, A. M. S. Silva, M. G. P. M. S. Neves, J. A. S. Cavaleiro, Â. Cunha, J. P. C. Tomé, Journal of Photochemistry and Photobiology, 14 (2015) 1853.

Biocompatible Indium phthalocyanine with near-infrared absorption as contrast agent for photoacoustic imaging

Ana C. S. Lobo[1], Fábio A. Scharberle[1], Vanessa A. Tomé[1], Mário J. F. Calvete[1], Mariette M. Pereira[1], Carlos Serpa[1] and Luis G. Arnaut[1,*]
[1]Coimbra Chemistry Centre, University of Coimbra, 3004-535 Coimbra, Portugal
*lgarnaut@ci.uc.pt

Photoacoustic imaging (PAI) is a biomedical imaging modality that involves the detection of an ultrasound wave generated by laser, designated as photoacoustic signal. The photoacoustic signal is produced when molecules absorb pulsed light and the excess of energy is quickly released to a medium as thermal energy, generating acoustic waves with high frequency. Photoacoustic imaging combines the high-contrast and spectroscopic-based specificity of optical imaging with the high spatial resolution of ultrasound imaging [1]. This imaging technique has been applied to small animal studies and, more recently, has been implemented in clinical diagnosis.

The challenge remains in the development of contrast agents for PAI that increase the resolution and the sensitivity of the technique to detect early stage diseases. The ideal contrast agents should absorb light in the phototherapeutic window, transform light into thermal energy in pico-microseconds and present no generation of reactive oxygen species that could lead to phototoxicity [2].

In this study we present the characterization of an Indium Phthalocyanine (InPc) which the synthesis of has been previously described [3]. InPc presents remarkable features for absorbing light with high efficiency between 830-850 nm and almost 100% deactivation from the excited states through thermal release; a highly valuable characteristic for a photoacoustic contrast agent. In vitro studies with murine breast adenocarcinoma cell line showed that InPc have no dark-toxicity or phototoxicity with incubation up to 30 µM. The generation of the photoacoustic signal in vitro allowed the cellular-uptake profile of the phthalocyanine to be followed. Our results validate the sensitivity and ability of InPc to be applied as a promising, biocompatible photoacoustic contrast agent.

Fig.1. Schematic representation of indium phthalocyanine.

Acknowledgements
The Coimbra Chemistry Centre is supported by the Fundação para a Ciência e a Tecnologia (FCT), Portuguese Agency for Scientific Research, through the projects PTDC/QEQ-MED/3521/2014, Pest-OE/QUI/UI0313/2014. ACSL is supported by Portuguese Science Foundation (ref. PD/BD/132524/2017).

References

[1] L.V. Wang, S. Hu, Science, 335 (2012) 335:1458.
[2] J. Weber, P. C. Beard, S. E. Bohndiek, Nature Methods,13 (2016) 8:639.
[3] A.C.S. Lobo, A.D. Silva,V.A Tomé, S.M.A. Pinto, E.F.F. Silva, M.J.F. Calvete, C.M.F. Gomes, M.M. Pereira, L.G. Arnaut, J. Med. Chem, 59 (2016) 10:4688.

Chalcones as modulators of neutrophils' oxidative burst, in physiological and hyperglycemic conditions

Adelaide Sousa[1,*], Daniela Ribeiro[1], Catarina M. Correia[2], Vera L. M. Silva[2], Artur M. S. Silva[2], Eduarda Fernandes[1], Marisa Freitas[1]

[1]LAQV-REQUIMTE, Applied Chemistry Laboratory, Department of Chemical Sciences, Faculty of Pharmacy of the University of Porto, Porto, Portugal

[2]QOPNA & LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, Aveiro, Portugal

**up201404164@ff.up.pt*

Hyperglycemia is a characteristic condition of diabetes *mellitus* (DM). In the last years, several epidemiological studies have reported inflammation as the essential etiological factor that links the chronic hyperglycemic status and DM complications. Neutrophils, the body's first-line-defense cells, are greatly involved in the perpetuation of the inflammatory response contributing to the onset and progression of late diabetic complications, through an excessive production of reactive species (RS), known as oxidative burst. Sustained high RS levels associated to its deficient removal by antioxidants, results in a condition that is commonly designated as oxidative stress (OS). There is a growing scientific interest in finding compounds capable of modulating OS during hyperglycemic conditions and consequently, playing an important role in the improvement of DM complications. Chalcones (1,3-diaryl-2-propen-1-one), open chain flavonoids with a three-carbon α, β-unsaturated carbonyl system joining the two aromatic rings (A and B), are natural and bioactive compounds found in plants and citrus fruit. Biological effects of these compounds have been extensively studied, more precisely in the modulation of several therapeutic targets for the treatment of DM [1-2].

The aim of this study was to evaluate the ability of a panel of 25 structurally related chalcones [varying the number and position of several substituents (hydroxyl, methoxyl, methyl or chlorine)], to modulate RS production by human neutrophils, in physiological (5.5 mM glucose) and in hyperglycemic conditions (30 mM glucose), simulating a DM status. For this purpose, human neutrophils were isolated and stimulated with phorbol 12-myristate-13-acetate, which induces the production of RS. RS were then detected by a chemiluminescent probe, luminol [3].

Most of the tested chalcones exhibited an interesting modulatory effect against neutrophil's oxidative burst, with IC_{50} values ≤ 10 μM. The majority of the tested chalcones presented similar effects in physiological and hyperglycemic conditions. Moreover, the substitution pattern expressively influenced the inhibitory activity of chalcones against RS production by human neutrophils, in both conditions. The most active chalcone presents a hydroxyl group at position 2' of the A ring and a methoxyl and a hydroxyl groups at positions 3 and 4, respectively, of the B ring. The results obtained suggest that chalcones can be considered a group of promising compounds able to modulate OS in high-glucose conditions, characteristic of DM.

Acknowledgments

The work was supported by UID/QUI/50006/2019 with funding from FCT/MCTES through national funds and "Programa Operacional Competitividade e Internacionalização" (COMPETE) (POCI-01-0145-FEDER-029241).

References

[1] S. Rocha, D. Ribeiro, E. Fernandes, M. Freitas, Current Medicinal Chemistry, 25 (2018).

[2] S. Rocha, A. Sousa, D. Ribeiro, C. M. Correia, V. L. M. Silva, C. M. M. Santos, A. M. S. Silva, A. N. Araujo, E. Fernandes, M. Freitas, Food & Function, (2019). *(In press).*

[3] M. Freitas, G. Porto, J. L. F. C. Lima, E. Fernandes, Clinical Biochemistry, 41 (2008) 570-575.

Síntese de derivados de imidazole e avaliação do potencial anticancerígeno em linhas celulares do carcinoma de células renais

A. Sousa[1,*], M. Costa[2,3] , O. Pontes[2,3], M.F. Proença[1]

[1] Centro de Química, Campus de Gualtar, Universidade do Minho, 4710-057 Braga, Portugal
[2] Instituto de Ciências da Vida e da Saúde (ICVS), Escola de Medicina, Universidade do Minho, Campus de Gualtar, Braga, Portugal
[3] ICVS/3B's – PT Laboratório Associado, Braga/Guimarães, Portugal

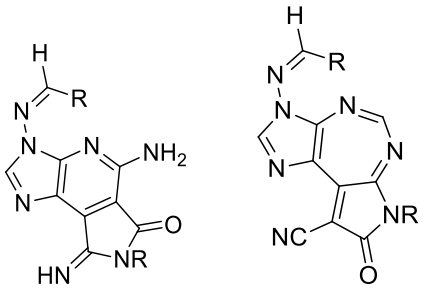
**pg33720@alunos.uminho.pt*

O carcinoma de células renais é um dos principais tipos de cancro que afeta o sistema urulógico. O tratamento desta doença é um objetivo dificil de alcançar uma vez que é cada vez mais recorrente o surgimento de resistência aos fármacos existentes, por parte das células tumorais.[1,2]

A proteína m-TOR é um dos principais alvos nas terapias utilizadas para o tratamento desta doença.[1,2]
Um screening virtual realizado a uma biblioteca de compostos sintetizados anteriormente pelo grupo de investigação, permitiu identificar uma seleção de moléculas, contendo o núcleo de imidazole, como potencialmente ativas nesta proteína.

As imidazo-piridinas **A** e imidazo-diazepinas **B**, identificadas neste estudo, podem ser preparadas a partir de imidazolil-pirrolonas, usando abordaqens sintéticas desenvolvidas no grupo de investigação.

Esta apresentação focará a síntese e caraterização de um conjunto de moléculas contendo os núcleos de imidazo-piridina (**A**) e imidazo-diazepina (**B**) que foram posteriormente submetidos para testes biológicos de forma a avaliar a sua potencial atividade em linhas celulares do carcinoma de células renais.



A **B**

Fig.1. Estruturas derivadas de imidazo-piridinas (**A**) e imidazo-diazepinas (**B**)

Agradecimentos
Agradecemos o apoio financeiro da UMinho, FCT e FEDER-COMPETE através do Centro de Química (UID/QUI/00686/2013 e UID/QUI/0686/2016), e a bolsa de Doutoramento da aluna Olívia Pontes (SFRH/BD/128850/2017). O espectómetro Bruker Avance III 400 pertence à Rede Nacional de RMN (RNRMN) e foi adquirido no âmbito do Programa Nacional de Reequipamento Científico, contrato REDE/1517/RMN/2005, com fundos do POCI 2010 (FEDER) e FCT.

Referencias

[1] Abe, H. & Kamai, T. Recent advances in the treatment of metastatic renal cell carcinoma. *Int. J. Urol.*, **2013**, 20, 944–55.

[2] Patard, J. J. *et al.* ICUD-EAU international consultation on kidney cancer 2010: Treatment of metastatic disease. *European Urology,* **2011**, 60, 684–690.

Interaction of dietary polyphenols with the endothelium: when nutrimetabolomics meets biophysics

Ana Reis[1,*], Sara Rocha[1], Jose Luis Quesada[2], Victor de Freitas[1]

[1]REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal
[2]Cardiovascular Biochemistry, Biomedical Research Institute IIB Sant Pau, Sant Antoni Ma Claret, 167, Barcelona, Spain

**e-mail del autor de contacto [anpereira@fc.up.pt]*

Dietary polyphenols are known for their antioxidant health benefits and improved vascular function. The study of polyphenol-lipid interactions is gaining increasing interest given the rising incidence of diet-related diseases such as obesity, diabetes and hypertension and the potential for polyphenol-rich diets in the quest for personalized nutritional strategies ("personalized nutrition") in the prevention, treatment, and management of non-communicable diseases in an increasingly aging society.

However, in their journey across the human epithelium (oral, stomach, gut and endothelium) polyphenols undergo an array of distinct chemical modifications that need to be taken into account in membrane and cellular models as they affect not only the chemical properties of polyphenols but also their physical interaction with epithelial lipids. In addition to this, the epithelium has distinct nuances in their lipid composition that is likely to affect the polyphenol's permeability, transport, and biological activity.

Following our interest on the health beneficial effects of diet-rich diets to the endothelial function in scenarios of hypercholesterolemia, we are currently exploring the polyphenol metabolome in triglyceride-rich lipoproteins (LDL and VLDL) collected from diabetic patients. Preliminary findings showed that the content of polyphenols is changed in hyperglycemia conditions suggesting that lipid environments influences the distribution of polyphenols transported. Information on the panel and content of polyphenol metabolites transported by lipoproteins will be used in permeability studies of polyphenol metabolites in epithelial model membranes.

The preliminary findings obtained from the metabolomic screening will be used to fine-tune the experimental conditions in model membrane studies and provide clues on the influence of lipid environments on the permeation, transport and biological activity of ingested polyphenols with particular emphasis on non-communicable diseases.

Agradecimientos
The authors acknowledge the financial support provided by Portuguese National Funds (NORTE-01-0145-FEDER-000011) and FEDER-Interreg España-Portugal Programme (Project ref. 0377_IBERPHENOL_6_E), and the facilities provided by REQUIMTE/LAQV through UID/QUI/50006/2019 with funding from FCT/MCTES through national funds and co-financed by FEDER under the Partnership Agreement PT2020.

Referencias

[1] A. Reis, M. Fonseca, V de Freitas, A. Rivas-Urbina, J.L. Quesada. Author, "Distribution of polyphenols across lipoprotein sub-populations in Health and Diabetes Mellitus", Free Rad Biol Med. 120 (2018) S132.

Synaptosomes as membranar models to study the effects of carotenoids on lipid peroxidation

Daniela Ribeiro[1,*], Pedro Nicola[1], Marta Silva[1], Marisa Freitas[1], Félix Carvalho[2], Eduarda Fernandes[1]

[1]LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal

[2]UCIBIO, REQUIMTE, Laboratory of Toxicology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal

**dsribeiro@ff.up.pt*

Synaptosomes are sub-cellular fractions, derived from neurons, functioning as anucleated cells that remain enzymatically and metabolically active. As the majority of the brain is constituted by lipids, it constitutes an excellent model to the study of the pro- *versus* antioxidant effects of a diversity of compounds, namely lipophilic ones. Moreover, synaptosomal membranes are particularly susceptible to the deleterious effects promoted by the reactive species produced during oxidative stress, as they suffer a chain reaction designated as lipid peroxidation [1,2]. Carotenoids are known lipophilic bioactive compounds widely distributed in nature and daily present in our diet. Despite the variety of biological properties attributed to carotenoids, their pro- and/or antioxidant activities are still controversial [3]. The main aim of this work was to develop a synaptosomal model to evaluate peroxynitrite anion ($ONOO^-$) and hydrogen peroxide (H_2O_2) - induced lipid peroxidation and evaluate carotenoids pro- *versus* antioxidant activities.

Synaptosomes were isolated from rat brain tissue, based on a previously described protocol [4]. In order to establish the methodological procedures, various parameters were optimized: concentration of synaptosomal proteins, concentration of $ONOO^-$ and H_2O_2 for lipid peroxidation induction, and incubation time of synaptosomes with $ONOO^-$ or H_2O_2. The optimized methods were defined as: synaptosomes (with a protein concentration of 0.1 mg/mL), incubated with $ONOO^-$ (10 mM) or H_2O_2 (0.125 % v/v), for 15 min, at 37 ºC. Following this optimization process, β-cryptoxanthin, β-carotene, and its physiological metabolites, *trans*- β-apo-8'-carotenal and β-ionone, were added during the synaptosomes preparation step, aiming their incorporation into the synaptosomes and subsequent evaluation of their effect on $ONOO^-$ and H_2O_2 - induced lipid peroxidation, by the thiobarbituric acid reactive substances (TBARS) method.

This work allowed the development of a micro-analysis assay, using synaptosomes, that enabled the high-throughput screening of the effects of carotenoids against $ONOO^-$ and H_2O_2 - induced lipid peroxidation. In both cases, the tested carotenoids and metabolites presented distinctive effects on lipid peroxidation, from the inhibition to the induction. The obtained results endorse the current doubts about the promising potential of carotenoids as antioxidants. Likewise, this work highlights the importance of tested concentrations and oxidative environment under which the different carotenoids are tested, indicating the need of harmonized procedures for this type of studies.

Acknowledgments

This work was supported by UID/QUI/50006/2019 with funding from Fundação para a Ciência e Tecnologia / Ministério da Ciência, Tecnologia e Ensino Superior (FCT/MCTES) through national funds, and "Programa Operacional Competitividade e Internacionalização" (COMPETE) (PTDC/QEQ-QAN/1742/2014 - POCI-01-0145-FEDER-016530).

References

[1] J. Jhou, H. Tai, Neurol Ther, 6(Sup 1) (2017) 57.
[2] Q. Guo, B. Zhao, M. Li, S. Shen, W. Xin, Biochim Biophys Acta, 1304(3) (1996) 210.
[3] D. Ribeiro, M. Freitas, A. Silva, F. Carvalho, E. Fernandes. Food Chem Toxicol, 120 (2018) 681.
[4] D. Barbosa, J. Capela, J. Oliveira, R. Silva, L. Ferreira, F. Siopa, P. Branco, E. Fernandes, J. Duarte, M. Bastos, F. Carvalho, Br J Pharmacol, 165 (2012) 1017.

Photoactive Cellulose Supported Materials for Antimicrobial Photodynamic Therapy (aPDT)

Carlos J. P. Monteiro[1*], Maria G. P. M. S. Neves[1], Adelaide Almeida[2]. M. Amparo F. Faustino[1]

[1]QOPNA & LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2]CESAM, Department of Biology, University of Aveiro, 3810-193 Aveiro, Portugal
**cmonteiro@ua.pt*

The advent of drug-resistance among pathogenic microbes is a severe concern and recent strategies have focused on the development of novel treatment options and alternative antimicrobial therapies. Antimicrobial Photodynamic Therapy (aPDT) involves the combination of photoactive dyes and harmless visible light to produce reactive oxygen species that can selectively kill microbial cells and is being recognized as an effective method to inactivate a broad spectrum of microorganisms, including those resistant to conventional antimicrobials/biocides [1]. In the last few years, the development and biological assessment of new photosensitizers for aPDT were accompanied by their immobilization in different supports having in mind the extension of the photodynamic principle to new applications, such as wound disinfection, sterilization of medical materials and surfaces in different contexts (industrial, household and hospital) or prevention of microbial contamination in packaged food. In the field of medical sciences, functionalized cellulose based materials has attracted much attention [2,3]. Cellulose is the most abundant natural biopolymer, considered a great starting material for developing new and more sustainable materials from renewable resources. As cellulose owns a carbohydrate nature, it has inherent compatibility with biological tissues and, consequently, possesses unique utility with respect to their bioavailability, biocompatibility and biodegradability considerations [4]. Photosensitizers for aPDT can become more efficacious when adsorbed, entrapped, or linked to cellulose like supports. In addition, these cellulose-based systems provide an increase in the surface area, are able to achieve the targeted drug delivery, as well as used for the preparation of packaging materials with improved mechanical strength, barrier, and antimicrobial properties. In this communication, we intended to summarize recent work considering a diversity of photosensitizers supported in cellulose or cellulose derivative materials to achieve an effective photoinactivation with particular attention to the chemistry behind the preparation of the photosensitized-cellulose functional materials.

Acknowledgements
The authors thank University of Aveiro and FCT/MCT for the financial support provided to QOPNA research Unit (FCT UID/QUI/00062/2019), the Associate Laboratory CESAM (FCT UID/AMB/50017/2019) and to Project PREVINE - FCT-PTDC/ASP-PES/29576/2017), through national funds (OE) and where applicable co-financed by the FEDER-Operational Thematic Program for Competitiveness and Internationalization-COMPETE 2020, within the PT2020 Partnership Agreement. Thanks are also due to the Portuguese NMR and Mass Networks.

References

[1] R. Yin, T. Agrawal, U. Khan, G. K. Gupta, V. Rai, Y. Y. Huang, M. R. Hamblin, Nanomedicine 10 (2015) 2379.
[2] M. Q. Mesquita, C. J. Dias, M. Neves, A. Almeida, M. A. F. Faustino, Molecules 23 (2018) 2424.
[3] E. Alves, M. A. F Faustino, M. Neves, A. Cunha, H. Nadais, A. Almeida, J. Photochem. Photobiol. C-Photochem. Rev. 22 (2015) 3.
[4] R. J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood, Chem. Soc. Rev. 40 (2011) 394.

Development of new anticancer metallodrugs

L. Monteiro [1,2*], R. Mendes [1,2], F. Paz [1,2], C. Silva [3,4], F. Martel [3,4], B. J. M. Leite Ferreira [1,2], T. M. Santos [1,2]

[1]Dep. de Química da Universidade de Aveiro, Campus Universitário de Santiago 3810-193 Aveiro, Portugal;
[2]CICECO, Aveiro Institute of Materials, 3810-193 Aveiro, Portugal;
[3]Unidade de Bioquímica, Dep. de Biomedicina da Faculdade de Medicina da Universidade do Porto, Alameda Prof. Hernâni Monteiro, 4200-319 Porto, Portugal;
[4]I3S, Instituto de Investigação e Inovação em Saúde, 4200-135, Porto, Portugal.

*luispedromonteiro@ua.pt

Chemotherapy success relays on low-molecular-weight drugs that have the ability to destroy cancer cells or to control proliferation. However, there are several side effects associated to the use of these drugs, mainly because they act both on cancer cells and healthy cells [1]. The use of metallodrugs to fight cancer started with Pt(II)-based drugs, but although they continue to be widely used, their harsh limitations are well known [2]. Those drawbacks prompted the need to exploit metallodrugs with different transition metals. Different metal ions can lead to alternative features of coordination modes, geometries and redox potential .That flexibility makes them an appealing to the development of new therapeutic agents [3]. The use of *pre-active* drugs as ligands is a good example on how the metal complexes can changing/improving the activity of the parent drugs [4].

The present work shows results from the synthesis and full characterization of novel metallodrugs which have been tested for their CT-DNA and BSA binding properties as well as for their anti-cancer behaviour. *In vitro* biological assays, like viability percentage, lipid peroxidation and glutathione levels, were also carry out in against breast cancer cells lines.

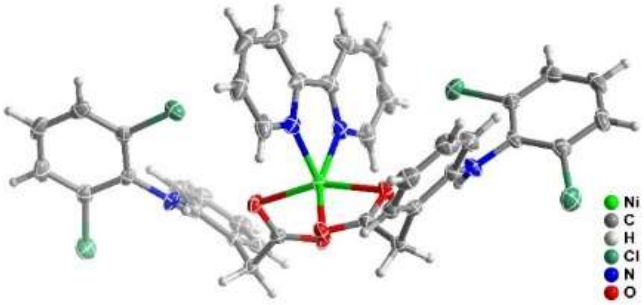


Fig. 1: Structure of one of the metallodrugs

Acknowledgements
The costs resulting from the FCT hirings is funded by national funds (OE), through FCT, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decreet-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES.

References

1. Nussbaumer, S., Bonnabry, P., Veuthey, J. L., Fleury-Souverain, Talanta, 85(5) (2011) 2265.
2. Kostova, I., Recent Patents on Anti-Cancer Drug Disco., 1(1) (2006) 1.
3. Jia, P.; Ouyang, R.; Cao, P.; Tong, X.; Zhou, X.; Lei, T.; Zhao, Y.; Guo, N.; Chang, H.; Miao, Y.; Zhou, S. J. Coord. Chem., 70(13) (2017) 2175.
4. Ogodo, U.P., O.O. Abosede, J. Applied Sci. & Environm. Management, 22(12) (2019) 371.

Novel 9-substituted-acridine derivatives as potential Acetylcholinesterase's inhibitors

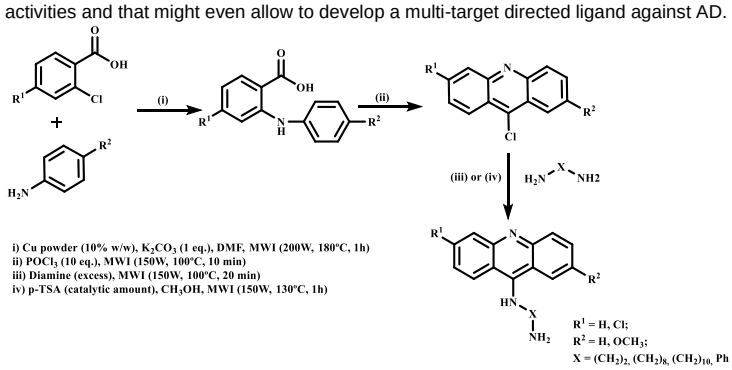
Carlos F. M. Silva[1], Diana C. G. A. Pinto[1], Artur M. S. Silva[1]

[1] Department of Chemistry & QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal

**silva.c@ua.pt*

Acridines are an interesting group of nitrogen-containing heterocyclic compounds, mainly due to its wide range of pharmaceutical properties.[1,2] The unique physical and chemical properties of this type of compounds allows several derivatives to be associated with numerous bioactivities, such as anti-inflammatory, anti-cancer, antimicrobial, antitubercular, antiparasitic, antimalarial, antiviral and fungicidal activities. Moreover, thanks to its structural similarity with tacrine, this type of compounds has also been evaluated for its potential action against Alzheimer's Disease (AD), with some 9-substituted-acridine derivatives already being described for these purposes.[3,4]

Based on these evidences, our work consisted in the development of 9-substituted-acridine derivatives that might act as acetylcholinesterase's (AChE) inhibitors. To accomplish these compounds, two different 9-chloroacridines reacted with distinct types diamines, leading to a small library of compounds (**Scheme 1**) to be evaluated for its ability to inhibit AChE. From preliminary results, some of these compounds have already revealed promising inhibitory activities, with one of them presenting IC_{50} values in the µM range, leaving room for further modifications to improve its activities and that might even allow to develop a multi-target directed ligand against AD.



Scheme 1. Synthetic route of 9-substituted-acridine derivatives

Acknowledgements:
Thanks are due to the University of Aveiro and FCT/MCT for the financial support for the QOPNA research Unit (UID/QUI/00062/2019) through national founds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement, and to the Portuguese NMR Network. Carlos F. M. Silva also thanks FCT for his PhD grant (PD/BD/135103/2017).

References:

[1] Zhang B, Li X, Li B, et al. Acridine and its derivatives: a patent review (2009 - 2013). Expert Opin. Ther. Pat. 2014;24:647–664.

[2] Gensicka-Kowalewska M, Cholewiński G, Dzierzbicka K. Recent developments in the synthesis and biological activity of acridine/acridone analogues. RSC Adv. 2017;7:15776–15804.

[3] Csuk R, Barthel A, Raschke C, et al. Synthesis of monomeric and dimeric acridine compounds as potential therapeutics in Alzheimer and prion diseases. Arch. Pharm. (Weinheim). 2009;342:699–709.

[4] Makhaeva GF, Lushchekina S V, Boltneva NP, et al. 9-Substituted acridine derivatives as acetylcholinesterase and butyrylcholinesterase inhibitors possessing antioxidant activity for Alzheimer's disease treatment. Bioorganic Med. Chem. 2017;25:5981–5994.

Discovery of azaaurones as potent antimycobacterial agents

Francisca Lopes[1*], André Campaniço[1], Marta P. Carrasco[1], Mathew Njoroge[2], Ronnett Seldon[2], Kelly Chibale[2], João Perdigão[1], Isabel Portugal[1], Digby F. Warner[2], Rui Moreira[1]

[1]Instituto de Investigação do Medicamento (iMed.ULisboa), Faculdade de Farmácia, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal
[2]University of Cape Town, Cape Town, South Africa
**e-mail fclopes@ff.ul.pt*

Tuberculosis (TB) remains one of the most lethal infectious diseases worldwide, ranking above HIV and malaria. The emergence of multidrug-resistant tuberculosis (MDR-TB) and extensively drug-resistant tuberculosis (XDR-TB) pose serious health threats, with strains resistant to first-line and multiple second-line antibiotics [1].

The discovery of new TB drugs is a challenging task because the conversion of hits into novel optimized leads suitable for selection as clinical candidates is hampered by the poor efficacy in eliminating *M. tuberculosis* within different host compartments, as well as a lack of knowledge about the specific target(s) inhibited and/or upregulated [2].

Herein we report the screening of an in-house small library of aurones and their isosteric counterparts, azaaurones and *N*-acetylazaaurones, against *Mycobacterium tuberculosis*. Aurones were inactive at 20 µM, while azaurones and *N*-acetylazaaurones emerged as the most potent compounds, with several derivatives displaying MIC_{99} values ranging from 0.4 to 2.0 µM. In general, (*Z*) isomers were more potent than (*E*) counterparts. In addition, several *N*-acetylazaaurones were found to be active against multidrug resistant (MDR) and extensively drug resistant (XDR) clinical *M. tuberculosis* isolates. The anti-mycobacterial mechanism of action of these compounds remains to be determined, however a preliminary mechanistic study confirmed that they do not inhibit the mycobacterial cytochrome bc1 complex. Additionally, microsomal metabolic stability and metabolite identification studies revealed that *N*-acetylazaaurones are deacetylated to their azaaurone counterparts. Overall, these results demonstrate that azaaurones and their *N*-acetyl counterparts represent a new entry in the toolbox of chemotypes capable of inhibiting *M. tuberculosis* growth.

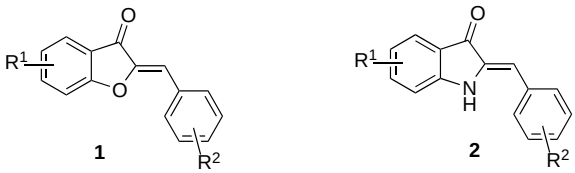


Fig.1. Chemical structures of aurones (**1**) and azaaurones (**2**)

Agradecimientos
This work was supported by projects Pest-OE/SAU/UI4013/2014 (FCT), and PTDC/MED-FAR/30266/2017 (FCT and FEDER). We also acknowledge FCT for fellowships SFRH/BD/61611/2009 (MC), SFRH/BD/131896/2017 (AC), SFRH/BPD/95406/2013 (JP) and SFRH/BSAB/113783/2015 (FL).

Referencias
[1] Global Tuberculosis Report 2018. Genebra: World Health Organization; 2018
[2] Kumar A, Chettiar S, Parish T. Expert Opin Drug Discov., 12 (2017);12:1.

Aspectos químicos y nutricionales del filete de *Aloe vera*

José Pinela[1,*], Mikel Añibarro-Ortega[1], Lillian Barros[1], Soraia P. Silva[2], Elisabete Coelho[2], Manuel A. Coimbra[2], Isabel C.F.R. Ferreira[1]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]QOPNA & LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
*jpinela@ipb.pt

El *Aloe vera* (*Aloe barbadensis* Mill.) es una planta suculenta de la familia Asphodelaceae actualmente naturalizada en muchos países tropicales y subtropicales. En la medicina tradicional, se ha utilizado ampliamente durante siglos para tratar trastornos de la piel y otras enfermedades, así como por su efecto purgante [1]. Hoy en día, esta especie se usa como ingrediente para alimentos funcionales, cosméticos y medicamentos [2]. Las hojas son la parte más utilizada de la planta, en la que se pueden identificar dos fracciones principales, la corteza externa y el parénquima interno conocido como pulpa o filete. Aunque hay varios estudios sobre el *Aloe vera* [1,2], muchos de ellos tienen descripciones confusas, principalmente sobre el interior de la hoja, debido a los diferentes términos que se han usado indistintamente. En este sentido, en este trabajo se realizó una caracterización del valor nutricional y composición química del parénquima interno de la hoja (filete), que es la parte comestible de la planta.

El filete de las hojas de *Aloe vera* fue separado de la cáscara y se determinó el contenido en humedad. Después, la muestra se liofilizó y se pulverizó y se determinó el contenido en proteína, grasa, cenizas, hidratos de carbono disponibles y fibra alimentaria. También se determinó la composición en ácidos orgánicos, ácidos grasos, tocoferoles, azúcares libres y polisacáridos de alto peso molecular utilizando diferentes técnicas cromatográficas. El perfil en compuestos fenólicos se caracterizó en un extracto hidroetanólico mediante HPLC-DAD-ESI/MS^n.

Se verificó que el filete corresponde aproximadamente al 58% de la masa de la hoja de *Aloe* vera y que su mayor constituyente es el agua (98%). En base seca, la fibra alimentaria resultó ser el macronutriente predominante (50.1%), constituida principalmente por manano (posiblemente acemanano), seguida por los hidratos de carbono disponibles (37.4%). Apenas 1% en grasa, 2.6% en proteína y 9% en cenizas, hacen que el filete sea un alimento de bajo poder calórico (4,5 kcal/100 g fw y 270 kcal/100 g dw). También se detectaron cantidades interesantes de α-tocoferol (5 mg/100 g dw) y ácido málico (5 g/100 g dw). Respecto al perfil fenólico, se detectaron de forma predominante cromonas (5.5 mg/g extracto) y antronas (5.3 mg/g extracto), incluyendo aloesina y aloínas A y B, respectivamente.

El filete fresco de *Aloe vera* es un alimento bajo en calorías debido a su alto contenido en agua y bajo contenido en grasa. Además, se destaca por su contenido en tocoferoles, ácido málico y cromonas [3]. Todo esto hace que el filete de *Aloe vera* sea un ingrediente interesante para ser explorado tanto por la industria alimentaria como por la industria cosmética.

Agradecimientos
Los autores agradecen a la Fundación para la Ciencia y la Tecnología (FCT, Portugal) y al FEDER (Fondo Europeo de Desarrollo Regional) en el marco del Programa PT2020 por el apoyo financiero a CIMO (UID/AGR/00690/2019) y los contratos de investigación de J. Pinela y L. Barros (financiación nacional de FCT, a través del contrato-programa de empleo científico institucional); al Proyecto AllNat - POCI-01-0145-FEDER-030463 (PTDC/EQU-EPQ/30463/2017), financiado por fondos del FEDER a través de COMPETE2020 - Programa Operacional de Competitividad e Internacionalización (POCI) - y por fondos nacionales a través de FCT/MCTES; al programa FEDER-Interreg España-Portugal por el apoyo financiero a través del proyecto 0377_Iberphenol_6_E; al Proyecto TRANSCoLAB (0612_TRANS_CO_LAB_2_P); y a la empresa "aCourela do Alentejo" por haber suministrado el material vegetal.

Referencias
[1] D.I. Sánchez-Machado, J. López-Cervantes,… A. Sanches-Silva, Trends Food Sci. Technol. 61 (2017) 94.
[2] K. Eshun, Q. He, Crit. Rev. Food Sci. Nutr. 44 (2004) 91.
[3] M. Añibarro-Ortega, J. Pinela, L. Barros, et al., Antioxidants, 8 (2019) 444.

QS27

Automated Microwave-assisted Synthesis for PET Radiochemistry

Ângela C.B. Neves[1*], Ivanna Hrynchak[1], V.H. Alves[1], Inês C.F. Fonseca[1], M.M. Pereira,[2] Amílcar Falcão[1,3], A.J. Abrunhosa[1]

[1]ICNAS/CIBIT - Institute for Nuclear Sciences Applied to Health - University of Coimbra
Pólo das Ciências da Saúde, Azinhaga de Santa Comba, 3000-548 Coimbra, Portugal
[2]Coimbra Chemistry Center, Chemistry Department, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal
[3] Laboratory of Pharmacology, Faculty of Pharmacy, University of Coimbra
**angela.neves@uc.pt*

Microwave dielectric heating has proven to be a highly effective source for a wide range of chemical transformations. This source of heating increases reaction yields and provides cleaner reaction mixtures [1,2]. Due to the short half-life of commonly used radionuclides for Positron Emission Tomography (PET) such as fluorine-18 (110 minutes) and gallium-68 (68 minutes) the reduction of reaction times and increase in yields is of critical importance. Moreover, considering the radioactive nature of the compounds, automation of the synthesis is mandatory. In order to optimize reaction time and yields, the main goal of this work was to implement an automated method using microwave technology to synthesize radiopharmaceuticals for PET imaging.

No-carrier-added fluoride-18 was produced by an IBA Cyclone® 18/9 cyclotron. $^{68}GaCl_3$ was obtained from a GalliaPharm® Ge-68/Ga-68 Generator from Eckert & Ziegler Radiopharma. Radiolabeling reactions were performed in a PET-Wave Discover® from CEM and an automatic module Trasis AllinOne®. Microwave heating was adapted to an existing automated setup in our site and tested for the production of commonly used radiopharmaceuticals such as [^{18}F]FDG, [^{18}F]FDOPA, [^{68}Ga]DOTANOC and [^{68}Ga]PSMA.

Azeotropic drying of [^{18}F]KF and subsequent [^{18}F]fluorination of mannose triflate were performed with a radiochemical yield of 78% and a reduction in time of 40%. Fluorination of 6-nitroveratraldehyde was performed with a radiochemical yield of 100% with a reduction in time of 60%. We also tested the setup in the radiolabelling of peptides (DOTANOC and PSMA) with ^{68}Ga, achieving 100% reaction in 1.5 minutes, instead the 10 minutes with conventional heating (reduction of 85%)[3]. Acid hydrolysis, in HCl or HI 37%, of protected [^{18}F]FDOPA was performed in 4 minutes, instead of 20 minutes by conventional heating, reducing in 84% the reaction time.

Radiosynthesis using microwave was performed with good radiochemical yields in a substantially shorter reaction time than conventional heating. These results suggest that the incorporation of microwave technology could provide a substantial advantage in the synthesis of radiopharmaceuticals with application in PET.

Acknowledgments
The authors wish to thank the financial support from Program COMPETE 2020 through project DOPAPET-DCP: POCI-01-0247-FEDER-023474. Ângela Neves also thank FCT and ICNAS-P for her PhD grant PD/BDE/135132/2017.

References
[1] PET Chemistry The Driving Force in Molecular Imaging. A. F. S. Stone-Elander, N. Elander, J.-O. Thorell, Springuer, 2007.
[2] Microwaves and Metals. M. Gupta, W.W.L. Eugene, Wiley, 2007.
[3] VH Alves, MIM Prata, AJ Abrunhosa, M Castelo-Branco, Journal of Radioanalytical and Nuclear Chemistry, 2015.

QS28

Estudo da fase inicial de agregación do β-amiloide

Mercedes Novo, Sonia Freire, Wajih Al-Soufi
Universidade de Santiago de Compostela, Facultade de Ciencias, Campus Universitario s/n, Lugo, Spain
**m.novo@usc.es*

A enfermidade de Alzheimer é unha enfermidade neurodexenerativa que constitúe a forma de demencia máis común nas persoas de idade avanzada e ten un forte impacto na sociedade actual. Asóciase á presenza das chamadas placas senís, que están formadas por fragmentos de proteínas chamados β-amiloide. Sin embargo, nos últimos anos atopáronse evidencias de que son os seus precursores, os pequenos agregados de β-amiloide formados nas fases iniciais, os que teñen efecto neurotóxico [1]. Ademais, entre os diferentes tipos de amiloide, o que está formado por 42 aminoácidos (Aβ42) considérase o máis tóxico pola súa maior tendencia a agregarse [2].

O obxectivo deste traballo é estudar a fase inicial do proceso de agregación do Aβ42 co fin de coñecer o mecanismo polo que ten lugar e caracterizar os agregados formados. Para elo utilizamos unha técnica espectroscópica de gran sensibilidade, a Espectroscopia de Correlación de Fluorescencia (FCS), que non só nos da información sobre o tamaño e a proporción dos agregados en función do tempo e da concentración de amiloide, senón que tamén nos permite estimar a concentración real de amiloide nas mostras, que é un dato crucial en estudos cuantitativos.

Estudouse a dependencia do proceso de agregación co tempo de incubación e coa concentración total de Aβ42. Os resultados obtidos mostran que o tamaño dos agregados non depende nin do tempo nin da concentración, mentres que a súa proporción si que aumenta drasticamente ao incrementar a concentración de amiloide, independentemente do tempo de incubación. De feito, a formación de agregados só é significativa cando a concentración total de amiloide supera unha certa *concentración crítica de agregación* (*cac*). Utilizando un modelo desenvolvido no grupo de investigación [3] foi posible levar a cabo unha análise cuantitativa dos datos experimentais de agregación e determinar dita concentración crítica [4]. Ademais, estimouse o tamaño dos agregados, que están formados por unhas 50 moléculas de amiloide [4].

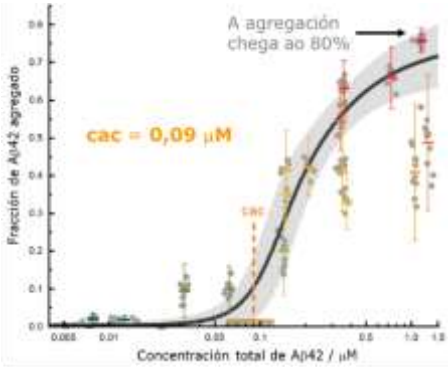


Fig.1. Formación de agregados de Aβ42 en función da concentración

Agradecementos
Este estudo foi financiado polo Ministerio de Ciencia e Innovación e pola Xunta de Galicia. S. F. agradece á Xunta de Galicia por unha bolsa predoutoral.

Referencias

[1] P. T. Lansbury, H. A. Lashuel, Nature 443 (2006) 774.
[2] G. Bitan, M. D. Kirkitadze, A. Lomakin, S. S. Vollers, , G. B. Benedek, D. B. Teplow, PNAS 100 (2003) 330.
[3] W. Al-Soufi, L. Piñeiro, M. Novo, J. Colloid Interface Sci. 370 (2012) 102.
[4] M. Novo, S. Freire, W. Al-Soufi, Scientific Reports 8:1783 (2018).

QUÍMICA TEÓRICA

molUP: How to start a computational QM/MM study of an enzyme?

Henrique S. Fernandes[1,*], Sérgio F. Sousa[1], and Nuno M.F.S.A. Cerqueira[1]
[1]UCIBIO@REQUIMTE, BioSIM, Dpt. Biomedicina, Faculdade Medicina, Universidade do Porto, Alameda Professor Hernâni Monteiro, 4200-319 Porto, Portugal
*hfernandes@med.up.pt

Nowadays, computational methods, as quantum mechanics and hybrid quantum mechanics/molecular mechanics (QM/MM), are standard approaches to study catalytic mechanisms. Together with experimental evidence, these techniques can provide an accurate and atomistic-detailed characterization of entire catalytic mechanisms.
Usually, the catalytic mechanism of an enzyme starts with the preparation of a crystallographic structure (e.g. deposited on Protein Data Bank) and consequent geometry relaxation using MM. Then, the most relevant species for the catalysis are assigned to the QM region in a hybrid QM/MM system. Afterwards, the QM/MM calculations can be performed using Gaussian [1] software, one of the most used software in the field. Besides this workflow is quite standard, the preparation of input files and subsequent analysis of outputs are often difficult tasks. Therefore, we developed molUP [2] plugin for VMD [3], which is an open-source plugin that covers the entire workflow from preparing input files to analyze results.
molUP provides a user-friendly GUI that helps users to load an AMBER minimization or Molecular Dynamics (MD) simulation and prepare the first Gaussian input file. During the preparation process, users can interactively choose the atoms that should be included in the QM region; freeze the position of certain atoms; adjust atomic charges; modify bond lengths, angle amplitudes, and dihedrals torsions; add or remove atoms/molecules; assign MM parameters; and provide input keywords for the Gaussian calculation. Once the input file is saved, it is ready to be launched using Gaussian software. After the end of the calculation, the resulting output file can be loaded using molUP. At this stage, molUP includes a set of tools for analysis and preparation of new input files for subsequent calculation. Along with the structural inspection allowed by the VMD, molUP shows energy profiles, representation and animation of vibrational frequencies, and thermodynamics results.
molUP intends to improve the entire process associated with the study of catalytic mechanisms using Gaussian software. Thus, the complete workflow is lightened, ensuring better tools, fewer issues, and more time for the computational chemist to devote to chemical reasoning.
molUP is available for Linux, macOS, and Windows at **biosim.pt/molup**

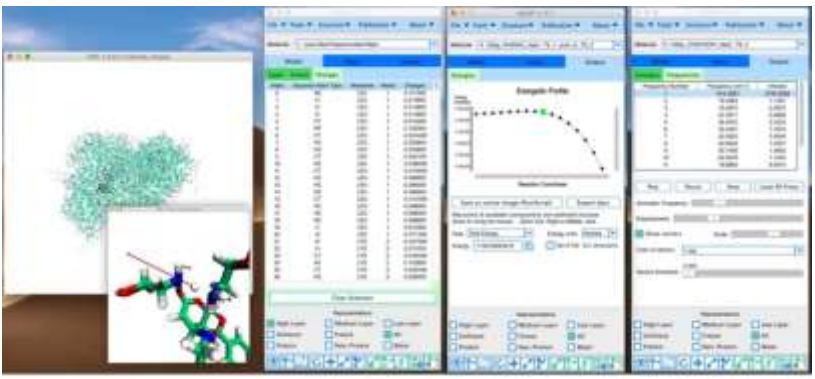


Fig.1. Screenshots of molUP plugin for VMD.

Agradecimientos
Fundação para a Ciências e Tecnologia (SFRH/BD/115396/2016, IF/01310/2013, IF/00052/2014, UID/Multi/04378/2019, PTDC/QUI-QFI/31689/2017).

Referencias
[1] M.J. Frisch, *et al.*, Gaussian 09, Gaussian, Inc. (2009)
[2] H.S. Fernandes, M.J. Ramos, N.M.F.S.A. Cerqueira, J Comput Chem, 39 (2018) 19.
[3] W. Humprey, A. Dalke, K. Schulten, J Mol Graph, 14 (1996) 1.

Using DFT and Semi-Empirical Methods as Alternative to QM/MM Approach to Study Biological Systems: Interaction of phenanthroline derivatives with duplex DNA and G-quadruplexes

Adrià Gil[1,2*], Ángel Sánchez-González[1], Iker Ortiz de Luzuriaga[2,3], Sawssen Elleuchi[4], Khaled Jarraya[4], Xabier Lopez[3,5], Maria José Calhorda[1]

[1]BioISI – Biosystems and Integrative Sciences Institute, DQB, Faculdade de Ciências, Universidade de Lisboa, Campo Grande 1749-016, Lisboa, Portugal

[2]CIC Nanogune, Tolosa Hiribidea 76, 20018, Donostia – San Sebastian, Basque Country, Spain

[3]Universidad del País Vasco / Euskal – Herriko Unibertsitatea, Facultad de Ciencias Químicas, Donostia – San Sebastián, Basque Country, Spain

[4]University of Sfax, Laboratory of Inorganic Chemistry, Sfax, Tunisia

[5]DIPC – Donostia International Physics Center, Computational Chemistry and Physical Chemistry, Donostia – San Sebastián, Basque Country, Spain

*agmestres@fc.ul.pt; a.gil@nanogune.eu

DFT and semi-empirical methods were used to study the interaction of two isomers of the [Mo(η^3-C_3H_5)Br(CO)$_2$(phen)] metal complex with DNA to gain isight on the comprehension and rationalization of its experimentally observed cytotoxicity.[1] Regular duplex chains of DNA and G-quadruplexes were considered to analyze several modes of interaction for the [Mo(η^3-C_3H_5)Br(CO)$_2$(phen)] metal complex. From a methodological point of view, the DFT treatment of the whole systems, ~500 atoms for the regular duplex DNA and ~1000 atoms for the G-quadruplex, including van der Waals contributions at the LMKLL/DP2P level with the SIESTA software [2] gives excellent results at a reasonable computing time. PM6-DH2 [3],[4] and PM7 [5] semi-empirical methods including also dispersión perform quite well for the geometries but the energetics of the system are not correctly described. From a chemical point of view the [Mo(η^3-C_3H_5)Br(CO)$_2$(phen)] metal complex prefers the intercalation rather than the groove binding in the case of the regular DNA duplex, whereas for the G-quadruplex a system in which the [Mo(η^3-C_3H_5)Br(CO)$_2$(phen)] is totally inside the G-quadruplex is the most stable. Energy Decomposition Analysis and topological studies were also carried out to know the nature of the interaction and our results confirm the importance of the role of weak interactions. The cytotoxicity of [Mo(η^3-C_3H_5)Br(CO)$_2$(phen)] seem to be related to a subtle balance between the stabilizing weak interactions and the destabilizing steric contribution. The entropic factor associated to the solvation effects results also of great importance.

Acknowledgements

We thank the Fundação para a Ciência e Tecnología for financial support by means of the project PTDC/QUI-QFI/29236/2017. A. G. is thankful to Diputación de Gipuzkoa for current funding in the frame of Gipuzkoa Fellows program.

References

[1] D. Bandarra, M. Lopes, T. Lopes, J. Almeida, M. S. Saraiva, M. V. Días, C. D. Nunes, V. Félix, P. Brandão, P. D. Vaz, M. Meireles, M. J. Calhorda, J. Inorg. Biochem., 104 (2010) 1171.

[2] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, J. Phys. Condens. Matter., 14 (2002) 2745.

[3] J. Rezác, J. Fanfrlik, D. Salahub, P. Hobza, J. Chem. Theory Comput., 5 (2009) 1749.

[4] M. Korth, M. Pitonák, J. Rezác, P. Hobza, J. Chem. Theory Comput., 6 (2010) 344.

[5] J. Stewart, J. Mol. Model., 19 (2013) 1.

Application of QM/MM Methods in the study of the reactivity of the enzyme Tryptophan Synthase

Carla S. Silva Teixeira[1,*], **Sérgio F. Sousa**[1], **Nuno M. F. S. A. Cerqueira**[1]
[1]UCIBIO@REQUIMTE, BioSIM, Departamento de Biomedicina, Faculdade de Medicina da Universidade do Porto, Alameda Professor Hernâni Monteiro, 4200-319, Porto, Portugal
*cteixeira@med.up.pt

Tryptophan Synthase (TSase) is an enzyme that has been pointed as emergent therapeutic target for the treatment of tuberculosis. The interest in TSase has been driven by the fact that it is not expressed in mammals but, has a vital importance for bacteria survival. This is the case of *M. tuberculosis*, where it catalyses the last two steps in the tryptophan biosynthetic pathway. Several experimental studies have proved its therapeutical value [1] and, recently, several inhibitors of TSase have been developed, with promising results. Inspite of all the interest devoted to it, the exact catalytic mechanism of this enzyme has remained unexplained at the atomic level. The fact that TSase is a multifunctional enzyme, with two dimers (α and β), each one with two independent active sites, interconnected by a 25 Å tunnel, has made it a challenging enzyme, from the catalytic point of view.
The α-active site of TSase catalyzes the reversible formation of glyceraldehyde-3-phosphate (G3P) and indole from indole 3-glycerolphosphate (IGP). The β-active site then catalyzes the condensation of indole and serine (Ser) to tryptophan (Trp) in a pyridoxal phosphate (PLP) dependent reaction.

Quantum mechanics/molecular mechanics (QM/MM) calculations were used to analyze and explain the two reactions catalyzed by this enzyme.

Globally, the obtained results provide an atomistic description of all the reactions, including the transition state structures and the free energetic profile of the full catalytic process [2]. The results agree very well with the available experimental data [3,4] and this knowledge can now be used to develop new specific inhibitors against tuberculosis.

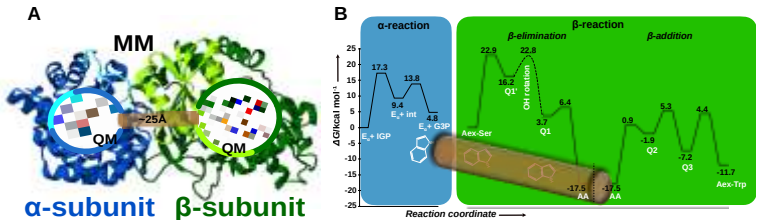


Fig.1. A) New cartoon representation of the TSase model. The α-monomer is represented in blue and the β-monomer in green. Both substrates (IGP in α-active site and PLP in β-active site) are represented in CPK. The atoms represented in licorice and CPK were considered in the QM layer of the QM/MM model. B) Energy profile of the reactions analyzed in the α and β-active sites of TSase

Agradecimientos
Foundation for Science and Technology (FCT) through the PhD grant number SFRH / BD / 114886/2016, the project PTDC/QUI-QFI/31689/2017, IF /01310/2013 and IF/00052/2014, national funds and FEDER co-founding under the partnership agreement with PT2020. This work was also supported by the Applied Molecular Biosciences Unit- UCIBIO which is financed by national funds from FCT/MCTES (UID/Multi/04378/2019).

Referencias
[1] Zhang, Y. J.; Reddy, M. C.; Ioerger, T. R.; Rothchild, A. C.; Dartois, V.; Schuster, B. M.; Trauner, A.; Wallis, D.; Galaviz, S.; Huttenhower, C.; Sacchettini, J. C.; Behar, S. M.; Rubin, E. J., Cell, 155 (2013) 1296-308.
[2] Teixeira. C. S S.; Ramos, M. J.; Sousa, S. F., Cerqueira, N. M. F. S .A., ChemCatChem, (2019) Accepted Author Manuscript.
[3] Ahmed, S. A.; Hyde, C. C.; Thomas, G.; Miles, E. W., Biochemistry, 26 (1987) 5492-8.
[4] Pioselli, B.; Bettati, S.; Mozzarelli, A., FEBS letter, 579 (2005) 2197-202.

Estimación de datos termodinámicos en dímeros de lignina mediante química computacional

Rodríguez-Olalde Nancy Eloísa[1,*], Navarro-Santos Pedro[2], López-Albarrán Pablo[3]

[1,3]Facultad de Ingeniería en Tecnología de la Madera, Universidad Michoacana de San Nicolás de Hidalgo, Edificio D, Francisco J. Múgica, 58040 Morelia, Michoacán, México.
[2]Instituto de Investigaciones Químico Biológicas, Universidad Michoacana de San Nicolás de Hidalgo, Edificio B-1, Francisco J. Múgica, 58040 Morelia, Michoacán, México.
*nrodriguez@umich.mx

La lignina es uno de los principales componentes de la biomasa y representa de un 16 a 33 % de la omposición total [1]. Es un polímero con estructura compleja que se forma a partir de los alcoholes *p*-coumarílico, coniferílico y siringílico los cuales dan origen a los monómeros identificados comounidades H, G y S respectivamente cuya abundancia depende del origen, en maderas suaves launidad G representa del 90 al 95 % y el resto de unidad S, en maderas duras las unidades G y Sestán presentes en igual cantidad [2]. Mediante oxidación enzimática las unidades formadoras se transforman en radicales libre modo quinona que llevan a cabo el proceso de polimerización, uniéndose principalmente mediante los enlaces b-O-4, a-O-4, b-5, 4-O-5, 5-5, b-1 y b-b [3]. La lignina puede ser aislada de la biomasa mediante procesos que hidrolizan de forma selectiva los polisacáridos y dejan la lignina como residuo sólido junto con algunos carbohidratos o, puede aislarse mediante procesos que la degradan a fragmentos solubles a determinados pH para después separarla mediante precipitación. Dependiendo del proceso de aislamiento, la estructura nativa de la lignina se modifica obteniendo una mezcla de fragmentos con distintos grados de polimerización y propiedades significativamente distintas [4]. El potencial de transformación de la lignina depolimerizada es muy amplio: producción de calor mediante su combustión, obtención de metanol, etanol, propanol, butanol, dimetil éter, fibras de carbón, compuestos aromáticos, resinas, adhesivos, aditivos para concreto entre otros [5]. Debido a la variabilidad estructural en la lignina depolimerizada y con el fin de evaluar las posibles rutas de transformación, es de gran utilidad la caracterización. En el presente trabajo mediante química computacional, se calculan los datos termodinámicos energía libre de Gibbs estándar (D$G°$), entalpía de reacción estándar (D$H$$%&'°), entropía de reacción estándar (D$S$$%&'°) y capacidad calorífica molar (*Cmp)* de lignina de madera suave depolimerizada considerando como compuesto modelo dímeros formados por unidades guayacil-guayacil (G-G) unidos mediante los enlaces b-O-4, a-O-4, b-5, 4-O-5, 5-5, b-1 y b-b considerando únicamente la ruta química para su formación. Para cada enlace se realiza una búsqueda conformacional, se optimizan las estructuras más estables utilizando B3LYP/6-311+g(d,p) y para la evaluación de los datos termodinámicos se utiliza Thermo.pl. De acuerdo a los resultados la reacción con mayor espontaneidad es la formación del enlace b-b, para todos los enlaces la espontaneidad se favorece a temperaturas bajas ya que todas las reacciones son exotérmicas y presentan D$S$$%&'° < 0. La capacidad calorífica molar (*Cmp)* a 298 K tiene valores de 378 a 446 *J/mol K*, experimentalmente se reportan valores de 242 y 289 *J/mol K* para ligninas con peso molecular menor al peso de los dímeros estudiados [6]. Los datos obtenidos son útiles para realizar análisis termodinámicos y evaluar procesos de transformación, software como ASPEN pueden alimentarse de estos datos y analizar moléculas de complejidad mayor como la lignina.

Agradecimientos
Los autores agradecen el apoyo del Programa para el Desarrollo del Personal Docente (PRODEP) mediante el proyecto de incorporación nuevo PTC-241 y a la Coordinación de la Investigación Científica de la UMSNH mediante el proyecto CIC-3757967.

Referencias

[1] Wood, Chemistry, Ultrastructure, Reactions, Fengel, D., Wegener, G., Ramegen, Verlag Kessel, 2003.
[2] Lignin and Lignans Advances in Chemistry, Heitner, C., Dimmel, D. R., Schmidt, J. A. (First Edition), Boca Ratón, CRC Press, 2010.
[3] Chakar, F. S., Ragauskas, A. J. Industrial Crops and Products, 20 (2004) 131.
[4] Pooya A., Inderwildi, O. R., Farnood, R., King, D. A. Renewable and Sustainable Energy Reviews, 21 (2013) 506.
[5] Top Value Added Chemicals from Biomass Volume II Results of Screening for Potential Candidaters from Biorefinery Lignin. Holladay, J., Bozell, J., White, J., & Johnson, D. Oak Ridge TN Pacific Northwest National Laboratory (2007).
[6] Voitkevich, O. V., Kabo, J. G., Blokhin, A. V., Paulechka, Y. U. Journal of chemical engineering data, 57 (2012) 1903.

COMUNICACIONES POSTER

QUÍMICA ALIMENTARIA

Chemical characterization and antioxidant activity of sweet cherry by-products: stems and pits

Sílvia Afonso[1, *], Alfredo Aires[1], Ivo Oliveira[1], Anne S. Meyer[2], Berta Gonçalves[1]
[1]CITAB-UTAD, Quinta de Prados, 5000-801, Vila Real, Portugal
[2]Technical University of Denmark, DTU Building 221, DK-2800 Kgs. Lyngby, Denmark
*safonso@utad.pt

Sweet cherry is one of the most appreciated fruit by consumers in the temperate areas of Europe [1,2], due to its organoleptic characteristics, but also by the consumers' awareness of their health benefits [3]. Worldwide sweet cherry production has been increasing in the last years (2008–2017, latest FAO available data) from 1.85 to 2.44 million tons, with Turkey, USA, Iran as the main producers accounting for about 50% of the total world production, and USA, Turkey and Chile the main exporters [4]. Portugal is also well-known producer of sweet cherries, with latest data referring 19563 tons of cherries annually [4], providing some of the first cherries of Europe.

Agricultural production and food industry residues and wastes are a considerable percentage (over 30%) of worldwide agricultural productivity and include the lignocellulosic materials, fruit and vegetable wastes [5]. The production and processing of sweet cherry generates quantities of by-products, namely the stems and pits [6] that, as for many other agricultural wastes and by-products, are gaining new interest, in order to find ways to achieve their valorisation [7]. Although cherry stems have been known in traditional medicine, with several properties, namely as sedative, diuretic and anti-inflammatory [8], their study, as well as the characterization of pits has only recently received attention. Several hydroxycinnamic acids, namely *ρ*-coumaric, ferulic, caffeic, chlorogenic and neochlorogenic acid were reported in *P. avium* stems [8, 9] and cherry pits contain phenolics including anthocyanins [10].

Hence, the objective of this work is to provide a preliminary study on the chemical composition and antioxidant activity of sweet cherry stems and pits. For this, four different cultivars (*Burlat*, *Early Bigi*, *Lapins* and *Van*), grown in an orchard located in Resende – Portugal, were studied. The content in total phenolics and flavonoids, ortho-diphenols, saponins and antioxidant activity (DPPH, FRAP and ß carotene) was accessed. In all the studied parameters, stems presented higher content of compounds (with some exceptions for saponins) when compared to pits. Stems showed an increased activity in DPPH and FRAP assays, while ß carotene results are similar for stems and pits, the exception being ß carotene. Comparing cultivars, and for both stems and pits, significant differences were observed in all parameters. In stems, higher overall results were recorded for cv *Lapins* in DPPH and FRAP, while in pits higher values were observed in cv *Early Bigi* for both methods. These results are part of an ongoing comprehensive study regarding the composition and bioactivity of stems and pits from sweet cherry, in order to achieve the valorisation of these by-products.

Agradecimientos
Sílvia Afonso is grateful to FCT, MCTES and FSE for the PhD Fellowship SFRH/BD/139922/2018. This work is supported by National Funds by FCT - Portuguese Foundation for Science and Technology, under the project UID/AGR/04033/2019.

Referencias

[1] A. Di Matteo, R. Russo, G. Graziani, A. Ritieni, C. Di Vaio, *Journal of the Science of Food and Agriculture*, m97 (2017) 2782.
[2] V. Usenik, J. Fabčič, F. Štampar, *Food Chemistry*, *107 (2008)* 185.
[3] F. Blando, B. Oomah, *Trends in Food Science & Technology, 86 (2019) 517.*
[4] FAOSTAT, 2017. F.A.O. FAOSTAT. Food and Agriculture Organization of the United Nations (2017). http://www.fao.org/faostat/en/#rankings/countries_by_commodity
[5] J. Ugwuanyi, B. McNeil, L. Harvey, in Biotechnology for Agro-Industrial Residues Utilisation, P.S. Nigam, A. Pandey (Eds). Springer, Dordrecht. 2009, 77.
[6] J. Švarc-Gajić, V. Cerdà, S. Clavijo, R. Suárez, P. Mašković, A. Cvetanović, C. Delerue-Matos, V. Novakov, *Journal of Chemical Technology & Biotechnology*, *93* (2018), 1627.
[7] F. Jesus, A. Gonçalves, G. Alves, L. Silva, *Food Research International*, *116 (2019)* 600.
[8] A. Aires, C. Dias, R. Carvalho, M. Saavedra, M, Acta Biochimica Polonica, 64 (2017) 265.
[9] C. Bastos, L. Barros, M. Dueñas, R. Calhelha, M. Queiroz, C. Santos-Buelga, I. Ferreira, *Food Chemistry*, 173 (2015) 1045.
[10] A. Chaovanalikit, R. Wrolstad, *Journal of Food Science*, 69 (2004) FCT67.

Atividade anti-inflamatória e imunomoduladora de extratos de *Lentinula edodes*

Diana Almeida[1,2*], Guilhermina Marques[3,4], Fernando M. Nunes[1,5], Amélia M. Silva[2,4]

[1]Departamento de Química, ECVA, Universidade de Trás-os-Montes e Alto Douro (UTAD), Vila Real, Portugal
[2]Departamento de Biologia e Ambiente, ECVA, (UTAD), Vila Real, Portugal
[3] Departamento de Agronomia, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal
[4]CITAB, Centro Investigação em Tecnologias Agro-Ambientais e Biológicas, UTAD, Vila Real, Portugal
[5]CQ-VR Centro de Química – Vila Real, UTAD, Vila Real, Portugal
**dianapfalmeida95@gmail.com*

Durante séculos os cogumelos foram consumidos por populações de muitas comunidades devido às suas propriedades medicinais e nutricionais. Atualmente, os principais cogumelos comercializados são *Agaricus bisporus*, seguido de *Lentinula edodes* e *Pleurotus spp*. *Lentinula edodes* que também é designado por shiitake, é o segundo cogumelo mais cultivado no mundo e designado como cogumelo medicinal. Os cogumelos têm sido também usados na investigação para estudar as suas propriedades funcionais e medicinais para uso farmacêutico. Da sua composição destaca-se o facto de serem constituídos por compostos medicinais/bioativos, como polissacarídeos, terpenóides, lípidos e esteróis, que têm uma boa atividade no tratamento de vários tumores e infeções (e.g. [1]).

Neste estudo usou-se o cogumelo *Lentinula edodes* que foi liofilizado, sujeito ao método de extração com água e etanol, os extratos foram sujeitos a diálises e com posterior purificação de algumas frações recorrendo a cromatografia de troca iónica, como descrito em [1]. De maneira a obtermos extratos isentos de contaminação bacteriana, implementámos um protocolo de eliminação de endotoxinas dos extratos. O efeito destes extratos foi avaliado na proliferação celular, usando diferentes concentrações e o modelo celular de macrófagos de murganho, RAW 264.7, sendo a viabilidade celular avaliada pelo método de Alamar Blue [2]. Também foi avaliado o efeito dos extratos na atividade anti-inflamatória, usando a mesma linha celular, por quantificação do óxido nítrico (NO) libertado pelo método de Griess, tal como descrito em [3].

Verificou-se que os extratos não demonstraram ser citotóxicos a nenhuma das concentrações testadas. Mas foram encontradas diferenças significativas tanto na viabilidade celular como na atividade anti-inflamatória. Observou-se ainda um efeito imunomodulador dos extratos.

Agradecimentos: a investigação foi financiada por verbas da Fundação para a Ciência e Tecnologia (FCT), adstritas aos centros de investigação CITAB (UID/AGR/04033/2019), e CQ-VR (PEst-OE/QUI/UI0616/2014), e pelo Projeto FUNGITECH –Tecnologia e inovação na cadeia de produção do shiitake e de outros cogumelos com valor nutracêutico e medicinal, N.º 33788, financiado pelo Fundo Europeu de Desenvolvimento Regional (FEDER) através do NORTE 2020 (Programa Operacional Regional do Norte 2014/2020.

Referências:

[1] M.K. Lemieszek, F.M. Nunes, C. Cardoso, G. Marques, W. Rzeski (2018). Carbohydrate Polymers, 197; 598-607.
[2] T. Andreani, C.P. Kiill, A.L. de Souza, J.F. Fangueiro, L. Fernandes, S. Doktorovova, D.L. Santos, M.L. Garcia, M.P. Gremião, E.B. Souto, A.M. Silva (2014) Colloids Surf., B, 123, 916–923.
[3] C. Martins-Gomes, M. Taghouti, J. Schäfer, M. Bunzel, A.M. Silva, F.M. Nunes, F. M. (2018). Journal of Functional Foods, 43, 154–164.

Las algas como nueva materia prima para la obtención de pigmentos

A.G Pereira [1,2], A. Carreira-Casais[2,3], P.G. Oliveira [1], C. Jiménez López [1,2], C.S.P.L. Lopes [1], Lillian Barros [2], M.A. Prieto [1], Isabel C.F.R. Ferreira [2], J. Simal-Gandara [1*]

[1] Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain.
[2] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3] Departamento de Química-Física, Centro de Investigaciones Biomédicas de Galicia (CINBIO), Universidade de Vigo, E-36310, Vigo, España

**e-mail del autor de contacto: jsimal@uvigo.es*

Debido a la enorme controversia a la que están sometidos los aditivos artificiales por sus efectos adversos, en la actualidad la gente demanda productos más naturales y más sanos. Es por ello que encontrar nuevos pigmentos naturales es de gran interés debido al uso masivo de este tipo de aditivos en la industria alimentaria [1].

Una posible solución es extraer pigmentos a partir de algas debido a la gran variedad de pigmentos que presentan, entre los que cabe destacar los carotenoides, la clorofila y las ficobilinas. La cantidad de cada uno de estos pigmentos determinará el color del alga en cuestión, permitiendo diferenciarlas en algas verdes, pardas y rojas, estudiándose los tres tipos de algas en este estudio. La concentración de estos compuestos es una de las razones por las cuales se ha promovido su cultivo a gran escala [2].

Para llevar a cabo la extracción se empleó un método de extracción sólido-líquido con 5 solventes distintos, los cuales se caracterizan por tener distinta polaridad. Estos solventes fueron cloroformo, etanol, acetato de etilo, acetona, hexano y agua. El proceso se llevó a cabo durante 24 h a 50ºC con dos lavados, uno a las 16 h y otro a las 20 h.

El análisis obtenido proporciona datos importantes que permiten la comparación entre diferentes solventes de extracción, en términos de eficiencia, y la consecuente toma de decisiones relacionadas. A nivel industrial, estas metodologías reducen los costos relacionados con la energía, el consumo de solventes, la inversión en equipos, etc. y es que lograr las condiciones óptimas y maximizar las respuestas es un paso importante para guiar la elección de un proceso adecuado y sostenible.

En conclusión, este estudio contribuye a la valorización de las especies de algas que son comunes en la región noroeste de España mediante la obtención de colorantes como alternativa a los más comúnmente utilizados, los cuales son conocidos por sus efectos adversos. Además, este tipo de pigmentos tienen otra serie de ventajas, como que provienen de recursos naturales y no requieren grandes extensiones para su cultivo.

Agradecimientos
A AlgaMar por el material de algas proporcionado (www.algamar.com). A MICINN por el apoyo financiero para el investigador Ramón & Cajal de M.A. Prieto. A la Xunta de Galicia y a la Universidad de Vigo por el apoyo financiero a los investigadores predoctorales A.G. Pereira y P.G. Oliveira. A la Xunta de Galicia por el "Programa de axudas á etapa predoutoral de la Xunta de Galicia" para los investigadores predoctorales de A.G. Pereira y Paula G. Oliveira. A Xunta de Galicia por el apoyo financiero de Axudas Conecta Peme del Proyecto IN852A 2018/58 NeuroFood. Los autores también agradecen a Interreg España- Portugal por el apoyo financiero a través del proyecto 0377_Iberphenol_6_E.

Referencias

[1] S.M. Zakaria, S.M.M. Kamal, Subcritical Water Extraction of Bioactive Compounds from Plants and Algae: Applications in Pharmaceutical and Food Ingredients, Food Eng. Rev. 8 (2016) 23–34. doi:10.1007/s12393-015-9119-x.
[2] S. Kraan, Pigments and minor compounds in algae, in: Funct. Ingredients from Algae Foods utraceuticals, 2013. doi:10.1533/9780857098689.1.205

Efeito do silicato de cálcio na composição química de *Pleurotus ostreatus* var. Florida

Rossana V. C. Cardoso[1,2], Ângela Fernandes[1], Márcio Carocho[1], Diego Cunha Zied[3], João C.M. Barreira[1], Ana M. Gonzaléz-Paramás[2], Lillian Barros[1], Isabel C.F.R. Ferreira[1,*]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2] Grupo de Investigación en Polifenoles (GIP), Unidad de Nutrición y Bromatología, Facultad de Farmacia, Universidad de Salamanca, Campus Miguel de Unamuno, E-37007 Salamanca, España
[3] Faculdade de Ciências Agrárias e Tecnológicas (FCAT), Universidade Estadual Paulista, Campus Dracena, 17900-000 São Paulo, Brazil
*iferreira@ipb.pt

Os cogumelos são um alimento muito apreciado desde tempos imemoriais pelo seu sabor e elevado valor nutritivo. Uma das espécies que tem suscitado maior interesse nos últimos anos é *Pleurotus ostreatus*, devido à sua facilidade de cultivo, potencial económico e qualidade nutricional, bem como pelas suas propriedades terapêuticas e biológicas [1]. O silício (Si) desempenha um papel importante na nutrição mineral dos cogumelos e plantas; é utilizado com o intuito de aumentar a produtividade uma vez que aumenta a disponibilidade de nutrientes, favorece o crescimento da biomassa, e confere resistência ao stresse biótico e abiótico [2]. São vários os estudos que descrevem a influência da suplementação de cálcio e silício na qualidade do substrato para o cultivo do *P. ostreatus* [3].
Neste estudo, amostras de *Pleurotus ostreatus* var. Florida foram suplementadas com silicato de cálcio (0,5, 1, 2 e 4%) com o intuito de verificar o efeito na composição química. Os açúcares livres e tocoferóis foram analisados por cromatografia líquida de alta eficiência acoplada a um detetor de índice de refração e fluorescência, respetivamente; e os ácidos gordos foram determinados por cromatografia gasosa acoplada a um detetor de ionização em chama [4].
Foram identificados três açúcares livres, sendo o manitol o maioritário. Verificou-se um aumento nos teores de açúcares totais com a suplementação de 2% de silicato de cálcio. Nos tocoferóis foram identificados 3 isoformas (α, β e γ-tocoferol), e verificou-se um aumento de quase 30x do teor de γ-tocoferol nas amostras suplementadas com 2% de silicato de cálcio (143 µg/100 g massa seca) comparativamente com o controlo (5 µg/100 g ms). Relativamente aos ácidos gordos, não se obtiveram diferenças acentuadas em comparação com o controlo.
Verificou-se que o silicato de cálcio contribuiu para uma melhoria do perfil químico, nos parâmetros avaliados, de *P. ostreatus*. Desta forma, esta substância poderá ser utilizada para suplementar o substrato de crescimento dos cogumelos, obtendo compostos essenciais para a dieta.

Agradecimentos
Os autores agradecem à Fundação para a Ciência e Tecnologia (FCT, Portugal) e à FEDER, no âmbito do Programa PT2020, pelo apoio financeiro ao CIMO (UID/AGR/00690/2019), Concessão da bolsa de doutoramento de R.V.C. Cardoso (SFRH /BD/137436/2018). L. Barros, J.C.M. Barreira, A. Fernandes e M. Carocho também agradecem o financiamento nacional da FCT - Fundação para a Ciência e Tecnologia, PI, através do contrato de programa institucional de emprego científico para seus contratos. Este trabalho é financiado pelos Fundos Europeus Estruturais e de Investimento (FEEI) por meio do Programa Operacional Regional Norte 2020, no âmbito do Projeto Mobilizador ValorNatural®; e à FEEI através do Programa de Desenvolvimento Rural (PDR2020).

Referências
[1] B. B. Teimoori, H. R. Pourianfar, M. J. Moeini, J. Janpoor, International Journal of Advanced Research, 2 (2014) 915–921.
[2] C. A. de Souza, Tese mestrado, Universidade Federal de Goiás, Goiânia-Goiás, Brasil, (2014).
[3] T. Thongsook, T. Kongbangkerd, Food Science and Technology International, 17 (2011) 351–365.
[4] R.V.C. Cardoso, Â. Fernandes, J.C.M. Barreira, S.C. Verde, A. L. Antonio, A.M. Gonzaléz-Paramás, L. Barros, I.C.F.R. Ferreira, Food Chemistry, 278 (2019) 760-766.

Caracterização e quantificação de açúcares presentes na abóbora de chila através de cromatografia iónica

Tiago E. Coutinho[1,2*], Amélia M. Silva[2,3] Fernando M. Nunes[1,4]

[1]CQ-VR, Centro de Química de Vila Real, UTAD, Vila Real, Portugal
[2]Departamento de Biologia e Ambiente, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal
[3]CITAB, Centro Investigação em Tecnologias Agro-Ambientais e Biológicas, UTAD, Vila Real, Portugal

[4]Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Vila Real, Portugal
**tecoutinho@utad.pt*

Os alimentos são fonte de nutrientes essenciais para o funcionamento do organismo, e são fontes de moléculas que influenciam o metabolismo celular, designadas de componentes bioativas. No que diz respeito a subprodutos, cerca de 1/3 do peso das frutas e dos legumes na forma de casca, sementes e peliculas são eliminados durante a sua preparação, criando um desperdício e por vezes também uma diminuição nutricional da fruta ou do vegetal. Hoje em dia, há várias tentativas de incluir esses subprodutos, ou compostos extraídos destes na dieta, pois estes são ricos em compostos bioativos. A *Cucurbita ficifolia* Bouché (abóbora chila) surgiu no méxico, sendo utilizada na medicina tradicional para tratar diabetes tipo 2, febre e para curar feridas, a polpa da abóbora chila é comumente utilizada na alimentação principalmente na preparação de doces cristalizados e de sobremesas.

O objetivo deste trabalho foi a identificação e quantificação dos açúcares presentes em diferentes frações (aquosa e metanólica) de extratos hidro-etanólicos da polpa e da casca da *Cucurbita ficifolia*.

Nesse sentido, a casca e a polpa de abóbora chila foram separadas, liofilizadas e trituradas. Posteriormente, foi efetuada uma extração hidro-etanólica (20:80 v/v) da polpa e da casca, estes extratos foram fracionados utilizando o método de extração em fase sólida, obtendo-se a fração aquosa e metanólica de cada extrato. Depois de liofilizadas as frações foram sujeitas a uma hidrólise ácida, sendo de seguida injetadas e analisadas por cromatografia iónica de alta eficiência com deteção de pulso amperométrico (*ICS-3000, Dionex*), para caracterização e quantificação de açúcares presentes em cada fração.

Observou-se que: i) a extração hidro-etanólica da polpa teve maior rendimento que a extração da casca, ii) as frações aquosas dos dois extratos tiveram maior rendimento que as frações metanólicas, podendo ser justificados pela natureza dos compostos presentes na abóbora chila. Na identificação e quantificação de açúcares, verificamos que as frações aquosas contêm maior quantidade de açúcares que as frações metanólicas de ambos os extratos, sendo a glucose o açúcar maioritário em todas as frações. A arabinose foi identificada somente nas frações metanólicas de ambos os extratos.

Conclui-se, portanto, que a polpa de abóbora chila contém maior quantidade de açúcares, verificando-se diferenças significativas no teor em açúcares nas diferentes partes da abóbora e nos diferentes tipos de fracionamentos de extratos.

Agradecimentos: esta investigação foi financiada por verbas da Fundação para a Ciência e Tecnologia (FCT), adstritas aos centros de investigação CITAB (UID/AGR/04033/2019) e CQ-VR (PEst-OE/QUI/UI0616/2014),

Soluções corantes baseadas em emulsões duplas incorporando extrato de *Sambucus nigra* L.: Desenvolvimento e teste em diferentes matrizes alimentares

Teixeira, L.G.[1,2,3], Rezende, S.C.[1,2], Fernandes, I.P.[1,2], Reis F.S.[1], Barros L.[1], Barreira J.[1] Leimann, F.V.[3], Ferreira, I.C.F.R.[1], Barreiro, M.F. [1,2,*]

[1]Centro de Investigação de Montanha (CIMO) e [2]Laboratório de Processos de Separação e Reação – Laboratório de Catálise e Materiais (LSRE-LCM), Instituto Politécnico de Bragança, Portugal

[3]Programa de Pós-Graduação em Tecnologia de Alimentos (PPGTA), Universidade Tecnológica Federal do Paraná-Campus Campo Mourão, via Rosalina Maria dos Santos, 1233, CEP 87301-899, Campo Mourão, Paraná, Brasil.

barreiro@ipb.pt

As antocianinas são pigmentos vegetais hidrossolúveis, pertencentes à classe dos flavonoides apresentando propriedades edulcorantes e bioativas. São caracterizadas por conferirem cor na gama do vermelho a violeta. No entanto, para aplicações industriais, estes pigmentos apresentam problemas de variabilidade da cor com o pH, temperatura, presença de humidade e luminosidade [1]. Neste contexto, estudaram-se extratos obtidos a partir de bagas de *Sambucus nigra* L., reconhecidas pelo seu elevado teor em antocianinas, como soluções corantes para a área alimentar. Para o efeito, procedeu-se à estabilização do extrato através da preparação de emulsões duplas (água/óleo/água, A/O/A). A obtenção do extrato corante foi efetuada por trituração das bagas, seguindo-se da secagem do sumo obtido por *spray-drying* para obtenção da correspondente forma em pó. A preparação das emulsões duplas foi realizada adaptando a metodologia descrita por Paula et al. [2], podendo ser descrita como dividida nas duas etapas seguintes: i) preparação da emulsão primária, por emulsificação da fase aquosa (55 mg/L do extrato e 5% de polirricinoleato de poliglicerol (PGPR)) em óleo de milho (razão A/O 0,4) utilizando uma velocidade de homogeneização de 20000 rpm durante 5 min; e ii) preparação da emulsão dupla por dispersão da emulsão primária numa fase aquosa secundária contendo Tween 80 e goma arábica, em diferentes proporções. A emulsão A/O/A final foi preparada utilizando diferentes proporções de emulsão primária/fase aquosa secundária recorrendo a um homogeneizador a 6000 rpm durante 2 min. As emulsões produzidas foram analisadas por microscopia ótica (MO) para avaliar o tamanho e morfologia das gotículas. Adicionalmente, procedeu-se ao teste das emulsões como agentes corantes estáveis ao pH, usando para o efeito matrizes alimentares com diferentes valores de pH, nomeadamente iogurte líquido natural (pH 4,65), bebida biológica de arroz (pH 6,01), leite (pH 6,47) e bebida biológica soja (pH 7,92), tendo-se feito a comparação com o uso direto do extrato de *S. nigra* **(Figura 1)**. Posteriormente procedeu-se à avaliação da cor de acordo com os parâmetros L*, a* e b*. Os resultados obtidos apontam para uma melhor estabilidade da cor e menor variabilidade desta com o pH. Em síntese, a estratégia testada revelou-se promissora tendo em vista o desenvolvimento de formulações corantes, para a área alimentar, baseadas em corantes naturais ricos em antocianinas. Esta estratégia poderá ser aplicada a outros setores industriais.

Figura 1. Aplicação direta do extrato de *S. nigra* e comparação com o uso das emulsões duplas nas diferentes matrizes alimentares testadas.

Agradecimentos

Laboratório Associado LSRE-LCM (UID/EQU/50020/2019) financiado por fundos nacionais através da FCT/MCTES (PIDDAC) e FCT e CIMO (UID/AGR/00690/2019) através do FEDER no âmbito do Programa PT2020. Projeto Valor Natural (Norte-01-0247-FEDER024479) através do FEDER no âmbito do Programa PT2020. Ao financiamento nacional da FCT, P.I., através do contrato de programa institucional de emprego científico de L. Barros e I.P. Fernandes.

Referências

[1] Smeriglio A.; Barreca D.; Bellocco E.; Trombetta D. *Phytotherapy Research*. **2016**, *30*, 1265-1285.

[2] Paula D A. *et al*. *International Journal of Biological Macromolecules*. **2018**, 117, 665- 672.

Nova estratégia de coloração de produtos lácteos usando extratos antociânicos de flores comestíveis

Tânia C.S.P. Pires[1,2], Maria Inês Dias[1], Lillian Barros[1], João C.M. Barreira[1], Celestino Santos-Buelga[2], Isabel C.F.R. Ferreira[1,*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]Grupo de Investigación en Polifenoles (GIP-USAL), Facultad de Farmacia, Universidad de Salamanca, Campus Miguel de Unamuno s/n, 37007 Salamanca, España.
*iferreira@ipb.pt

Dos vários produtos lácteos fermentados, o iogurte é certamente um dos mais populares, sendo amplamente consumido em todo o mundo devido às suas propriedades organoléticas e nutricionais [1]. Alguns iogurtes disponíveis no mercado são preparados utilizando corantes artificiais. No entanto, as recentes preocupações com a segurança de alguns desses corantes artificiais incentivaram o desenvolvimento e a aplicação de alternativas naturais. As flores comestíveis ricas em pigmentos naturais surgem assim como uma das respostas para o desenvolvimento de novas estratégias de coloração de produtos alimentares [2]. O objetivo do presente trabalho centra-se na utilização de extratos ricos em antocianinas de pétalas comestíveis de *Rosa damascena* "Alexandria" com *R. gallica* "French" enxertada em *R. canina*, como uma alternativa ao E163 (extrato comercial de antocianinas) para a coloração de produtos lácteos (especificamente, iogurtes). O extrato aquoso antociânico de pétalas de rosa foi caracterizado quanto ao seu perfil fenólico de antocianinas por HPLC-DAD-ESI/MS. Posteriormente, foi feita a sua incorporação em iogurtes naturais e avaliada a estabilidade cromática durante dois períodos distintos (dia de preparação e após 7 dias de armazenamento a 4 ^{o}C). Foi ainda avaliada a composição nutricional (métodos AOAC), em açúcares livres (HPLC-RI) e em ácidos gordos (GC-FID) nos produtos desenvolvidos. Foram preparadas duas amostras controlo: i) sem adição de agente corante e ii) com adição do corante comercial - E163.

Relativamente ao perfil de antocianinas do extrato aquoso de rosa, foram identificados dois compostos antociânicos, sendo a cianidina-3,5-*O*-diglúcosido a molécula maioritária (13,19 ± 0,01 µg/g extrato), representado 98% da composição fenólica. A aditivação de produtos lácteos tem que ter em conta a aceitabilidade por parte dos consumidores, e por isso é altamente dependente da sua aparência e propriedades reológicas. É por isso crucial que os novos produtos desenvolvidos sejam muito semelhantes aos já existentes no mercado. Os iogurtes preparados com o extrato antociânico de pétalas de rosa revelaram uma composição nutricional, e um perfil em açúcares e ácidos gordos muito semelhantes às amostras preparadas com o corante E163 e às amostras sem aditivação ao longo dos 7 dias de armazenamento.

As pétalas de rosa apresentam-se assim como uma potencial alternativa de coloração (amarelo-laranja) para produtos lácteos sem detrimento das características mais aceitáveis por parte dos consumidores. Com a incorporação destes extratos naturais para o desenvolvimento de novos produtos alimentares de alto valor agregado, potencia-se também a funcionalização dos mesmos e por isso com efeitos benéficos para a saúde do consumidor.

Agradecimentos
FCT e FEDER sob o Programa PT2020 pelo apoio financeiro ao CIMO (UID/AGR/00690/2019), bolsa individual de doutoramento de T.C.S Pires (SFRH/BD/129551/2017) e aos contratos de M.I. Dias, L. Barros and J. Barreira (através de fundos nacionais da FCT, no âmbito da celebração do contrato-programa de emprego científico institucional). Ao FEDER-Interreg España-Portugal pelo financiamento ao projeto 0377_Iberphenol_6_E e TRANSCoLAB 0612_TRANS_CO_LAB_2_P; FEDER através do Programa Operacional Regional Norte 2020, no âmbito do Projeto NORTE-01-0145-FEDER-023289 (DeCodE) e projeto Mobilizador Norte-01-0247-FEDER-024479: ValorNatural®. Governo espanhol pelo apoio ao GIP-USAL (AGL2015-64522-C2-2-R).

Referencias
[1] Caleja, C., Barros, L., Antonio, A.L., Carocho, M., Oliveira, M.B.P.P., Ferreira, I.C.F.R. Food Chemistry, 210 (2016), 262–268.
[2] Pires, T.C.S.P.; Dias, M.I.; Barros L.; Barreira, J.C.M.; Santos-Buelga, C.; Ferreira, I.C.F.R. LWT - Food Science and Technology, 97 (2018) 668–675.

VALORIZAÇÃO DE CLADÓDIOS DE *OPUNTIA FICUS-INDICA* (L.) MILLER

L. Espírito Santo[1,2,3], M. A. Nunes[1], A. Gomes[1], A. S. G. Costa[1], A. Rocha[1,3], M. B. P. P. Oliveira[1*]
[1]LAQV@REQUIMTE, Faculdade de Farmácia, Universidade do Porto, Porto, Portugal
[2]Faculdade de Ciências, Universidade do Porto, Porto, Portugal
[3]Faculdade de Ciências da Nutrição e Alimentação, Universidade do Porto, Porto, Portugal
* beatoliv@ff.up.pt

Opuntia ficus-indica (L.) Miller, vulgarmente conhecida em Portugal como figueira-da-índia, é um cato originário da América do Sul [1]. Desde 2008, o seu cultivo intensivo e ordenado ganhou mais expressão na produção de frutos [2]. Com o aumento desta produção, aumenta a disponibilidade de cladódios (caules), preocupação para os produtores devido ao seu potencial invasivo [3].

Os cladódios não fazem parte do padrão alimentar português, mas a sua valorização para consumo alimentar pode contribuir para a disponibilidade de alimento. Nessa perspetiva, este estudo teve como objetivo avaliar a composição nutricional e o teor de antioxidantes de quatro variedades, duas que produzem figos brancos, uma laranja e uma vermelha.

Para a caracterização nutricional recorreu-se aos métodos oficiais AOAC [4], tendo a humidade das amostras sido determinada com uma balança de infravermelhos. O teor de hidratos de carbono disponível foi calculado por diferença. Para determinar os compostos bioativos utilizaram-se diferentes solventes: água a 100%, água/etanol (50/50; v/v) e etanol a 100% e procedeu-se à avaliação do teor de fenólicos totais e a atividade antioxidante pelos métodos de inibição de DPPH$^{\bullet}$ e de FRAP.

A composição nutricional das diferentes variedades de cladódios estudados é apresentada na tabela 1. O solvente 100% água extraiu maior teor de fenólicos totais, bem como exibiu maior atividade antioxidante.

Numa perspetiva de assegurar o acesso a alimentos e promover a diversidade alimentar, este estudo, pretende promover o uso dos cladódios na alimentação da população portuguesa, tendo em consideração o seu teor em fibra.

Tabela 1. Composição nutricional de quatro variedades de cladódios

Variedades de cladódios	Humidade (%)	Gordura*	Proteína*	Cinzas*	Fibra Total*	Hidratos de carbono*
Branca do Arrepiado	8,05 ± 0,39	1,17 ± 0,03	4,90 ± 0,37	17,21 ± 0,22	40,00 ± 1,11	36,88 ± 1,51
Branca da Barquinha	8,39 ± 0,21	1,24 ± 0,02	7,62 ± 0,77	20,35 ± 0,15	26,45 ± 0,02	44,99 ± 0,28
Laranja de Olaia	7,59 ± 0,06	1,30 ± 0,01	4,14 ± 0,37	26,99 ± 0,72	35,61 ± 1,36	32,44 ± 0,65
Vermelha de Olaia	10,63 ± 0,35	1,73 ± 0,33	3,48 ± 0,36	20,70 ± 0,04	22,95 ± 0,23	51,18 ± 0,57

* Resultados apresentados em g/100g de peso seco

Agradecimentos:
Os autores agradecem o financiamento do projeto UID/QUI/50006/2019, através de fundos nacionais da FCT/MCTES (Portugal). Os autores agradecem também ao produtor Paulo Costa (Torres Novas), por gentilmente fornecer as amostras

Referências:

[1] A. M. Rodrigues, F.I.P., C. M. G. Reis and M. Blasco, *Nutritional Value of Opuntia Ficus-Indica Caldodes from Portuguese Ecotypes.* Bulgarian Journal of Agricultural Science, 22 (No 1) 2016: p. 40-45.
[2] *A Cultura da Figueira-da-índia e a Valorização Agroindustrial do Fruto*. Instituto Nacional de Investigação Agrária e Veterinária, I.P. (INIAV, I.P.) ed. 2016. 101.
[3] Shackleton, S., D. Kirby, and J. Gambiza, *Invasive plants – friends or foes? Contribution of prickly pear (Opuntia ficus-indica) to livelihoods in Makana Municipality, Eastern Cape, South Africa.* Development Southern Africa, 2011. 28(2): p. 177-193.
[4] *AOAC. Official Methods of Analysis of AOAC International, 19th Edition AOAC International 2012: Maryland, EUA.*

Propriedades bioativas de infusões potenciadas pela mistura de plantas

Cristina Caleja[1], Tiane C. Finimundy[1,2,*], Carla Pereira[1], Lillian Barros[1], Ricardo C. Calhelha[1], Marina Sokovic[3], Marija Ivanov[3], Ana Maria Carvalho[1], Eduardo Rosa[2], Isabel C.F.R. Ferreira[1]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
[2]CITAB - University of Trás-os-Montes and Alto Douro (UTAD), Department of Agronomy, Vila Real, Portugal.
[3]University of Belgrade, Department of Plant Physiology, Institute for Biological Research "Siniša Stanković", Bulevar Despota Stefana 142, 11000 Belgrade, Serbia.
**tiane@ipb.pt*

A preparação de infusões a partir de plantas aromáticas e medicinais é uma técnica utilizada desde a antiguidade [1]. As plantas podem ser utilizadas sozinhas ou misturadas para agregar valor nutricional, sabor ou potenciar alguma bioatividade [2,3]. Com este intuito, foram preparadas misturas de cinco espécies de plantas: *Erica australis* L. (EA), *Genista tridentata* L. (GT), *Melissa officinalis*, L. (MO), *Mentha spicata* L. (MS) e *Prunella vulgaris* L. (PV) em diferentes proporções (M1 – 20% PV, 40% GT e 40% MS; M2 – 30% EA, 30% PV e 40% MO; M3 – 30% PV, 35% MO e 35% MS). As misturas foram analisadas em termos de valor nutricional (açucares livres, HPLC-RI), composição fenólica (HPLC/DAD-ESI/MS) e bioatividade (propriedades antioxidantes, antimicrobianas, citotóxicas e anti-inflamatórias). A atividade antioxidante foi avaliada através da inibição da peroxidação lipídica (TBARS) e da hemólise oxidativa (OxHLIA); a atividade antimicrobiana foi testada em bactérias Gram + (*Bacillus cereus* e *Listeria monocytogenes*) e Gram - (*Escherichia coli* e *Salmonela typhimurium*) e fungos (*Aspergillus niger*, *Aspergillus versicolor*, *Penicillium funiculosum* e *Penicillium verrucosum),* usando o método da microdiluição em placa; para a avaliação da atividade citotóxica usou-se o método colorimétrico da sulforrodamina B em quatro linhas tumorais humanas (MCF-7, NCI-H460, HeLa e HepG2) e uma cultura primária de células não-tumorais de fígado de porco (PLP2); para a atividade anti-inflamatória, utilizou-se a linha de macrófagos RAW 246.7.

A mistura M1 apresentou a maior quantidade de hidratos de carbono e de frutose bem como a maior concentração de compostos fenólicos totais, com prevalência de flavonóides, principalmente derivados de quercetina. Os resultados da atividade antioxidante e antibacteriana não foram significativos, no entanto a amostra M1 apresentou uma boa atividade antifúngica contra *Penicillium funiculosum* (MFC: 0,5 mg/mL), com um valor igual ao do controlo positivo de cetoconazol (MFC: 0,5 mg/mL). A M2 apresentou a melhor atividade citotóxica, em especial para a linha celular HepG2, com um GI_{50} de 166±10 µg/mL, e uma atividade anti-inflamatória moderada (GI_{50}: 324±3 µg/mL). Este trabalho demonstrou o potencial das infusões de diversas misturas de plantas e o seu benefício para a saúde humana, bem como a sua possível aplicação na indústria alimentar ou farmacêutica.

Agradecimentos

Os autores agradecem à Fundação para a Ciência e a Tecnologia (FCT, Portugal) e ao FEDER no âmbito do programa PT2020 pelo apoio financeiro ao CIMO (UID/AGR/00690/2019); financiamento nacional da FCT, PI, através do contrato de programa institucional de emprego científico para o contrato de L. Barros e R.C. Calhelha; o contrato de C. Pereira através da celebração contrato de programa previso no nº 4, 5 e 6 do artigo 23º do Decreto-Lei nº 57/2016, de 29 de agosto, alterado pela Lei nº 57/2017, de 19 de julho; FEDER-Interreg España-Portugal pelo apoio financeiro através do projeto 0377_Iberphenol_6_E; FEDER através do Programa Operacional Regional Norte 2020, no âmbito do Projeto NORTE-01-0145-FEDER-023289: DeCodE; e à empresa Ervital (Castro Daire, Portugal) pela cedência das amostras

Referências

[1] V. Farzaneh, I.S. Carvalho, Industrial Crops and Products, 65 (2015) 247.
[2] A.C. Kaliora et al., Food Chemistry, 142 (2014) 233.
[3] H. Aoshima, S. Hirata, S. Ayabe, Food Chemistry, 103 (2007) 617.

Controlo da qualidade do teor de CO_2 em água mineral engarrafada

Gomes B. Vânia[1,2*], João M. Isabel[2]

[1]Águas do Vimeiro, S.A., Rua da Ribeira, 2560-084, Maceira, Torres Vedras, Portugal
[2]Instituto superior de Engenharia de Lisboa, Rua Conselheiro Emidio Navarro, 1, 1959-007 Lisboa, Portugal

**vaniabernardesgomes@hotmail.com*

Este trabalho descreve a implementação e uso de cartas de controlo para monitorizar o teor de CO_2 em água mineral gaseificada. O teor de CO_2 na água gaseificada engarrafada é uma característica da qualidade muito importante e deve ser monitorizado e controlado numa primeira fase logo na linha de produção de forma a garantir que o processo de produção é estável e previsível ao longo do tempo.
O processo de carbonatação consiste na dissolução do CO_2 na água o qual pode ocorrer de uma forma natural, como é o caso das águas minerais naturais que absorvem o CO_2 diretamente de aquíferos do subsolo ou pode ser um processo artificial no qual o CO_2 é misturado com a água utilizando-se para tal um pré-saturador e saturador com duas colunas para efetuar a mistura da água e do dióxido de carbono. Foram estudados dois tipos de produto de água mineral carbonatada engarrafada em PET e vidro respetivamente. O controlo da qualidade do teor de CO_2 na água mineral engarrafada, quer em PET quer em vidro foi implementado diretamente na linha de produção.
A determinação do teor do CO_2 em linha foi realizada recorrendo à medição da temperatura e da pressão de cada garrafa de acordo com o plano amostral selecionado, considerando para tal amostras com a dimensão de quatro unidades e utilizando a lei de Henry para a determinação do teor de CO_2 [1,2]. Na fase I de implementação do controlo estatístico da qualidade recolheram-se os dados do processo, colocou-se o processo sob controlo estatístico e determinaram-se os limites de controlo experimentais a utilizar na fase II. Com o processo de produção em linha sob controlo estatístico foi possível determinar os parâmetros do processo, nomeadamente médias e desvios padrão e com base na especificação técnica previamente estabelecida determinar a capacidade do processo [3].
Por analise dos índices de capacidade do processo foi possível concluir que o processo é capaz de cumprir com a especificação técnica na linha de enchimento PET com índices de capacidade elevados. Já na linha de enchimento vidro o processo registou índices de capacidade mais baixos sendo marginalmente capaz e a necessitar de intervenção no sentido de proceder ao aumento de capacidade com consequente melhoria da qualidade do processo de produção
A implementação do controlo estatístico do processo na linha de produção com utilização de cartas de controlo de médias e de amplitudes revelou-se muito adequado uma vez que sendo uma ferramenta visual é de fácil utilização e implementação e permitiu à empresa um melhor conhecimento do seu processo e um contributo para a melhoria contínua do mesmo [4].

Agradecimentos
Um agradecimento às Águas do Vimeiro, S.A. pela possibilidade de realização deste trabalho.

Referencias

[1] R. Sander. Atmospheric Chemistry and Physics, 15(8), (2015), 4399-4981
[2] E.A. Moelwyn-Hughes, D. Lewis. J. Electrochem. Soc,107(5), (1960), 124c-125c.
[3] Introduction to Statisticaly Quality Control, D.C. Montgomery, 7th edition, Wiley, 2012.
[4] Applied Statistics and Probability for Engineers, D.C. Montgomery, G.C. Rungers, 6th edition, Wiley, 2014.

Effect of a biosurfactant from the corn-milling industry on anthocyanins extracted during winegrape skin maceration

A. López-Prieto[1,*], G. Scalzini[2], M. A. Paissoni[2], V. Englezos[2], S. Giacosa[2], L. Rolle[2], S. Río Segade[2,*], B. Pérez Cid[3], A.B. Moldes[1], J.M. Cruz[1].

[1]Chemical Engineering Department, School of Industrial Engineering – Centro de Investigación Tecnológico Industrial (MTI), University of Vigo, Campus As Lagoas-Marcosende, 36310, Vigo, Spain

[2]Università degli Studi di Torino, Dipartimento di Scienze Agrarie, Forestali e Alimentari. Largo Paolo Braccini 2, 10095 Grugliasco (TO), Italy

[3]Food and Analytical Chemistry Department, Faculty of Chemistry, University of Vigo, Campus As Lagoas-Marcosende, 36310 Vigo, Spain

**alexlopez@uvigo.es; susana.riosegade@unito.it*

Abstract

Biosurfactants are surface-active compounds obtained as secondary metabolites by microbial production that help in the stabilization of emulsions and solubilization of hydrophobic substances in formulations [1]. They are biocompatible and biodegradable compounds found in agro-industrial wastes like corn steep liquor (CSL), a fermented residual stream from the corn-milling industry [2].

In winemaking, the extraction of grape phenolic compounds is of great relevance for the production of quality red wines. In particular, anthocyanins are responsible for the red color of grapes and wines. These red pigments are released in the first steps of maceration from the skins into the juice/wine where they can undergo chemical reactions or be adsorbed by grapes solid parts and yeast lees, leading to a reduction in color stability. Besides their total content, the different reactivity of anthocyanins depends on structural features such as hydroxylation pattern, as well as on their involvement in polymerization and copigmentation reactions [3]. With the aim of improving the color characteristics of red wines by hindering the degradation of anthocyanins extracted from the grape skin, a biosurfactant obtained from CSL was added in the hydroalcoholic extracting solution. Two red winegrape varieties (*Vitis vinifera* L. cv. Cabernet sauvignon and Aglianico) were studied for anthocyanin content, polymerization, copigmentation and color parameters during simulated skin maceration for 7 days at 25 °C.

The results obtained showed that the addition of a biosurfactant from CSL improves color intensity from the beginning of maceration without an increase in tonality. The effect was particularly significant for Cabernet sauvignon, probably due to the limited presence of malvidin-3-glucoside in grapes, which is the most stable form and, therefore less prone to oxidation. At the end of maceration, the color loss decreased down to –4.3% in Aglianico and Cabernet sauvignon, when compared with the control without biosurfactant addition. While total anthocyanin content was not affected by the addition of the biosurfactant extracted from CSL in the two varieties studied, a higher copigmentation ratio was observed for Cabernet sauvignon after 7 days of maceration. Another important aspect to take into account is the positive effect of the biosurfactant extract, regarding to the defense of all individual anthocyanin forms, particularly after 6 h of simulated maceration. When maceration progressed, this protective effect was evident for cyanidin-3-glucoside and delphinin-3-glucoside, which are very reactive due to the presence of two and three hydroxyl groups in the B ring [4], respectively, and therefore easily degraded. These preliminary results highlighted the effectiveness of the biosurfactant extracted from CSL to protect and stabilize the color traits during simulated maceration of red winegrapes. However, further studies will be carried out to confirm these results in real winemaking.

Acknowledgements

This study was supported by the Spanish Ministry of Economy and Competitiveness (MINECO) under the project RTI2018-093610-B-100. A. López-Prieto expresses his gratitude to the University of Vigo for his pre-doctoral scholarship.

References

[1] D. F. K. Santos, R. D. Rufino, J. M. Luna, International Journal of Molecular Sciences 17 (2016) 1.

[2] X. Vecino, L. Barbosa-Pereira, R. Devesa-Rey, J. M. Cruz, A. B. Moldes, Journal of Agricultural and Food Chemistry, 62 (2014) 5451

[3] V. A. P. de Freitas, A. Fernandes, J. Oliveira, N. Teixeira, N. Mateus, OENO One, 51 (2017) 1.

[4] P. Sarni, H. Fulcrand, V. Souillol, J. M. Souquet, V. Cheynier, Journal of the Science of Food and Agriculture, 69 (1995), 385.

Biosurfactant obtained from a corn residual stream as agent for improving water solubility of copper oxychloride pesticide: a comparative study

A. López-Prieto[1,*], B. Pérez Cid[2], A.B. Moldes[1], J.M. Cruz[1]
[1]Chemical Engineering Department, School of Industrial Engineering – Centro de Investigación Tecnológico Industrial (MTI), University of Vigo, Campus As Lagoas-Marcosende, 36310, Vigo, Spain
[2]Food and Analytical Chemistry Department, Faculty of Chemistry, University of Vigo, Campus As Lagoas-Marcosende, 36310 Vigo, Spain
*alexlopez@uvigo.es

Abstract

For the last decade, the introduction of new restrictions in relation with the use of pesticides and the increase in crop production has caused that the agrochemical industry had to search for new formulations focused on the use of more biodegradable and eco-friendly substances. Moreover, the disadvantage of some organic and inorganic pesticides is their low water solubility. Therefore, high concentrations of chemical surfactants and emulsifiers have to be employed to improve pesticides water solubility. Among the active principles, those based on copper oxychloride are the most popular to treat and preserve crops from pests, showing, nevertheless, a poor solubility in water. Additionally, restrictions by the EU are related with the use of copper and amide based pesticides [1], therefore, new formulations are needed to reduce the use of these substances in the final product. In this sense, microbial surfactants, also named biosurfactants, appear as a possible alternative to chemical surfactants to obtain eco-friendlier pesticides.

In general, biosurfactants are defined as surface-active compounds produced by microorganisms that are able to reduce the surface tension of water allowing the solubilization of hydrophobic substances [2]. Some biosurfactants can be extracted from agro-industrial residues such as corn steep liquor (CSL), a residual stream from the corn-milling industry where they are produced due to the spontaneous growth of a Bacillus strain [3]. In addition, the biosurfactant obtained from CSL has shown promising results as antimicrobial agent, increasing even more the interest for its incorporation in pesticides [4].

The aim of this work was to evaluate the solubility of copper oxychloride in presence and absence of a biosurfactant extracted from CSL, with chloroform or ethyl acetate, in comparison with a chemical surfactant (Tween 80). Experiments were carried out by triplicate using fixed concentration of copper oxychloride (4 g/L) in the presence of different concentrations (2 and 20 g/L) of the tested bisourfactant, as well as a comercial chemical surfactant (Tween 80). The mixture was stirred during 20 min, at room temperature, centrifuged and filtered (0.45 µm) to remove the non-solubilized copper oxychloride. The amount of pesticide solubilized in the supernatant solution was quantified by Flame Atomic Absorption Spectroscopy (FAAS).

The results showed that it is possible to dissolve around 90 % of the copper active principle tested, when using concentrations of 4 g/L of copper oxychloride in the presence of 20 g/L of the biosurfactants extracted from CSL with ethyl acetate, whereas Tween 80 was only able to solubilize less than 1 % of copper oxychloride. When using the biosurfactants extracted from CSL with chloroform, it was observed that it was solubilized less than 50 % of the active principle.

Based on these results, it can be concluded that biosurfactants produced in CSL can play an important role in the formulation of eco-friendlier biopesticides, promoting a circular economy, althought attention should be paid on the extractive prodecure in order to obtain biosurfactants with optimum emulsifier properties.

Acknowledgements
This study was supported by the Spanish Ministry of Economy and Competitiveness (MINECO) under the project RTI2018-093610-B-100. A. López-Prieto expresses his gratitude to the University of Vigo for his pre-doctoral scholarship.

References
[1] EU (2009/32/EC). European Comission (2009)

Influência do ciclo de crescimento no perfil fenólico e nas propriedades bioativas de *Cynara cardunculus* L. var *altilis*

Filipa Mandim[1,2], Maria Inês Dias[1], José Pinela[1], Spyridon Petropoulos[3], Lillian Barros[1], Celestino Santos-Buelga[2], Isabel C.F.R. Ferreira[1,*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Bragança, Portugal
[2]GIP-USAL, Faculdad de Farmacia, Universidad de Salamanca, Salamanca, Espanha
[3]University of Thessaly, Department of Agriculture, Crop Production and Rural Environment, Magnissia, Greece
**iferreira@ipb.pt*

Cynara cardunculus L., também conhecida por cardo, é uma planta herbácea da família Asteraceae, compreendendo três variedades: cardo selvagem (var. *sylvestris*), cardo cultivado (var. *altilis*) e alcachofra (var. *scolymus*) [1]. Os seus capítulos florais são utilizados em diversas receitas, bem como na medicina tradicional devido a propriedades diuréticas, coleréticas e hepatoprotetoras. Esta espécie apresenta diversas aplicações industriais, sendo utilizada na produção de queijo, biomassa, bioenergia, produtos farmacêuticos, etc. [2]. As suas propriedades e aplicações têm enaltecido o seu consumo e utilização e, consequentemente, o seu cultivo e valor económico [3,4].

Estimulado pelo crescente interesse comercial associado ao cardo, o presente estudo visa a análise da composição fenólica e das propriedades bioativas dos capítulos florais de *Cynara cardunculus* var. *altilis* cultivados na Grécia e colhidos em cinco fases distintas do seu ciclo de crescimento. As amostras foram submetidas a extrações hidrometanólicas e a composição fenólica dos extratos obtidos foi determinada por HPLC-DAD-ESI/MS. A atividade citotóxica foi avaliada pelo método colorimétrico da sulforrodamina B em linhas celulares tumorais humanas (MCF-7, NCI-H460, HeLa e HepG2) e numa cultura primária de células não tumorais de fígado de porco (PLP2). Por sua vez, a atividade anti-inflamatória foi analisada pela inibição da produção de NO em macrófagos de rato ativados com lipopolissacárido. A atividade antioxidante foi avaliada através dos ensaios celulares TBARS e OxHLIA.

Foram identificados nove compostos fenólicos nos extratos dos capítulos florais do cardo. O ácido 3,5-*O*-dicafeoilquínico e a apigenina-*O*-glucurónido foram os compostos detetados em maior quantidade. Foi observado que o teor em compostos fenólicos diminui com o aumento do estado de maturação dos capítulos florais. Relativamente à atividade citotóxica, os capítulos imaturos apresentaram maior atividade contra as células tumorais testadas, exceto para a linha MCF-7 (carcinoma de mama), para a qual estados de maturação mais avançados revelam maior atividade. Os extratos dos capítulos imaturos revelaram também maior potencial anti-inflamatório e capacidade de inibir a formação de TBARS. Por outro lado, os extratos dos capítulos florais colhidos mais tardiamente apresentaram capacidade de proteger os eritrócitos dos radicais livres gerados no sistema de reação. A heterogeneidade dos resultados revelou que outros compostos além dos polifenóis poderão estar relacionados com as bioatividades estudadas.

Este estudo comprovou o alto potencial biológico dos capítulos florais do cardo e o seu possível uso como potencial fonte de importantes compostos bioativos. No entanto, são necessários mais estudos para compreender quais os compostos responsáveis pelas propriedades bioativas demonstradas.

Agradecimentos
Os autores agradecem à Fundação para a Ciência e Tecnologia (FCT, Portugal) e FEDER, no âmbito do Programa PT2020 pelo apoio financeiro ao CIMO (UID/AGR/00690/2019), aos contrato-programa de emprego científico institucional de M. I. Dias, J. Pinela e L. Barros. Os autores agradecem também ao programa FEDER-Interreg Espanha-Portugal pelo apoio financeiro através do projeto 0377_Iberphenol_6_E.

Referencias

[1] B. de Falco, G. Incerti, M. Amato, V. Lanzotti, Phytochemistry Review, (2015), 993.
[2] J. Gominho, M. D. Curt, A. Lourenço, J. Fernández, H. Pereira, Biomass and Bioenergy, 109 (2018) 257.
[3] J. Gominho, M. D. Curt, A. Lourenço, J. Fernández, H. Pereira, Biomass and Bioenergy, 109 (2018), 257.
[4] E. Christaki, E. Bonos, P. Florou-Paneri, International Journal of Science and Technology, 2 (2012), 64.
[5] .

Distribuição e atividade antioxidante do hidroxitirosol e seus ésteres em sistemas emulsionados

Alfredo Esteves[1*], Marlene Costa[1], Fátima Paiva-Martins[1], Sónia Losada-Barreiro[1,2], Carlos Bravo-Díaz[2], Luís S. Monteiro[3]

[1]REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, Porto, Portugal

[2]Universidade de Vigo, Faculdade de Química, Departamento de Química Física, Vigo, Espanha

[3]Centro de Química, Universidade do Minho, Braga, Portugal

**up201305498@fc.up.pt*

O controlo da oxidação lipídica é importante no desenvolvimento de novas estratégias para a preparação de alimentos mais saudáveis e com maior prazo de validade. A adição de antioxidantes (AOs) aos produtos alimentares é uma das práticas mais utilizadas na indústria alimentar para retardar ou inibir a oxidação lipídica. A eficiência antioxidante depende tanto da velocidade de reação dos AOs com os radicais quanto da sua concentração no local da reação, que nos sistemas emulsionados acredita-se ser a região interfacial.

O hidroxitirosol (HT) é um composto fenólico presente no azeite, que se destaca pelas suas propriedades antioxidantes e efeitos benéficos para a saúde. Sintetizaram-se derivados hidrofóbicos do HT de modo a analisar os efeitos da hidrofobicidade do AO na distribuição e na estabilidade oxidativa de emulsões e nanoemulsões de óleo de peixe em água[1].

Os resultados mostram que a eficiência dos ésteres do HT aumenta com o aumento da sua hidrofobicidade até um máximo no derivado octilo, após o qual diminui em ambos os sistemas emulsionados. A variação observada na eficiência com o comprimento da cadeia alquílica do AO é paralela à percentagem de AO na região interfacial. As concentrações interfaciais são 20-170 vezes (dependendo de Φ_I e do sistema emulsionado utilizado) mais altas que a concentração do AO no sistema. Alterações na razão O/A podem ser usadas para otimizar as concentrações interfaciais dos AOs hidrofóbicos (octilo e laurilo de hidroxitirosol) ou hidrofílicos (hidroxitirosol), mas não os dos AOs de hidrofobicidade intermediária (acetato de hidroxitirosol). Os resultados fornecem, pela primeira vez, evidências experimentais de que a variação na eficiência de séries homólogas de AOs em sistemas emulsionados são devidas a diferenças nas suas concentrações interfaciais, confirmando que existe uma relação direta entre a concentração AO e a região interfacial dos sistemas emulsionados e a sua eficiência.

Agradecimentos: O trabalho foi apoiado por UID/QUI/50006/2019 com financiamento da FCT/MCTES através de fundos nacionais e pela PTDC/OCE-ETA/32492/2017 – POCI-01-0145-FEDER-032492 - PHENOLIVA e Marlene Costa agradece à FCT pela bolsa de doutoramento (SFRH/BD/100889/2014).

[1] M. Costa, S. Losada-Barreiro, F. Paiva-Martins, C. Bravo-Díaz, L. S. Romsted, Food Chem, 2015, 175, 233-342

Evaluation of the prebiotic galacto-oligosaccharides addition in the traditional Portuguese cake "*bolo-de-arroz*"

R. Moreira[2,*], C. Amorim[1], S.C. Silvério[1], B. Cardoso[1], L.R. Rodrigues[1]
[1]CEB-Centre of Biological Engineering, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[2]Chemical Engineering Department, Universidade de Santiago de Compostela, Campus Vida, 15782, Santiago de Compostela, Spain
**ramon.moreira@usc.es*

The global epidemic of overweight and obesity have become a major public health problem in several parts of the world. The increasing prevalence of those medical conditions is associated with many diet-related chronic diseases (diabetes mellitus, cardiovascular disease, etc.). The consumers prefer low-sugar and functional food products. In this context, prebiotics compounds have attracted global attention as functional food ingredients due to their beneficial effects over several physiological functions, namely on the gastrointestinal tract [1]. Prebiotic Galacto-oligosaccharides (GOS) are recognized as safe food ingredients and are used in the EU from two decades [2].

In this study, traditional Portuguese cakes "bolo-de-arroz" were produced containing (a) 100% of sugar (100), (b) 75% of sugar supplemented with 0,9% GOS (75GOS), and compared with commercial bolo-de-arroz (commercial). Physical features (apparent density and porosity), optical properties (colour) and textural characterization (texture profile analysis) were measured after 1 day of baking and during 5 days of storage. Water adsorption isotherms at 20ºC were determined by gravimetric method using saturated salt solutions.

Table shows some results of tested samples after 1 day of baking. No significant differences were found between 75GOS and commercial samples and 100 sample show higher porosity values and lowest apparent density. Color parameters were invariant for the GOS addition. Textural results indicate that low sugar content promotes the interactions between proteins and starch and hardness, gumminess and chewiness increased. On the other hand, water adsorption isotherms can be classified as type II and they were satisfactorily modelled by means of Oswin model.

Table. Physical, optical and textural properties of tested cakes (1 day after baking): bolo-de-arroz with 100% of sugar (100), 75% of sugar and 0.9% GOS (75GOS) and (commercial) bolo-de-arroz

Property/Sample	100	75GOS	Commercial
Baking Loss (%)	9.4 ± 1.0	9.1 ± 0.3	-
Apparent density (g/cm^3)	0.28 ± 0.01	0.36 ± 0.01	0.33 ± 0.03
Apparent Porosity (%)	74.3 ± 0.1	68.37 ± 0.76	67.7 ± 1.5
Color			
L*	65.6 ± 0.89	68.03 ± 1.58	57.2 ± 1.9
a*	-2.2 ± 0.05	-2.49 ± 0.09	-1.4 ± 0.3
b*	23.3 ± 0.26	26.65 ± 0.69	26.1 ± 1.0
Hardness (g)	205 ± 47	372 ± 49	209 ± 35
Adhesiveness (g.cm)	-0.005 ± 0.001	-0.016 ± 0.017	-0.04 ± 0.04
Adhesive Force (g)	-1.2 ± 0.8	-0.8 ± 0.3	-1.0 ± 0.2
Springiness (cm)	0.89 ± 0.02	0.86 ± 0.01	0.82 ± 0.02
Cohesiveness (-)	0.702 ± 0.02	0.60 ± 0.04	0.39 ± 0.03
Resilience (-)	0.279 ± 0.01	0.23 ± 0.02	0.13 ± 0.01
Gumminess (g)	127 ± 60	185 ± 93	81 ± 16
Chewiness (g.cm)	113± 53	159 ± 80	67 ± 13

Agradecimientos
CA and BC acknowledge their grants (UMINHO/BPD/4/2019 and SFRH/BD/132324/2017) from FCT. This study received financial support from UID/BIO/04469/2019 unit; COMPETE 2020 (POCI-01-0145-FEDER-006684), FoSynBio (POCI-01-0145-FEDER-029549), NewFood (NORTE-01-0246-FEDER-000043) and BioTecNorte (NORTE-01-0145-FEDER-000004). R. Moreira acknowledges the financial support to the Xunta de Galicia and FEDER by the project (EDD431B 2019/01).

Referencias

[1] G.R. Gibson et al. Nature Reviews Gastroenterology & Hepatology, (2017) 14.
[2] J. Van Loo, P. Coussement, L. DeLeenheer, H. Hoebregs, G. Smits, G. Critical Reviews in Food Science and Nutrition, (1995) 35.

Fraccionamiento de polisacáridos sulfatados de *Bifurcaria bifurcata*

Gonçalves, C., Sineiro, J.*, Moreira R.
Departamento de Enxeñería Química, Universidade de Santiago de Compostela, Campus Vida, 15782, Santiago de Compostela, España
**jorge.sineiro@usc.es*

Bifurcaria bifurcata es un alga perteneciente a la familia *Sargassaceae* cuya distribución abarca desde el Sur de Marruecos hasta el Noroeste de Irlanda. Su hábitat se encuentra en la zona supralitoral y en la zona intermareal media. De su composición han sido ampliamente caracterizados sus terpenos, compuestos principalmente por diterpenos lineales (Muñoz et al., 2013). No hay mucha literatura respecto a los carbohidratos de este alga, que en ensayos preliminares mostró un contenido en sulfatos y cenizas significativamente más altos que fucales como *Fucus vesiculosus* o *Ascophyllum nodosum*. Es por ello que en este trabajo se aislaron fracciones de carbohidratos de distinto peso molecular medio y en relación a su grado de sulfatación.

Materiales y métodos

La extracción de fucoidano crudo se llevó a cabo siguiendo la metodología descrita por Wang et al., (2008). Se tomarion 400 g de alga en 4L. La suspensión se distribuyó en vasos de 250 mL y se autoclavó a 120ºC durante 3 h. Tras precipitar con $MgCl_2$ y etanol, el sobrenadante se dializó empleando membranas de 3500 Da. Se concentró en rotavapor y se precipitaron los carbohidratos con etanol absoluto hasta una concentración final del 80% (p/p). El sólido se secó a vacío a 45°C.

El fraccionamiento de los fucoidanos se realizó mediante cromatografía de intercambio aniónico, utilizando una columna de DEAE-Sepharose CL-6B, con un caudal de 150 mL/h. Se recolectaron fracciones con absorbancia apreciable con el método colorimétrico de azúcares totales de Dubois et al. (1956). Los sulfatos se determinaron por el método de Dogson (1961).

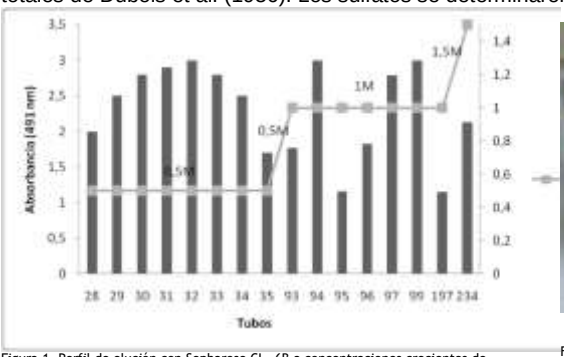


Figura 1. Perfil de elución con Sepharose CL–6B a concentraciones crecientes de Nacl(0,5, 1, 1,5 M)

Figura 2. Recolección de muestras con diverso contenido en carbohidratos.

Fracciones (V eluc.,mL)	Contenido carbohidratos (mg/L)	Cantidad recuperada (mg)	Contenido sulfatos (mg/L)
F1 (175-212)	218,4	10,70	-
F2 (212-219)	126,3	0,88	-
F3 (581)	131,0	0,92	-
F4(587)	223,0	1,56	63
F5(594)	86,2	0,60	1589
F6(601)	136,0	0,95	715
F7(608-622)	222,0	3,01	943
F8(1081)	85,4	0,60	-
F9(1458)	158,2	2,21	-

Tabla. Contenido en carbohidratos, volúmenes de elución, volumen y cantidad recuperada por fracción.

Resultados.

El mayor rendimiento en carbohidratos se obtuvo de fracciones sin sulfatación (F1). Se obtuvieron 4 fracciones significativas en rendimiento de carbohidratos y grado de sulfatación, siendo la fracción F6+F7 la de mayor rendimiento en carbohidratos con alto grado de sulfatación.

El análisis de carbono orgánico total y S elemental aportaron relaciones molares en F4 y F5 de 34 y 37 molC/molS, siendo las más sulfatadas, con relaciones fucosa/sulfato en torno a 2,7. Para F5, con rendimiento bajo, pero altamente sulfatada, se obtuvo 1,3. Las fracciones F5-F7 son de interés para evaluar actividades biológicas.

Agradecimientos. A la Xunta de Galicia y al FEDER por el proyecto (EDD431B 2019/01).

Referencias

[1] Wang et al., (2008). International Journal of Biological Macromolecules 42 (2008) 127–132.
[2] Dubois et al., (1956). Analytical Chemistry, 28(3), 350–356.
[3] Dogson et al., (1961). The Biochemical Journal, 78, 312–319.

Volatile, phenolic and fatty acid profiles of Portuguese almond cultivars

Ivo Oliveira[1,*], Anne S. Meyer[2], Sílvia Afonso[1], Alfredo Aires[1], Piebiep Goufo[1], Henrique Trindade[1], José Alberto Pereira[3], Berta Gonçalves[1]
[1]CITAB, UTAD, Quinta de Prados, 5000-801, Vila Real, Portugal
[2]Technical University of Denmark, DTU Building 221, DK-2800 Kgs. Lyngby, Denmark
[3]CIMO, ESA-Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
**ivo.vaz.oliveira@utad.pt*

The determination of chemical composition of fruit samples, associated with the use of statistical tests, has a wide application in sciences. Chemometrics is significant not only to compare cultivars and/or the effects of technological processes, but also to retrieve and interpret important information from the compositional profile patterns. Ultimately, the application of chemometrics, may be useful for varietal discrimination and authentication as well as to attest the application of determined technological processes.

In this work, the use of chromatographic equipment and techniques, such as solid phase head space microextraction (HS-SPME) and mass spectrometry-coupled gas chromatography (GC-MS), high performance liquid chromatography coupled to a diode array detector (HPLC-DAD-UV-VIS) or gas chromatography associated with a flame ionization detector (GC-FID) was applied to obtain profiles of volatile compounds, phenolic compounds and fatty acids, respectively, were applied to samples of almonds from traditional Portuguese cultivars, namely Amendoão, Bonita, Casanova, Molar and Pegarinhos.

The volatile profile of almonds included 20 compounds, although not all present in all cultivars. The total content of volatile compounds ranged from 22.6 µg / g fresh weight (FW) obtained for Molar cultivar up to 110.7 µg / g FW for Bonita cultivar. Major volatiles include the alcohol 3-methyl-1-butanol and the aldehydes benzaldehyde and hexanal. Twenty individual phenolic compounds were identified, nine of which were detected in all cultivars. In all samples, the most abundant one was catechin, and the sum of all individual phenolic compounds was higher in cv. Molar (3817 µg / 100 g FW), and the lowest content was found in Bonita (1436 / 100g FW). Eighteen fatty acids were identified in the studied almond cultivars, oleic and linoleic acids being the main ones, representing at least 77% of the total fatty acids.

The use of statistical tests such as Linear Discriminant Analysis (LDA) and Principal Component Analysis (PCA) allowed the recognition of patterns in the profiles of volatile compounds, phenolics and fatty acids that may be useful in cultivar identification, used for authenticity purposes, especially for cultivars included in the "Amêndoa Douro" Protected Designation of Origin.

Agradecimientos
Ivo Oliveira is grateful to FCT − Fundação para a Ciência e a Tecnologia (FCT), POPH-QREN and FSE for the Post-doctoral Fellowship SFRH/BPD/111005/2015. This work is supported by National Funds by FCT − Portuguese Foundation for Science and Technology, under the project UID/AGR/04033/2013.

Desenvolvimento e Aplicação de um Revestimento Conservante Natural para Fiambres; Perfil Físico-Químico e Estabilidade

Filipa A. Fernandes[1,2], Márcio Carocho[1], Sandrina A. Heleno[1], Paula Rodrigues[1], Lillian Barros[1,] e Isabel C. F. R. Ferreira[1,*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;
[2]Grupo de Nutrición y Bromatología, Departamento de Química Analítica y Alimentaria, Facultad de Ciencias de Ourense, Universidad de Vigo-Ourense Campus, E-32004 Ourense, Spain.
*iferreira@ipb.pt

Grande parte do plástico produzido é aplicado na conservação de alimentos, no entanto há cada vez mais estudos que confirmam a migração dos seus aditivos para as matrizes alimentares, sendo prejudiciais para a saúde do consumidor. É também notória a contribuição do plástico para a poluição do planeta. Assim, as indústrias procuram alternativas à utilização de plástico, sendo os revestimentos comestíveis e biodegradáveis uma opção viável [1,2]. O objetivo deste trabalho consistiu em verificar a eficácia de um revestimento conservante edível, à base de ingredientes naturais (extrato aquoso de alecrim e carragenina), através de estudos de crescimento microbiano e de características físico-químicas (textura, humidade e cor) em fiambre durante 15 dias de acondicionamento.

Para verificar o crescimento microbiano no fiambre, contaminaram-se amostras de fiambre, com diferentes microrganismos (coliformes e *Escherichia coli*; leveduras e bolores; bactérias psicrotróficas; e *Staphylococcus aureus*) que foram sujeitos a revestimentos de conservação distintos (revestimento edível, revestimento com filme de plástico comercial, ambos os revestimentos e, finalmente uma amostra sem qualquer tipo de revestimento, servindo de controlo). Foi posteriormente analisada a quantidade de microrganismos ao longo de 15 dias de acondicionamento a 5ºC pelo método da contagem em placa. A textura foi analisada através de um texturómetro (TA.XT Plus, Stable Micro Systems), a humidade foi calculada com base na perda de água durante o tempo de armazenamento, e a medição da cor foi realizada com um colorímetro (CR400 portátil da Konica Minolta).

De uma forma geral, em termos de carga microbiana, verificou-se que as amostras capazes de reter a humidade durante o tempo de armazenamento apresentam maior contagem de microrganismos. Para os coliformes, usados como indicadores de higiene sanitária e de contaminantes fecais, o fiambre imerso na solução conservante apresentou menor contagem, comprovando seu valor antimicrobiano em relação a estes microrganismos. Também se verificou, que para todos os microrganismos testados, nas etapas finas de armazenamento o fiambre com o revestimento natural apresentou maior atividade antimicrobiana, uma vez que a contagem de microrganismos foi menor. Em relação à textura, verificou-se que tanto o tempo como o tipo de armazenamento têm influência significativa. Assim, constatou-se que com o tempo a dureza das amostras sujeitas ao armazenamento com o revestimento edível aumentou, embora a adesividade tenha sido reduzida. A elasticidade, a coesão e a resiliência não variaram muito ao longo do tempo em nenhum dos tratamentos aplicados, contudo houve uma alta variação na mastigabilidade. Relativamente à humidade, o revestimento edível não conseguiu manter a mesma percentagem de água no fiambre que o filme de plástico comercial (como era esperado), no entanto, obtiveram-se melhores resultados que na amostra controlo (sem qualquer tipo de revestimento). Para o parâmetro da cor, constatou-se que as amostras com o revestimento edível preservaram melhor a cor que as amostras armazenadas com filme plástico, pois as primeiras mostraram uma tendência amarelada ao longo do tempo, evitando um aumento da cor azul (cor indesejada para produtos à base de carne). Os resultados obtidos neste estudo mostram que a solução conservante apresenta um alto potencial na conservação de fiambre, o que tem suscitado um elevado interesse por parte da indústria alimentar.

Agradecimentos

Os autores agradecem à Fundação para a Ciência e a Tecnologia (FCT, Portugal e ao FEDER, no âmbito do programa PT2020 pelo apoio financeiro ao CIMO (UID/AGR/00690/2013); bolsa individual de doutoramento de Filipa Fernandes (SFRH/BD/145467/2019), Fundos nacionais através da FCT- Fundação para a Ciência e Tecnologia, I.P., no âmbito da Celebracção do contrato-programa de emprego científico individual de Sandrina Heleno e Institucional de Lillian Barros. Projeto *Mobiliizador* Norte-01-0247-FEDER-024479: ValorNatural® pelo contrato de Márcio Carocho.

Os autores agradecem ao "SONAE MC" pela doação do presunto utilizado neste trabalho.

Referências

[1] M. Carocho, S. Heleno, P. Rodrigues, M. F. Barreiro, L. Barros, I. C. F. R. Ferreira, LWT - Food Science and Technology, 104 (2019) 76-83.

[2] P. Cazón, G. Velazquez, J. A. Ramírez, M. Vázquez, Food Hydrocolloids, 68(2017), 136–148.

Otimização da extração de antocianinas a partir de epicarpos de jabuticaba e validação da capacidade corante do extrato numa matriz alimentar

Bianca R. Albuquerque[1,2], José Pinela[1], Lillian Barros[1], M. Beatriz P.P. Oliveira[2], Isabel C.F.R. Ferreira[1]*

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2]REQUIMTE/LAQV, Faculdade de Farmácia, Universidade do Porto, Rua Jorge Viterbo Ferreira, 280, 4050-313 Porto, Portugal

**iferreira@ipb.pt*

As incertezas a respeito do consumo seguro de alguns aditivos artificiais e a procura por alimentos mais saudáveis têm promovido a utilização de corantes naturais na indústria alimentar [1]. Nos últimos anos, a obtenção deste tipo de aditivos a partir de fontes naturais tornou-se numa área de investigação ativa e em crescimento [2]. Neste contexto, o epicarpo de jabuticaba, que normalmente não é consumido e muitas vezes descartado durante o processamento industrial, apresenta uma interessante composição em antocianinas, compostos com grande potencial para produção de agentes corantes com propriedades bioativas [3]. Por esta razão, a presente investigação teve como objetivos: i) otimizar a extração de antocianinas por maceração (ME) e ultrassons (UE) utilizando a metodologia de superfície de resposta; e ii) validar a capacidade corante do extrato obtido nas condições previamente otimizadas através da sua incorporação numa matriz alimentar, nomeadamente macarrones.

Para otimização por RSM, foi um desenho composto central de 5 níveis combinando as variáveis tempo, percentagem de etanol e temperatura ou potência. Os teores de delfinidina-3-*O*-glucósido e cianidina-3-*O*-glucósido, determinados por HPLC-DAD-ESI/MS, foram usados como variáveis de resposta. O software Design-Expert foi usado para construir e validar os modelos e obter as condições que maximizam a extração. O extrato obtido nas melhores condições foi posteriormente incorporado em macarrones a fim de se avaliar o potencial corante. Para isso, o produto formulado foi analisado quanto aos parâmetros de cor e valor nutricional ao longo do tempo de prateleira e os resultados foram comparados com os obtidos com um corante comercial à base de antocianinas.

Dentre as técnicas testadas, a ME foi a mais eficaz em extrair ambas as antocianinas identificadas no epicarpo de jabuticaba; este método permitiu extrair mais do dobro do conteúdo de antocianinas obtido com UE. Para maiores rendimentos, a extração ME necessitou de uma percentagem de etanol mais baixa e uma temperatura mais elevada, enquanto o processo UE foi caracterizado por um tempo de extração mais curto e uma elevada potência de ultrassons. Quanto aos macarrones formulados com o extrato antociânico, estes exibiram uma coloração estável e não apresentaram nenhuma diferença no valor nutricional quando comparados com macarrones formulados como o corante comercial.

Conclui-se que o epicarpo de jabuticaba é uma fonte interessante de antocianinas e que o método ME foi mais indicado para extração destes compostos. O extrato obtido nas condições ótimas incorporado em macarrones proporcionou uma coloração estável e não interferiu na composição nutricional do produto. O biorresíduo estudado apresentou, assim, potencial para produção de corantes naturais.

Agradecimentos

Os autores agradecem à Fundação para a Ciência e a Tecnologia (FCT, Portugal) e ao FEDER, no âmbito do programa PT2020, pelo apoio financeiro ao CIMO (UID/AGR/00690/2019); à FCT pela bolsa de doutoramento de B. Albuquerque (SFRH/BD/136370/2018) e pelos contratos-programa de emprego científico institucional de J. Pinela e L. Barros. Ao FEDER pelo financiamento através do Programa Operacional Regional Norte 2020 no âmbito do Projeto NORTE-01-0145-FEDER-023289 (DeCodE) e projeto *Mobilizador* Norte-01-0247-FEDER-024479 (ValorNatural); ao FEDER-Interreg España-Portugal pelo apoio financeiro através do projeto 0377_Iberphenol_6_E e ao projeto TRANSCoLAB (0612_TRANS_CO_LAB_2_P).

Referências

[1] N. Martins, C.L. Roriz, P. Morales, L. Barros, I.C.F.R. Ferreira, Trends Food Sci. Tech., 52 (2016) 1.

[2] J. Pinela, M.A. Prieto, M.F. Barreiro,… I.C.F.R. Ferreira, Innova. Food Sci. Emerg. Technol., 41 (2017) 160.

[3] P. Morales, L. Barros, M.I. Dias,… J.J. Berrios, Food Chem., 208 (2016) 220.

Influence of traditional extraction techniques on chemical composition of *Mentha pulegium* liqueurs

Rodríguez-Solana R.[1], Galego L.[2], Mansinhos I.[1], Gonçalves S.[1], Pérez-Santín E.[3], Romano, A.[1*]

[1]Centre for Mediterranean Bioresources and Food, Faculty of Sciences and Technology, University of Algarve, Campus de Gambelas, Ed. 8, 8005-139 Faro, Portugal
[2]Centre for Mediterranean Bioresources and Food, Higher Institute of Engineering, University of Algarve, Campus de Penha, 8005-139 Faro, Portugal
[3]Graduate School of Engineering and Technology, Universidad Internacional de La Rioja (UNIR), Logroño, Spain

**aromano@ualg*

Mentha pulegium L., commonly known as pennyroyal, is a medicinal and aromatic plant belonging to the *Lamiaceae* family and widely used in the preparation of different beverages such as liqueurs [1]. Herbal liqueurs are potential source of volatile and phenolic compounds with beneficial effects for human health [2]. Distillation (D), percolation (P), maceration (M), and hydro-alcoholic (HI) and aqueous (AI) infusions are the traditional extraction techniques used in liqueur elaboration [3]. The choice of the technique will depend on the sensorial attributes that the producer wants to give to the final product. The objective of this work was to assess the differences in volatile composition (determined by GC-MS and GC-FID), total phenolic content (TPC), and antioxidant capacity (AC) (evaluated by FRAP and TEAC assays) of liqueurs obtained by the abovementioned extraction techniques. Liqueur obtained by HI showed the highest TPC [446.80 ± 11.18 mg gallic acid equivalents (GAE)/L] and AC [FRAP: 888.05 ± 17.01 mg ascorbic acid equivalents (AAE)/L; TEAC: 1152.97 ± 29.80 mg Trolox equivalents (TE)/L] values, while that obtained by D showed the lowest (TPC: 15.23 ± 1.12 mg GAE/L; FRAP: 14.49 ± 0.21 mg AAE/L; TEAC: 6.22 ± 0.23 mg TE/L). *p*-Cymene, (-)-menthone, caryophyllene oxide and pulegone were the main plant compounds identified in the analysed liqueurs [4], although pulegone was the component found in largest quantities. According to the Committee of Herbal Medicinal Products (EMEA/HMPC/138386/2005) [5], pulegone is considered a hepatotoxin with a tolerable daily intake (TDI) set for food of 0.1 mg/kg bw. Considering an adult of 70 kg, and a consumption of pennyroyal liqueur of 50 mL (equivalent to a standard liqueur glass), the TDI of liqueurs obtained by HI, P, and M techniques exceed the recommended daily rate (values between 0.14 and 0.10 mg/kg bw). According to these results, a more exhaustive study should be carried out to determine the most appropriate plant material concentration and extraction technique used to obtain pennyroyal liqueurs with the highest values of TPC and AC, as well as with pulegone amounts less harmful to human health.

Agradecimientos
We are very grateful to Ángel R. de Lera and Rosana Álvarez from the Organic Chemistry Department, Faculty of Chemistry and Centro de Investigaciones Biomédicas (CINBIO), Universidade de Vigo, for their valuable contributions. This work received financial support from the project INTERREG - MD.Net: When Brand Meets People, and from the Foundation for Science and Technology (FCT), Portugal (SFRH/BPD/103086/2014).

Referencias

[1] L. Galego, V. Almeida, in Aguardente de frutos e licores do Algarve. História, técnica de produção e legislação. Colibri (Eds.), Lisboa, 2007.
[2] R. Rodríguez-Solana, J.M. Salgado, J.M. Domínguez, S. Cortés-Diéguez, Journal of the Institute of Brewing, 122 (2016) 653-660.
[3] T.E. Coldea, E. Mudura, Hop and Medicinal Plants, 23 (2015) 25-33.
[4] B. Teixeira, A. Marques, C. Ramos, I. Batista, C. Serrano, O. Matos, N.R. Neng, J.M.F. Nogueira, J.A. Saraiva, M.L. Nunes, Industrial Crops and Products, 36 (2012) 81-87.
[5] EMEA 2005. European Agency for the Evaluation of Medicinal products. Reference EMEA/HMPC/138386/2005 (https://www.ema.europa.eu/en/documents/public-statement/draft-public-statement-use-herbal-medicinal-products-containing-pulegone-menthofuran-revision-1_en.pdf)

Profiling of volatile carbonyl compounds in defective green coffee beans by means of a fan-assisted extraction process

João Rodrigo Santos*, José A. Rodrigues

REQUIMTE/LAQV – Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto
*jrodrigosantos@fc.up.pt

The quality evaluation of raw coffee beans is a very important task that defines the market price of this commodity. The presence of defective coffee beans within a green coffee batch is one of the quality's parameter greatly surveyed in coffee evaluation, since the presence of bean defects in the final coffee brew, deeply decreases the consumers' preference for this drink. The main coffee bean defects are the black, sour and immature beans. The presence of these beans is due to, e.g. overripe beans/ immature beans harvest and/or deficient post-harvest processing. In this work, profiling of the volatile carbonyl in defective green coffee beans was aimed. These compounds were selected as target compounds since they have been thoroughly studied in food samples due to their strong organoleptic impact. Therefore, the identification of carbonyl marker compounds of defective green beans can be viewed as an important chemical marker that help in green coffee bean quality evaluation.

A second aim of this work was to develop an extraction process for volatile compounds that avoided sample heating. This is a relevant feature since heating procedures, usually followed to help in the volatiles liberation, can easily adulterate food sample's chemical composition. To this end, the following extraction strategy was exploited: initially, a defined mass of sample and a recipient containing an acceptor solution are poured inside a closed flask featuring a fan in the inner part of the flask's cap (Fig.1). The idea of using a fan is to enhance volatile compounds mass transport from the solid sample to the acceptor solution. The flask is then closed, the fan turned on and, after a defined period, the acceptor solution is collected and analyzed by HPLC-DAD-MS/MS.

The experimental results concerning the impact of the fan upon the volatiles' compounds extraction shown that the strategy presented enable to significantly enhance the volatile compounds mass transfer process at room temperature conditions. The experimental results regarding the profile of volatile carbonyl compounds of defective beans of robusta and arabica coffee species enabled to identify some carbonyl compounds that occur in higher amounts in defective beans [1].

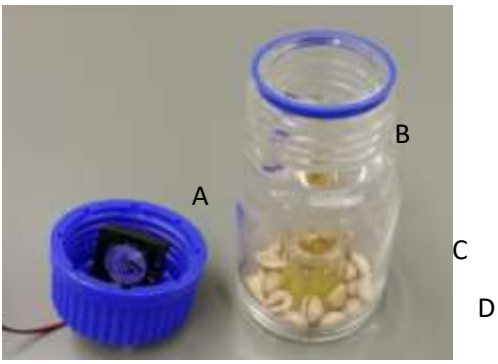


Fig.1. Fan-assisted extraction apparatus. A – cap with electric fan; B - 100 mL flask; C – container with acceptor solution; D - coffee sample.

Acknowledgments
The work was supported by UID/QUI/50006/2019 with funding from FCT/MCTES through national funds. J.R. Santos thanks FCT (Fundação para a Ciência e Tecnologia) for funding through program DL 57/2016 – Norma transitória.

References

[1] João Rodrigo Santos, José A. Rodrigues, Food Control, 108 (2020) 106879.

Evaluación del perfil fenólico individual de *Calluna vulgaris* (L.) y de su potencial bioactivo

Anxo Carreira-Casais[1,2], Paula García-Oliveira[2,3], Cristina Caleja [2] Eliana Pereira[2,*], M.A. Prieto[2,3], Jesús Simal-Gándara[3], Jorge Perez-Juste[1], Lillian Barros[2], Isabel C.F.R. Ferreira[2]

[1]Departamento de Química-Física, Centro de Investigaciones Biomédicas de Galicia (CINBIO) Universidad de Vigo E36310, Vigo, España

[2]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[3]Grupo de Nutrición y Bromatología, Facultad de Ciencias y Tecnología de los Alimentos, Universidad de Vigo, Campus de Ourense, E32004 Ourense, España.

**eliana@ipb.pt*

En la actualidad, existe una tendencia en el consumo de alimentos más nutritivos y que aporten beneficios para la salud [1]. En este contexto, el consumo de plantas ha demostrado ser beneficioso, debido a la presencia de diversos nutrientes y moléculas bioactivas con propiedades funcionales. Los polifenoles son un grupo de compuestos que, según diversos estudios, han demostrado propiedades antioxidantes, anti-inflamatorias, antimicrobianas y antitumorales, entre otros, ejerciendo efectos terapéuticos sobre diversas enfermedades [1,2]. Así en el presente trabajo se determinó el perfil individual de compuestos fenólicos en los extractos hidroetanólicos e infusiones obtenidas a partir de las flores de *Calluna vulgaris* (L.); así como las propiedades bioactivas a través de ensayos *in vitro* de actividad antioxidante y antimicrobiana.

Los compuestos fenólicos individuales se analizaron mediante HPLC-DAD-ESI/MS. La actividad antioxidante se evaluó a través de las metodologías de TBARS y OxHLIA; la actividad antimicrobiana se determinó usando el método de microdilución en bacterias Gram-positivas y Gram-negativas, y en hongos; y finalmente, la hepatotoxicidad se estimó usando un cultivo de células primarias no tumorales (PLP2) y aplicando el ensayo de sulforhodamina B.

En la evaluación del perfil fenólico individual, en ambos extractos evaluados (hidroetanólico e infusión) fue evidente la presencia de 20 compuestos fenólicos, de los cuales siete fueron identificados como ácidos fenólicos y trece como flavonoides. La quercetina-3-*O*-ramnosida se destacó como el compuesto principal. Con respecto a la actividad antioxidante, ambos ensayos testados mostraron valores promisorios de EC_{50}, que tradujeron el excelente potencial antioxidante de la especie. Lo mismo sucedió con la actividad antimicrobiana, donde se demostró el potencial bacteriostático, bactericida y fungicida contra las cepas de bacterias y hongos analizados. También fue probado la ausencia de toxicidad del estrato hidroetanólico y la infusión de *C. vulgaris*.

Este estudio concluyó que *C. vulgaris* es una flor rica en moléculas bioactivas, especialmente flavonoides y ácidos fenólicos, que pueden generar un gran interés en la industria alimentaria y farmacéutica.

Agradecimientos

Los autores agradecen a la FCT, Portugal y FEDER bajo el Programa PT2020 por el apoyo financiero a CIMO (UID/AGR/00690/2019). L. Barros agradece a FCT, P.I., a través del contrato institucional del programa científico de empleo; contrato de investigación de C. Caleja (proyecto AllNatt, POCI- 01-0145-FEDER-030463); y a lo Programa FEDER-Interreg España-Portugal pelo apoyo financiero a través del proyecto 0377_Iberphenol_6_E. Agradecen tambien al Ministerio de Ciencia, Innovación y Universidades por el soporte económico del investigador pre-doctoral Anxo Carreira Casais y a la Xunta de Galicia “Programa de axudas á etapa predoutoral da Xunta de Galicia” por el apoyo financiero a la investigadora pre-doctoral Paula García Oliveira. A la Xunta de Galicia por el soporte financiero de las “Axudas Conecta Peme” al proyecto IN852A 2018/58 NeuroFood.

Referencias

[1] P. B. Gollücke, R. C. Peres, D. A. Ribero, O. Aguiar in Polyphenols: Mechanisms of Action in Human Health and Disease, R.R Watson, V. R. Preedy, S. Zibadi (Eds.), Academic Press, 2018, 11.

[2] Manach, D. Milenkovic, T. Van de Wiele, A. Rodriguez-Mateos, B. de Roos, M. T. García-Conesa… C. Morand, Molecular nutrition & food research, 61(2017)

QUÍMICA Y MEDIOAMBIENTE

Construcción de un micro-prototipo de sistema de electrocoagulación para funcionamiento en flujo continuo

Acosta N. Gema[1, *], Bourdon G. Alejandro[2]
García B. Anguie[3], Ruiz L. Johann[4], Salazar R. Esteban[5]
[1]Universidad Militar Nueva Granada, Dirección, Bogotá, Colombia
gema.acosta@unimilitar.edu.co

De acuerdo con ensayos realizados con anterioridad para remoción de cromo(VI) en aguas y con el objetivo de implementar un sistema más eficiente, se propone diseñar y construir un reactor a escala para medir el tiempo de reacción por el método de electrocoagulación.

El tanque del reactor se fabrica tomando tubos PVC comerciales de 2,3 y 4 pulgadas. Para determinar el diámetro adecuado del orificio de salida se perfora el contenedor (6,12; 6,22 y 5,30) mm respectivamente, para permitir el flujo libre, de 500 mL de agua. Posteriormente a este orificio, se le coloca un tubo de 5,37 mm de diámetro con posición vertical al tanque, para simular el micro reactor midiendo el tiempo que tarda en desocuparse el tanque.

De la tabla 1, se puede establecer la ecuación a partir de datos experimentales $y = -0.0019x^2 + 0.4194x - 0.4554$, esta nos permite relacionar matemáticamente el diámetro interno del tanque (x), y el tiempo de desalojo (y), de 500 mL de solución acuosa, de igual forma la ecuación indica cual tamaño de diámetro del tanque es proporcional al tiempo de desalojo.

En todos los casos estudiados, al emplear el mismo tamaño para reducción de diámetro en la salida de los tanques, se encontró que disminuye el tiempo de desalojo. Finalmente, se seleccionó el tanque de 2 pulgadas debido a que muestra mayor precisión en los resultados, (menor desviación estándar).

El área de acceso al reactor debe ser de aproximadamente $22.64\ mm^2$ para obtener un tiempo de residencia de la solución contaminada en el reactor, cercano a 20 segundos. Basados en los resultados obtenidos hasta el momento, se proyecta que el reactor se pueda fabricar como un paralelepípedo con medidas internas: largo $200\ mm$, ancho (distancia entre placas) $10\ mm$ y profundidad $2.264\ mm$.

Tabla 1. Tiempo de desalojo respecto diámetro de reactor

Diámetro reactor [mm]	Tiempo de desalojo [s]
56,95	17,212
77,53	20,526
111,3	22,432

Referencias

[1] [1] G. Niño Eunice Acosta, A. B. García and C. A. C. Barrera, "EVALUACIÓN Y REGULACIÓN DE PARÁMETROS EN UN EQUIPO DISEÑADO PARA LA DISMINUCIÓN DE CROMO(VI), PROVENIENTES DE LA INDUSTRIA DE RECUBRIMIENTOS GALVÁNICOS/EVALUATION AND PARAMETERS REGULATION IN EQUIPMENT DESIGNED FOR DECREASE OF CHROMIUM(VI), COMING FROM GALVANIC COATINGS INDUSTRY: SCIENCE AND ENGINEERING NEOGRANADINA SCIENCE AND ENGINEERING NEOGRANADINA," Ciencia e Ingeniería Neogranadina, vol. 23, (1), pp. 107-116, 2013.

[2] BARRAZA, A. P. PROPUESTA DE TRATAMIENTO PARA EL AGUA RESIDUAL INDUSTRIAL. BOGOTÁ, COLOMBIA. (2016).

[3] Edwar Alejandro Aguilar Ascon , “EVALUACIÓN DE LA EFICIENCIA DE UNA CELDA DE ELECTROCOAGULACIÓN A ESCALA LABORATORIO PARA EL TRATAMIENTO DE AGUA”, UNIVERSIDAD NACIONAL MAYOR DE SAN MARCOS, 24P. (2015).

Elaboración de un montaje para hallar la curva de volumen de gases generados en un proceso de electrocoagulación

Acosta N. Gema[1, *], Bourdon G. Alejandro[2]
García B. Anguie[3], Ruiz L. Johann[4], Salazar R. Esteban[5]
[1]Universidad Militar Nueva Granada, Dirección, Bogotá, Colombia
gema.acosta@unimilitar.edu.co

Durante el proceso de electrocoagulación se generan gases en los electrodos, debido a los métodos electroquímicos propios de la técnica. Con el objetivo de establecer el volumen de gases generados, se propone realizar el montaje (Fig.1) y determinar la gráfica del volumen en función del tiempo, para orientar trabajos posteriores de caracterización de los gases. Con base en la composición de la mezcla gaseosa, se espera hacer disposición final de manera sustentable.
Los gases generados en el reactor se conducen a una bureta invertida, en cuya entrada se instala un generador de burbujas, para determinar la rapidez del flujo respecto al avance del proceso de electrocoagulación, con éste resultado poder generar la curva de volumen de gases generados en el desarrollo del tratamiento del agua.
Se determina que el montaje permite medir rapidez y velocidad de los gases producidos en una reacción.

RESULTADOS

- Foto del montaje. (vea figura 1).
- Se logra establecer el buen funcionamiento del montaje en cuanto a la medida del flujo de gases.
- Los diámetros de los ductos son suficientes para evitar presurización en el equipo.

SUGERENCIAS

- Humectar internamente la bureta con la sustancia antes de comenzar el proceso.
- Concentración aproximada tenso activo 5%, mayor concentración genera espuma.
- La manguera dentro de la probeta invertida debe estar por debajo de la escala de medida.
- Realizar ensayos preliminares de sellado para evitar fugas usando bicarbonato y ácido.
- Recomendable uso de manguera siliconada.
- Corregir el volumen del gas recogido con respecto a la altura de la columna de agua.

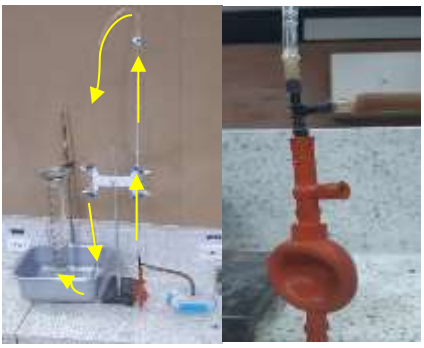


Figura 1. Montaje para medición de flujo de gases

Referencias
[1] Al-Qodah, Zakaria; Al-Shannag, Mohammad; Bani-Melhem, Khalid; Assirey, Eman; Mohd Adib Yahya; et al..Environmental Chemistry Letters; Dordrecht Tomo 16, N.º 3, (Sep 2018): 695-714. DOI:10.1007/s10311-018-
[2] Álvaro Arango Ruiz1. La electrocoagulación: una alternativa para el tratamiento de aguas residuales. 2005.
[3] ECKENFELDER, W.W. and CECIL, L. K. Application of New Concepts of PhysicalChemical Wastewater Treatment .Vanderbilt University; Nashville, TN.: Pergamon Press, Inc.

A comparison of three digestion methods to extract microplastics from marine plankton samples

Jose M. Andrade*, Adrián López-Rosales, Verónica Fernández-González, Purificación López-Mahía, Soledad Muniategui

Grupo de Química Analítica Aplicada e Instituto Universitario de Medio Ambiente (IUMA).
Universidade da Coruña. Campus da Zapateira s/m 15071, A Coruña, España.
*andrade@udc.es

The characterization of existing microplastics (MPs) in marine environmental samples is essential to know their impact and carry out actions to fight against this type of pollution of the oceans. However, there are still no standardized protocols or reference methods to determine them in the different environmental matrices. One of the least studied is plankton, which is of big importance in the food chain. It was reported that zooplankton can ingest microplastics [1,2], and in turn, fish could also incorporate them into their organisms by confusion or by ingestion of zooplankton [3].

The most widely adopted strategy for treating biological samples consists of digesting organic matter, filtering and identifying microplastics, generally with FTIR microscopy. The destruction of organic matter is usually based on enzymatic digestions, alkaline treatments (such as KOH), and oxidative treatments (such as H_2O_2). But the latter two still present many doubts about whether the polymers are totally preserved. This study compares three methods for the treatment of plankton samples: an alkaline treatment based on 10 % KOH; another enzymatic treatment combining SDS, protease and lipase; and a single treatment with SDS. In all three, a final step was performed with H_2O_2 to complete the destruction of organic matter. For these experiments, representative samples of Galician coastal plankton were generated, spiked with microplastics (range 300-70 µm).

Organic matter destruction was checked, and analytical recovery was evaluated for each type of plastic (PP, PS, PE, PET, PA and PVC). The characterization combines stereomicroscopy and FTIR microscopy (in reflectance mode). To save time in the search for microplastics with the FTIR microscope, aluminium plates with small cavities were designed to deposit a single suspicious microplastic per cavity.

All methods digest the organic matrix fine. But the results show doubts about the strict necessity of enzymes for this type of matrix in comparison with the use of SDS plus H_2O_2. Both methods show the same destruction of organic matter. The alkaline treatment could be harmful to PS if the incubation time is exceeded. The most suitable method appears to be the combined use of SDS and H_2O_2 due to its low cost and the negligible damage to the studied polymers.

Acknowledgements

The Spanish Government (Ministerio de Economía y Competitividad) and the JPI-Oceans European Program are acknowledged by the BASEMAN Project (PCIN-2015-170-C02-01, with FEDER funds). Thanks are given also to the Spanish Government by the CTM2016-77945-C3-3-R (ARPA-ACUA) Grant. The Galician Government ("Xunta of Galicia") is acknowledged for its support to the QANAP group (Programa de Consolidación y Estructuración de Unidades de Investigación Competitiva. Ref. ED431C 2017/28) partially financed by FEDER funds.

References

[1] Desforges J-PW, Galbraith M, Ross PS. Ingestion of Microplastics by Zooplankton in the Northeast Pacific Ocean. Arch Environ Contam Toxicol 2015;69:320–30. doi:10.1007/s00244-015-0172-5.
[2] Sun X, Li Q, Zhu M, Liang J, Zheng S, Zhao Y. Ingestion of microplastics by natural zooplankton groups in the northern South China Sea. Marine Pollution Bulletin 2017;115:217–24. doi:10.1016/j.marpolbul.2016.12.004.
[3] Kang J-H, Kwon O-Y, Shim WJ. Potential Threat of Microplastics to Zooplanktivores in the Surface Waters of the Southern Sea of Korea. Arch Environ Contam Toxicol 2015;69:340–51. doi:10.1007/s00244-015-0210-3.

AVALIAÇÃO DA CAPACIDADE DE COMPOSTO PRODUZIDO INDUSTRIALMENTE PARA REMOÇÃO DE PARACETAMOL DE ÁGUAS

O.T. Andrade[1], P. Bettencourt[1], P. Ramísio[2], F. Bento[1], D. Geraldo[1], M.F. Proença[1]

[1] Departamento de Química, Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal.

[2] Centro de Território, Ambiente e Construção, Escola de Engenharia, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal.

*andradeotilia33@gmail.com

O composto é um material produzido pela decomposição de matéria orgânica através de um processo denominado de compostagem. Neste processo ocorre uma estabilização da matéria orgânica, com formação de moléculas ricas em estruturas aromáticas contendo grupos hidroxilo e carbonilo [1]. Estas estruturas químicas, usualmente classificadas de substâncias húmicas, oferecem um enorme potencial para estabelecer interações intermoleculares. Esta potencialidade é altamente desejável, permitindo a sua utilização na construção de filtros para o tratamento terciário de águas residuais [2].

O paracetamol é um composto ativo amplamente utilizado como fármaco possuindo propriedades analgésicas e antipiréticas, sendo a sua administração feita em humanos ou animais, e posteriormente libertados no meio ambiente por várias vias. A ocorrência deste fármaco e seus metabolitos nas águas residuais é descrita como uma preocupação crescente, sendo nocivos para os organismos aquáticos e podendo mesmo apresentar riscos para a saúde humana [3].

Inserido no âmbito do projeto Res2ValHum [4], foi efetuado um estudo preliminar em *batch* onde se testou a remoção de paracetamol utilizando composto produzido industrialmente em túnel, a partir de resíduos urbanos provenientes de recolha seletiva. As soluções de paracetamol usadas tinham concentrações compreendidas entre 20 e 375 mg L^{-1} (C_0) e as massas de composto testadas foram entre 0,5 e 4,5 g ($m_{composto}$). Os ensaios foram realizados ao longo do tempo e monitorizados recorrendo a HPLC - DAD. Foi estudada a influência de parâmetros, como a concentração inicial de fármaco, a massa de composto, o pH e a presença de surfactantes (presentes em águas residuais, "águas cinzentas"). Verificou-se que a percentagem de remoção depende da massa de composto e da concentração inicial de paracetamol. Os resultados reportados na **Figura 1** foram calculados a partir das concentrações de paracetamol em solução medidas para um tempo de 60 min, C_{eq} (Concentração de equilíbrio).

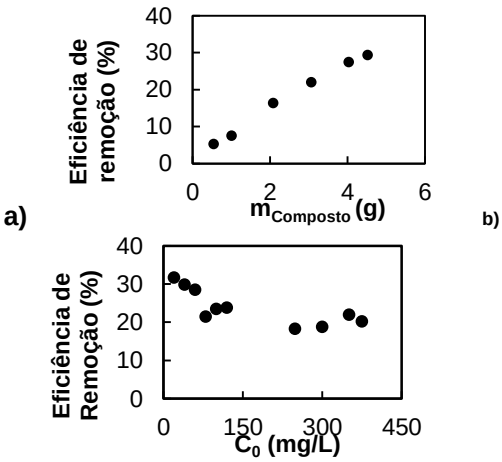


Fig 1. Eficiência de remoção do paracetamol, $(C_0-C_{eq})/C_0$, para diferentes: **a)** massas de composto (C_0 = 150 mg L^{-1}). **b)** concentrações de paracetamol ($m_{composto}$ = 2,5 g)

Agradecimentos

Este trabalho foi cofinanciado pelo Programa Interreg V-A Espanha-Portugal (POCTEP) 2014-2020 e a União Europeia através do Fundo Europeu de Desenvolvimento Regional - FEDER no âmbito do projeto RES2VALHUM - Valorização de Resíduos Orgânicos: Produção de Substâncias Húmicas (0366_RES2VALHUM_1_P).

Referências

[1] A. Cerda, A. Artola, X. Font, R. Barrena, T. Gea, A. Sánchez, Composting of food wastes, 248 (2018) 57–67.

[2] D.C.H. Seremeta, C.P. da Silva, R. Zittel, S.X. Campos, S. Xavier, Environmental Science and Pollution Research**,** 26 **(**2019) 797-805**.**

[3] G. Zhang, Y. Sun, C. Zhang, Z. Yu, Journal of Hazardous Materials 323 (2017) 719–729**.**

[4] Information on http://www.res2valhum.org

EXTRACCIÓN Y DETERMINACIÓN DE Cd, Pb, As y Sb EN AGUA EMPLEANDO REDES METALO-ORGÁNICAS DE LA FAMILIA UiO-66

Juan Carlos Becerra Rodríguez[1], Jorge Luis Guzmán Mar[1], Carlos Palomino Cabello[2], Gemma Turnes Palomino[2] y Laura Hinojosa Reyes[1*]

[1]Universidad Autónoma de Nuevo León, Facultad de Ciencias Químicas, Departamento de Ingeniería Química, Ave. Universidad S/N, Cd. Universitaria, San Nicolás de los Garza N.L. México, C.P. 66455.

[2]Universidad de les Illes Balears, Departamento de Química, , Carretera de Valldemossa, km 7.5, Palma, Illes Balears, España C.P. 07122

**e-mail del autor de contacto laura.hinojosary@uanl.edu.mx*

Una de las principales fuentes de contaminación por metales pesados en agua subterránea es la que procede de zonas mineras. En estos efluentes se han reportado la presencia de metales y metaloides como cadmio (Cd), plomo (Pb), arsénico (As) y antimonio (Sb) [1]. Los límites permisibles para estos metales y metaloides, según la NOM-201-SSA1-2015, son de 3 µg L^{-1} para Cd, 10 µg L^{-1} para As, 5 µg L^{-1} para Sb y 10 µg L^{-1} para Pb [2]. Desde hace unos años, gracias a su elevada área superficial y volumen de poros, así como a su fácil funcionalización con diferentes grupos funcionales [3], se viene estudiando el uso de las redes metalo-orgánicas (MOFs) como materiales adsorbentes para la extracción en fase sólida de diferentes contaminantes orgánicos e inorgánicos. Así, el objetivo de este estudio fue desarrollar un método analítico para la determinación de Cd, Pb, As y Sb en agua de una zona minera en San Luis Potosí (S.L.P.), México basado en el uso de las redes metal-orgánicas UiO-66, UiO-66-NH_2 y UiO-66-$(COOH)_2$ como adsorbentes para la extracción en fase sólida de los elementos indicados y de la Espectroscopia de Fluorescencia Atómica (AFS-HG) y Espectroscopia de Absorción Atómica (AAS) como métodos de detección. Los MOFs anteriormente indicados se prepararon y caracterizaron por SEM, XRD, FTIR y fisisorción de nitrógeno. Para la preconcentración se usaron 25 mg de adsorbente y 100 mL de una muestra de agua con una concentración conocida de los metales de interés. Como eluente se empleó 10 mL de HCl 1.2 M + tiourea 1.4 M. La cuantificación de los distintos elementos se llevó a cabo mediante AAS y HG-AFS. El muestreo de agua subterránea se realizó en seis puntos de la zona minera de S.L.P., México. Haciendo uso de un diseño central compuesto centrado en las caras se evaluó el efecto del pH de la disolución y el tipo de material adsorbente sobre la adsorción de Cd, Pb, As y Sb. Las mayores capacidades de adsorción para los metales estudiados (114.9 mg g^{-1} para Pb, 24.5 mg g^{-1} para Cd, 19.4 mg g^{-1} para Sb y 20.9 mg g^{-1} para As) fueron obtenidas con el material UiO-66-$(COOH)_2$ a pH 6. Los resultados de determinación después de la preconcentración se muestran en la Tabla 1 (n=5). El material UiO-66-$(COOH)_2$ permitió la preconcentración de Cd, Pb, As y Sb en muestras de agua subterránea obteniéndose límites de detección de entre 0.22 y 3.1 µg/L y porcentajes de recuperación de entre 74.1 y 112.7%.

Tabla 1. Concentraciones detectadas y porcentajes de recuperación (50 µg L^{-1} de c/u adicionado) de Cd, Pb, As y Sb en agua subterránea después de preconcentración con UiO-66-$(COOH)_2$

Muestra	As (µg L^{-1})	Recuperación As (%)	Sb (µg L^{-1})	Recuperación Sb (%)	Cd (µg L^{-1})	Recuperación Cd (%)	Pb (µg L^{-1})	Recuperación Pb (%)
Zona 1	35.4±1.4	91.2±3.5	5.4±2.7	76.2±1.2	ND*	90.0±3.8	17.0±1.4	86.8±0.2
Zona 2	35.6±0.8	92.6±0.9	22.0±0.3	74.1±3.4	ND*	81.0±3.4	24.0 ± 1.8	80.8±0.3
Zona 3	37.9±0.9	89.6±2.0	19.5±0.3	84.8±2.1	ND*	78.0±3.3	10.0 ±0.3	90.5±3.6
Zona 4	34.8±1.1	97.9±2.2	16.0±0.8	82.2±2.0	ND*	90.0±3.8	12.0 ± 1.1	88.9±2.2
Zona 5	27.6±1.1	87.0±1.6	6.7±1.8	80.9±3.2	ND*	84.0±3.6	12.0 ±1.4	93.5±4.2
Zona 6	25.7±1.4	112.7±2.6	11.7±1.5	78.5±2.2	ND*	94.5.±2.0	18.0 ±0.6	94.2±4.0

*LOD Cd= 2.3 µg L^{-1}, LOD Pb= 3.1 µg L^{-1} LOD As= 0.22 µg L^{-1} LOD Sb= 0.98 µg L^{-1}

Agradecimientos

Los autores agradecen a Universidad Autónoma de Nuevo León (PAICyT UANL 2019) y a CONACYT-México por el apoyo financiero, así como a la Agencia Estatal de Investigación (AEI) y al Fondo Europeo de Desarrollo Regional (FEDER) por su financiación a través del proyecto CTQ2016-77155-R (AEI/FEDER, UE).

Referencias

[1] H. Passow., Rothstein, A., and Clarkson, T. W. Pharmacological Reviews vol. 5, (1961) pp. 185–224.

[2] Secretaría de Salud, "NORMA Oficial Mexicana NOM-201-SSA1-2015, Disponible: http://dof.gob.mx/nota_detalle.php?codigo=5420977&fecha=22/12/2015. (2015)

[3] N. A. Khan and S. H. Jhung, J. Hazard. Mater., vol. 325 (2017) pp. 198–213

[4] J. H. Cavka, U. Olsbye, N. Guillou, S. Bordiga, and K. P. Lillerud, J. Am. Chem. Soc., vol. 6. (2008) pp. 1–19.

Metals concentrations and removal along the SBR Wastewater Treatment Plant of Torres Vedras, Portugal

P. Cantinho[1,2 *], M.M. Correia dos Santos[2], M. A. Trancoso[3], E. Cortês[4], M. Matos[1,5]

[1] Instituto Superior de Engenharia de Lisboa, ADEQ, R. Conselheiro Emídio Navarro, 1949-014, Lisboa, Portugal
[2] Centro de Química Estrutural, IST, UL, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[3] Laboratório Nacional de Energia e Geologia, LBB, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal
[4] Águas do Tejo Atlântico, Fábrica da Água de Alcântara, Avenida de Ceuta 1300-254, Lisboa, Portugal
[5] Instituto de Telecomunicações, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

**pcantinho@deq.isel.ipl.pt*

The concerns on metals in municipal Wastewater Treatment Plants (WWTPs) discharges are mainly related with its contents in sludge, which can prevent its application in land and so the recycling of valuable nutrients, and with the more restrictive limits foreseen for final effluents, due to the recent guidelines introduced by the European Water Framework Directive (EUWFD) [1]. The last upgrade of the EUWFD [2] lists 45 priority pollutants, whose emissions to the environment must cease (priority hazardous substances) or be reduced in order to meet the Environmental Quality Standards (EQS) and so achieve a good status for all surface waters in the future. Four metals were classified as priority substances, Cd, Hg, Ni and Pb, the top two also classified as hazardous. Other metals as As, Cu, Cr and Zn are also frequently included in the additional list of substances that may become classified as priority in the near future [3]. The literature review shows that the understanding of metals behaviour and fate throughout WWTPs is a crucial issue face to the more stringent discharge quality requirements for the final effluent and final sludge. Relevant data have been published in recent decades, but the findings still remain insufficient and quite contradictory in many fields [4][5], thus the need of more research is consensual, particularly by considering data collected from full scale WWTPs [5].

The present work is part of a larger one concerning Torres Vedras WWTP (SBR, low load, F/M=0.08 d^{-1}, SRT=8.7 d) (*Águas do Tejo Atlântico*), carried out with the final aim of establishing a simulation model that allows predicting the behaviour and fate of eight metals along the treatment. Experimental data were obtained from two sampling campaigns (Spring/Summer and Autumn/Winter) involving an exhaustive collection of composite samples in all flows of the liquid and solid phases of the treatment system. Metals determinations in the matrices were conducted according to in-house accredited methods at LNEG, carefully followed by actions of validation and quality control. Here, we present the results obtained in the characterization of As, Cd, Pb, Cu, Cr, Hg, Ni and Zn through the treatment system, namely its total and soluble concentrations in all the matrices and the removal/concentration ratios of total metals relative to the influent wastewater. Also, results for the metals overall removal efficiencies in the liquid phase of treatment are shown, and the quality of final effluent and sludge face to the current legal limits and to the future more restrictive scenarios are assessed.

The comparative analysis of the obtained total concentrations for As, Cd, Pb, Cu, Cr, Hg, Ni and Zn, in the raw wastewater (1.9, 0.3, 10.2, 58.7, 2.5, 0.7, 4.0 and 161.9 µg/L, respectively), final effluent (1.5, 0.3, 5.5, 7.0, 0.9, 1.0, 2.1 and 29.3 µg/L, respectively) and final sludge (5.6, 0.9, 28.9,170.9, 18.7, 0.6, 16.1 and 600.4 mg/kg d.w., respectively) with those reported in the literature [4][5], shows that they are all within the lower limit of the range of results found in other WWTPs worldwide. Metals overall removal efficiencies are about 80% for Cu and Zn, 64% for Cr, 45-50% for Pb and Ni and 20% for As; for Hg a negative removal is observed (-43%). Results for final effluent and sludge show compliance to the current legal limits. Regarding the EQS introduced by the EUWFD for priority metals, the final effluent only shows no compliance for Hg. Concerning the very stringent limits already set by some countries for final sludge, there is no compliance for Cu and Zn.

References

[1] Directive 2000/60/EC of 23 October 2000 of the European Community. Official Journal L 327 of 22.12.2000.
[2] Directive 2013/39/EU of 12 August 2013 of the European Community. Official Journal L 226 of 24.08.2013.
[3] S.M. Ruel, J.-M. Choubert, P. Ginestet, M. Coquery, *Water Science and Technology*, 57 (2008) 1935-1942.
[4] A.J. Hargreaves, C. Constantino, G. Dotro, E. Cartmell, P. Campo, *Environ.Technol. Reviews*, 7 (2018) 1-18.
[5] P. Cantinho, M. Matos, M.A. Trancoso, M.M. Correia dos Santos, *Int. J. Environ. Sci. Technol.*,13 (2016) 359-386.

Metals sorption and partitioning coefficients in all matrices of the Torres Vedras SBR WWTP, Portugal

P. Cantinho[1,2 *], **M.M. Correia dos Santos**[2], **M. A. Trancoso**[3], **E. Cortês**[4], **M. Matos**[1,5]

[1] Instituto Superior de Engenharia de Lisboa, ADEQ, R. Conselheiro Emídio Navarro, 1949-014, Lisboa, Portugal
[2] Centro de Química Estrutural, IST, UL, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[3] Laboratório Nacional de Energia e Geologia, LBB, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal
[4] Águas do Tejo Atlântico, Fábrica da Água de Alcântara, Avenida de Ceuta 1300-254, Lisboa, Portugal
[5] Instituto de Telecomunicações, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

**pcantinho@deq.isel.ipl.pt*

The literature review concerning the issue of metals behaviour and fate throughout WWTPs shows that, although relevant data have been published in recent decades, results are not consensual and more studies are needed, particularly from data obtained in full scale WWTPs [1]. Specifically, there are few published works reporting experimental values of metals sorption and partitioning coefficients (k_{sor} and K_D, respectively) from full scale WWTPs, and they do not usually distinguish between the different matrices [1][2]. Metals partitioning in the unit processes is a key point when intending to approach a model describing the fate and transport of metals in a WWTP; upon knowing this information together with that of solids generation/removal, the metal concentrations in the effluent and the metal removal efficiency can be estimated [3]. However, for each metal, it is required to differentiate k_{sor} and K_D according to the type of matrix, at least for the activated sludge, raw wastewater and final effluent, once they may be quite different due to the different physicochemical characteristics of the matrices [4]. In this context, the experimental results obtained within the present work aim to contribute with more in-depth data concerning this issue.

This work is part of a larger one concerning Torres Vedras WWTP (SBR, low load, F/M=0.08 d^{-1}, SRT=8.7 d) (*Águas do Tejo Atlântico*), carried out with the final aim of establishing a simulation model that allows predicting the behaviour and fate of eight metals along the treatment system. Experimental data were obtained from two sampling campaigns (Spring/Summer and Autumn/Winter) involving an exhaustive collection of composite samples in all flows of the liquid and solid phases of the treatment system. Metals (total and soluble) determinations in the matrices were conducted according to in-house accredited methods at LNEG, carefully followed by actions of validation and quality control.

This communication presents the ksor obtained for As, Cd, Pb, Cu, Cr, Hg, Ni and Zn, in all the matrices along the treatment system, and highlights the possible meaning arising from its relative comparison, and in relation to the amount and nature of the suspended solids present. These results, together with the obtained K_D (table 1), allow to estimate metals concentrations and partitioning through the WWTP.

Table 1. Partitioning coefficients, **K_D (L/kg) = {M_S}/{SS})/[M_d]**, obtained from experimental data along Torres Vedras treatment system; {M_s}: sorbed metal (µg); {SS}: Suspended Solids (kg); [M_d]: dissolved metal concentration (µg/L)

	log K_D (L/kg)							
Matrices	**As**	**Cd**	**Pb**	**Cu**	**Cr**	**Hg**	**Ni**	**Zn**
Raw Wastewater	2.9		4.1	4.6	3.7	2.0	2.8	3.5
Pre-treatment Effluent	2.8	3.8	4.1	4.8	3.7	3.6	3.4	3.6
Returned liquor from Thickening	3.6	3.3	4.5	5.1	4.2	3.2	3.7	4.2
Returned liquor from Dewatering	3.0		3.3	4.7	4.0	3.1	3.2	3.8
Biological Reactor (**SBR**)	3.6	3.3	4.1	5.0	4.6	3.0	3.7	4.2
Final Effluent	3.6		4.5	5.1	4.2	4.4	3.6	3.0
Sludge purge from SBR	3.5	3.5	4.1	5.0	4.5	3.2	3.8	4.4

References

[1] P.Cantinho, M. Matos, M.A. Trancoso, M.M. Correia dos Santos, *Int. J. Environ. Sci. Technol.*,13 (2016) 359-386.
[2] A.J. Hargreaves, C. Constantino, G. Dotro, E. Cartmell, P. Campo, *Environ.Technol. Reviews*, 7 (2018) 1-18.
[3] Wang, J., Huang, C.P., Allen, H. E., *Water Research*, 40 (2006) 1333-2340.
[4] M. Pomiès, J.-M.Choubert, C. Wisniewski, M. Coquery, *Science of the total Environment* 443 (2013) 733-748

Formas de hierro y aluminio en suelo rizosferico y no rizosferico desarrollado sobre cenizas volcánicas del Volcan Cotopaxi, Ecuador

Jaime Caza Caza[1*], Xose Luis Otero[1], Paulina Guevara Garcia[1,2]
[1] Departamento de Edafoloxía e Química Agrícola, Facultade de Biología Universidade de Santiago de Compostela, 15782 Santiago de Compostela, España
[2]Universidad de las Fuerzas Armadas ESPE, Av. El Progreso S/N, Sangolqui, Ecuador
*jaimehumberto.caza@rai.usc.es

Los páramos son ecosistemas neotropicales de alta montaña localizados entre el límite del bosque cerrado y las nieves perpetuas en los Andes [1]. Se caracterizan por la vegetación de poca altura y niveles altos de endemismo. Los suelos de los páramos del Ecuador se han desarrollado esencialmente sobre los depósitos piroclásticos resultantes de las erupciones de los numerosos edificios volcánicos, [2]. Pero su morfología y propiedades varían considerablemente según los principales factores de la pedogénesis, como la edad, la naturaleza, la composición química de los materiales y las condiciones climáticas.

Se determino las formas de hierro y aluminio en suelos Rizosfericos $_{(R)}$ y No Rizosfericos $_{(Bulk)}$ en la Chuquiragua, planta que crece en los páramos cercanos al volcan Cotopaxi (Ecuador), se muestreo la Rizosfera a profundidades de 0-10 cm y 10-20 cm y el suelo No rizosferico cercano a 50 cm. Las técnicas de la extracción selectiva para Al y Fe. Se uso los siguientes extractantes: (1) Pirofosfato sódico . Con el cual se solubilizan los complejos orgánicos de Al(piro) y Fe(piro). (2) Oxalato amónico 0.2 M tamponado a pH 3 [3]; este extractante es una mezcla de oxalato amónico y oxalato ácido en proporción 1:0.75 para la extracción de formas de Al(oxa) y Fe(oxa) ligadas a óxidos amorfos, óxidos hidratados, aluminosilicatos no cristalinos y a la M.O.(3) Ditionito–citrato sódico 0.5M en medio reductor [4], se solubilizan óxidos cristalinos de Fe, así como el Fe presente en compuestos inorgánicos no cristalinos. El Fe y Al total $_{(Fet\ y\ Alt)}$ se extrajeron por digestión ácida.

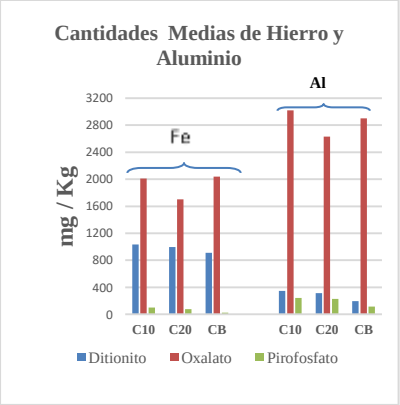


Fig. 1

En la fig.1 el Fe(oxa) y Al(oxa) es mayor que Fe(piro) y Al(piro), indicando mayor alteración mineral en el Bulk (CB) y la rizosfera (C10, C20). Los datos muestran diferencias significativas ($P < 0.05$) entre las formas de Fe(piro), Al(piro) en suelo rizosferico y bulk contrario a las formas extraídas con Fe (oxa) , Al(oxa).
La cantidad de Fe y Al siguen la secuencia Fe oxa >> Fe (piro) > Fe (dit) ; Al (oxa) >> Al (piro) > Al(dit) La relación del Fe(dit) con el Fe total (FeT) utilizada como índice de alteración [5] ,entre 4.0 % ± 0.56 - 4.5 % ± 1.4 expresa la transformación del hierro contenido en los silicatos ,en los óxidos de hierro pedogénicos. El Al (piro) con valores de 0.011% a 0.024%, afirma que los suelos son insipientes y ni el Fe ni Al representan un papel relevante en la floculación y la meta estabilización de materia orgánica.

Referencias

[1] P. Mena, C. A. S. Flores, R. Hofstede, C. Josse, S. Lasso, G. Medina, N. Ochoa y D. Ortíz, Páramo. Paisaje estudiado, habitado, manejado e institucionalizado, Quito: EcoCiencia/AbyaYala/ECOBONA, 2011.

[2] Quantin y Zebrowski, «Caractérisation et formation de la cangahua en Equateur.,» de *Suelos Volcánicos endurecidos*, Quito, 1997.

[3] L. C. Blakemore, P. L. Searle y B. K. Daly, «Soil bureau laboratory methods: A methods for chemical analysis of soils. New Zealand Soil Bureau,» *Scientific Report 10a.,* pp. 44-45, 1981.

[4] G. G. Holmgren, «A rapid citrate-dithionite extractable iron procedure,» *Soil Sci. Soc. Am,* nº 31, pp. 210 - 211, 1967.

[5] N. a. c. N. Kampf, «Óxidos de ferro: indicadores de ambientes pedogênicos e geoquímicos in Tópicos em Ciencia do Solo,» pp. 111 - 142, 2000.

Adsorción y desorción de aniones fluoruro y vanadato por dos Andosoles africanos

González Rodríguez, S.[1], Fernández-Marcos, M.L.[1,2,*]

[1]Universidad de Santiago de Compostela, Departamento de Edafología y Química Agrícola, Campus universitario s/n, 27002 Lugo, España
[2]Universidad de Santiago de Compostela, IBADER, Campus universitario s/n, 27002 Lugo, España
**mluisa.fernandez@usc.es*

Los Andosoles son suelos desarrollados preferentemente sobre materiales volcánicos, caracterizados por la presencia de materiales pobremente cristalinos, como oxihidróxidos de hierro y aluminio, alofano, imogolita, ferrihidrita y/o complejos Al-humus o Fe-humus, que les confieren carga variable, alta capacidad de retención de fosfato (y otros aniones), baja densidad aparente, formación de agregados estables, etc. La retención de ciertos aniones se produce por procesos de adsorción específica, mediante la formación de complejos de esfera interna con formas activas de Al y Fe.
El flúor es un elemento tóxico para las plantas, animales y el hombre. Los volcanes son una importante fuente natural de flúor. Diversas actividades antrópicas dan lugar a emisiones de flúor al ambiente. El vanadio es un elemento ubicuo en la litosfera, pero altamente tóxico a concentraciones elevadas. Es emitido en actividades mineras, así como por ciertas industrias y procesos de incineración. La forma más abundante en suelos es $H_2VO_4^-$. La adsorción de fluoruro o vanadato por los suelos es un proceso descontaminador que protege las aguas y la vegetación de la contaminación por estas especies.
Se estudia la adsorción/desorción de fluoruro y vanadato por dos horizontes A de suelos representativos de áreas volcánicas del África ecuatorial: un Andosol vítrico [1] desarrollado sobre materiales basálticos en Santo Tomé y Príncipe (0º20'00"N, 6º39'00"E) y un Andosol silándico desarrollado sobre cenizas volcánicas en Ruanda (1º36'32"S, 29º32'57"E). Los dos suelos son ácidos, con una textura franco limosa o franco arenosa. El Andosol vítrico de Santo Tomé presenta concentraciones moderadas de Fe y Al no cristalinos y una gran cantidad de oxihidróxidos de hierro cristalinos. Por el contrario, en el Andosol silándico de Ruanda las formas no cristalinas de hierro predominan sobre las formas cristalinas. Se determinaron las isotermas de adsorción, llevando los suelos al equilibrio con disoluciones que contenían hasta 100 mgL^{-1} de F o V. La desorción se llevó a cabo con $NaNO_3$ 0,02 M.
Las adsorciones de fluoruro y vanadato fueron muy elevadas. La adsorción de fluoruro varió entre 93 y 99% de la cantidad añadida en el Andosol silándico y entre 71 y 98% en el Andosol vítrico. La desorción varió entre 1 y 6% de la cantidad adsorbida en el Andosol silándico y entre 3 y 22% en el Andosol vítrico. La adsorción de vanadato varió entre 97 y 100% en el Andosol silándico y entre 96 y 100% en el Andosol vítrico, mientras la desorción varió entre 0,1 y 3% en ambos suelos. Las mayores adsorciones y menores desorciones de fluoruro en el Andosol silándico indican el papel predominante de los compuestos de Al y Fe no cristalinos en la adsorción de este anión. La fuerte adsorción de vanadato en ambos suelos sugiere que tanto formas de hierro y aluminio no cristalinas como compuestos cristalinos de hierro adsorben eficazmente este anión. Las isotermas de adsorción de fluoruro se ajustan bien al modelo de Temkin, mientras la adsorción de vanadato se ajusta al modelo de Freundlich. En el caso del fluoruro, las isotermas de adsorción y desorción son coincidentes, indicando la reversibilidad del proceso. Por el contrario, en la desorción de vanadato se observa un fenómeno de histéresis, particularmente en el Andosol silándico, lo que indica la irreversibilidad de la adsorción.
mbos suelos, particularmente el Andosol silándico, pueden jugar eficazmente un papel protector de otros compartimentos ambientales frente a la contaminación por flúor y son extraordinariamente eficaces frente a la contaminación por vanadio.

Referencias

IUSS Working Group WRB. 2015. World Reference Base for Soil Resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome.

SUSTAINABLE STRATEGIES AND TOOLS FOR WILDFIRES PREVENTION AND CONTROL: A DYNAMIC EVALUATION

Ahinara Francisco López[1], Andrés Lema Martínez[1], Pastora M. Bello Bugallo[1,*]

[1]School of Engineering, Universidade de Santiago de Compostela, Av. Lope Gómez de Marzoa, s/n, E-15782, Santiago de Compostela, Spain

**pastora.bello.bugallo@usc.es*

Forest areas are crucial for regulating the water cycle, absorbing CO_2 and providing close-to-nature recreation possibilities [1]. Strengthening efforts to manage forests sustainably is also central to the UN 2030 Agenda for Sustainable Development as forests play a multifunctional role that supports the achievement of most Sustainable Development Goals [2]. Wildfires must be considered in any forest management strategy, whose impacts ares site-specifc an context-dependent [3].

This work presents and analytical review of the existing works related to the forest wildfires management in the political and scientific databases. The references are analysed classifying them based on the field previously identified (such as risks, soil management, prevention, social, economic and environmental impact, and so on). A dynamic (before, during and after fire) evaluation of the strengths and weaknesses from a sustainable point of view is developed, and a general inventory of techniques of improvement (including best practices as well as technologies in the circular economy framework) is elaborated. Different historical case studies are selected and dynamically analysed. Some questions are analysed: how was the ecosystem before? What happened during the fire? How did the actors react? What could have been done? The chemical transformations due to the fire are considered to evaluate the energy and material flows, as well as the new compounds that appear in the area, and the valorisation processes are enumerated also in the inventory.

The results of this work permit to identify study areas unexplored or little explored in the wildfire prevention and control framework. Then the work will contribute also to improve the decision tools to evaluate risks to be applied to particular cases, and the inventories of best practices and/or technologies in a dynamic focus. Finally, the evaluation of the chemical transformations will contribute to best evaluate and reduce the impacts, including prevention and valorisation processes.

References

[1] European Commission. Environment. https://ec.europa.eu/environment/forests/index_en.htm (access date: October 2019)

[2] European Commission: COM (2019) 352 final- Communication from the Commission to The European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions Stepping up EU. Action to protect and restore the World's forests.

[3] Stavi, I. Wildfires in grasslands and shrublands: a review of impacts on vegetation, soil, hydrology, and geomorphology. Water 2019, 11, 1042.

Kinetic modelling of the hydrothermal carbonization of compost derived from Municipal Solid Waste

Fernanda F. Roman[1,2], Jose L. Diaz de Tuesta[1,2], Paulo Praça[3], Adrian M.T. Silva[2], Joaquim L. Faria[2], Helder T. Gomes[1,2,*]

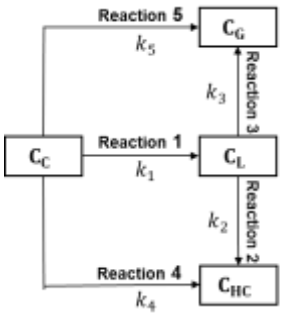
[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2]Laboratory of Separation and Reaction Engineering–Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[3]Resíduos do Nordeste, EIM, S.A. Empresa Intermunicipal, 5370-340 Mirandela, Portugal

htgomes@ipb.pt

Nowadays, municipal solid waste (MSW) management commonly includes a mechanical and biological treatment process (MBT). The solid stream from the anaerobic digestion of the organic fraction can be processed to obtain a compost, which can be used as fertilizer. However, compost production is higher than the existing demand, and the expected developments on up-coming directives ruling "End-of-waste" criteria are leading to barriers on the use of MSW-derived fertilizers [1]. Thus, the development of new alternatives for the treatment of organic wastes and compost valorization are necessary. This work deals with the valorization of compost from MBT, through the production of catalysts by Hydrothermal Carbonization (HTC) [2]. HTC of the compost was carried out in a Teflon vessel inserted in a stainless-steel body at different operating conditions (150-230 ºC,1-5 h, 1-4 g of compost, 30 mL). A Doehlert Matrix was considered to plan the experiments. The carbon balance and the kinetic equations were evaluated from experimental data reporting the carbon content in the liquid (estimated by TOC analysis) and solid phases (estimated by elemental analysis). A lumped kinetic model based on the elemental carbon content is proposed (Fig. 1), anticipating that the compost (C) undergoes reactions that originate liquid intermediates (L), reaction 1, and sequentially results in hydrochar (HC) and gases (G), reactions 2 and 3, respectively. In addition, it was assumed that HC and G were also produced from the compost directly, reactions 4 and 5, respectively. The highest kinetic constant at 190 ºC ($8.3\cdot10^{-4}$ min^{-1}) was found for the formation of the liquid soluble intermediates from compost (reaction 1), whereas the production of hydrochar from the liquid intermediates (reaction 2) shows the lowest kinetic constant ($3.1\cdot10^{-4}$ min^{-1}). The lowest activation energy was estimated for reaction 1 (23 $kJ\cdot mol^{-1}$), while reactions 2 and 4, related to the formation of hydrochar, resulted in the highest values (85 and 195 $kJ\cdot mol^{-1}$, respectively), meaning that the production of hydrochar strongly depends on the temperature.



$$\frac{dC_{c(t)}}{dt} = -C_{c(t)}(k_1 + k_4 + k_5)$$

$$\frac{dC_{L(t)}}{dt} = k_1 C_{C(t)} - C_{L(t)}(k_2 + k_3)$$

$$\frac{dC_{G(t)}}{dt} = k_3 C_{L(t)} + k_5 C_{c(t)}$$

$$\frac{dC_{HC(t)}}{dt} = k_4 C_{C(t)} + k_2 C_{L(t)}$$

Fig.1. Proposed mechanism for the thermochemical conversion of compost to hydrochar.

Acknowledgements

This work was financially supported by project "VALORCOMP - Valorización de compost y otros desechos procedentes de la fracción orgánica de los residuos municipales", 0119_VALORCOMP_2_P, and project "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", reference NORTE-01-0145-FEDER-000006, supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through FEDER; the Associate Laboratory LSRE-LCM - UID/EQU/50020/2019 - funded by national funds through FCT/MCTES (PIDDAC); and CIMO (UID/AGR/00690/2019) through FEDER under Program PT2020.

References

[1] H. Saveyn, P. Eder, End-of-waste criteria for biodegradable waste subjected to biological treatment (compost & digestate): Technical proposals, 2014.

[2] H. S. Kambo, A. Dutta, Renewable and Sustainable Energy Reviews 45 (2015) 359.

Elaboración de un montaje para hallar la curva de volumen de gases generados en un proceso de electrocoagulación

Acosta N. Gema[1, *], Bourdon G. Alejandro[2]
García B. Anguie[3], Ruiz L. Johann[4], Salazar R. Esteban[5]
[1]Universidad Militar Nueva Granada, Dirección, Bogotá, Colombia
gema.acosta@unimilitar.edu.co

Durante el proceso de electrocoagulación se generan gases en los electrodos, debido a los métodos electroquímicos propios de la técnica. Con el objetivo de establecer el volumen de gases generados, se propone realizar el montaje (Fig.1) y determinar la gráfica del volumen en función del tiempo, para orientar trabajos posteriores de caracterización de los gases. Con base en la composición de la mezcla gaseosa, se espera hacer disposición final de manera sustentable.
Los gases generados en el reactor se conducen a una bureta invertida, en cuya entrada se instala un generador de burbujas, para determinar la rapidez del flujo respecto al avance del proceso de electrocoagulación, con éste resultado poder generar la curva de volumen de gases generados en el desarrollo del tratamiento del agua.
Se determina que el montaje permite medir rapidez y velocidad de los gases producidos en una reacción.

RESULTADOS

- Foto del montaje. (vea figura 1).
- Se logra establecer el buen funcionamiento del montaje en cuanto a la medida del flujo de gases.
- Los diámetros de los ductos son suficientes para evitar presurización en el equipo.

SUGERENCIAS

- Humectar internamente la bureta con la sustancia antes de comenzar el proceso.
- Concentración aproximada tenso activo 5%, mayor concentración genera espuma.
- La manguera dentro de la probeta invertida debe estar por debajo de la escala de medida.
- Realizar ensayos preliminares de sellado para evitar fugas usando bicarbonato y ácido.
- Recomendable uso de manguera siliconada.
- Corregir el volumen del gas recogido con respecto a la altura de la columna de agua.

Figura 1. Montaje para medición de flujo de gases

Referencias

[1] Al-Qodah, Zakaria; Al-Shannag, Mohammad; Bani-Melhem, Khalid; Assirey, Eman; Mohd Adib Yahya; et al..Environmental Chemistry Letters; Dordrecht Tomo 16, N.º 3, (Sep 2018): 695-714. DOI:10.1007/s10311-018-

[2] Álvaro Arango Ruiz1. La electrocoagulación: una alternativa para el tratamiento de aguas residuales. 2005.

[3] ECKENFELDER, W.W. and CECIL, L. K. Application of New Concepts of PhysicalChemical Wastewater Treatment .Vanderbilt University; Nashville, TN.: Pergamon Press, Inc.

Comparison of glyphosate and imidacloprid induced toxicity using two cell models

Carlos Martins-Gomes [1,2,#,*], Tatiana Andreani [2,3,#], Amélia M. Silva[1,2]

[1]Department of Biology and Environment (DeBA-ECVA), University of Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5000-801 Vila Real, Portugal
[2]Centre for Research and Technology of Agro-Environmental and Biological Sciences (CITAB-UTAD), Quinta de Prados, 5000-801 Vila Real, Portugal
[3]Centro de Investigação em Química da Universidade do Porto, Departamento de Química e Bioquímica, Rua do Campo Alegre 687, 4169-007 Porto, Portugal.
[#]Equal contribution
**camgomes@utad.pt*

Damage caused by anthropogenic activities frequently originate in everyday actions that are essential to support the demand of a growing civilization. Agriculture, and its necessity of pesticides use, is a classical example, that in order eliminate pests (undesired plant species, insects, fungi) that decrease productions rate, often overlook the side effects of such use. The main issue concerning pesticides is that their toxicity is not restricted to the target species. Occupational and accidental exposures occur frequently, and there is also the risk of unaware exposition in the air, water or food, due to an extensive and uncontrolled use of pesticides in everyday activities. Among the pesticides widely used in agriculture, we can find glyphosate, an herbicide, and imidacloprid, an insecticide.

Our objective was to evaluate the toxicity induced by the exposure to glyphosate and imidacloprid, using Caco-2 (Human colorectal adenocarcinoma) and HepG2 cells, which mimic intestinal tract and after absorption the first passage effect, respectively. The cytotoxicity evaluation was performed by exposing the cells to different concentrations of both pesticides, for 24 and 48 hours using Alamar Blue® assay [1]. Results were compared with the control group (non-exposed cells) and are presented as cell viability (% of control).

Our results indicate that both cell lines exposed to glyphosate, at concentrations up to 1 mM, show no significant differences in cell viability, compared to control cells, regardless of the selected exposure time-points. Concerning imidacloprid cytotoxicity, the toxicity of the insecticide was cell line dependent. In Caco-2 cells, imidacloprid, at 1 mM, only produced a slight decrease in cell viability, after 24 h of exposure, whilst in HepG2 cells exposed to the same concentration the insecticide reduced the cell viability to ~14% of control. Increasing exposure time to 48 h, the toxicity of imidacloprid was also increased for both cell lines, being again HepG2 the most affected cell line. Additionally, morphological changes were observed in cells exposed to imidacloprid but not to glyphosate.

Imidacloprid proved to be more toxic than glyphosate to both human cell lines tested, with higher toxicity to the hepatic cell line, a representative of an organ with a major role in the metabolization and elimination of xenobiotic compounds.

Acknowledgments
This research was supported by the Portuguese Foundation for Science and Technology (FCT) through the research project SafeNPest - Synthesis and Environmental Safety of Nanopesticides, funded by POCI-01-0145-FEDER-029343, POCI-FEDER, that supported CMG (BIM/UTAD/13/2019); and through CITAB (UID/AGR/04033/2019).

References
[1] Andreani, T., Fangueiro, J.F., Severino, P., de Souza, A.L.R., Martins-Gomes, C., Fernandes, P.M.V., Calpena, A.C., Gremião, M.P., Souto, E.B., Silva, A.M., Nanomaterials 9(8), (2019) 1081.

Soil water interface monitoring: development of automatic analysis tools

Raquel B. R. Mesquita*, **António O. S. S. Rangel**

Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327, 4169-005 Porto, Portugal

**rmesquita@porto.ucp.pt*

Soil nutrient and contaminant testing has become a fundamental management tool for environmental and agricultural studies, at both local and international level. With the growing concern on soil contamination, and the increasing awareness of inorganic and organic contaminants effects on soil leachates and ground waters quality, to assess contaminant concentrations and to monitor nutrient levels has became a fundamental. The soil composition has a huge impact on the quality of surface and ground waters, due to run-off and leaching of nutrients and contaminants, respectively. In this scenario, this is also a major issue affecting the health and well being of the citizens, with a major social and economical impact. Conventional monitoring can hardly keep up with the ever-increasing demand of sample analysis as it relies on manual or mechanical soil sampling and atomic absorption/emission spectroscopy, leading to costly and time consuming assays. This cost limits the number of samples analyzed per field, making it difficult to characterize spatial or temporal variability in soil nutrient or contaminant concentrations. Additionally, the above-mentioned spectroscopic techniques only provide information on total elements content, and do not enable chemical speciation.

In this context, in this work, a number of flow-based methods were developed to provide automatic, portable and low cost tools capable of real-time monitoring of the soil leaching processes. These methods were tested at laboratory scale soil columns (LSSCs), where different types of soils and simulation of different scenarios for nutrients and contaminants leaching were performed. Sequential injection (SI) methods present advantageous characteristics such as high extent of automation, robustness, and versatility, making them a quite suitable choice for monitoring waters [1] and coupled to spectrophotometric detection enable to attain speciation, as toxicity is often dependent on the analyte form. Additionally, the potential of SI manifolds to be coupled to miniaturized reactors facilitated in-line simulations. The developed SI methods, intended to be used in a multiparamentric approach, include: i) a SI method for calcium and magnesium biparameric determination in rain water and leachates from LSSCs; ii) an in-line soil column coupled to a SI manifold for monitoring simulated leaching of micronutrients, namely Cu, Zn, Fe and iron complexes; iii) a SI method for quantification of bromate, as a potential emerging pollutant in irrigating waters; iv) phosphate assessment in both irrigating waters and leachates, exploiting the clean-up and pre-concentration capacity of a anion-exchange resin column.

All methodologies can be arranged in a single manifold, resulting a multiparametric determination of macronutrients (phosphate), micronutrients (calcium, magnesium, iron and iron complexes), oligoelements (copper and zinc) and emerging contaminants (bromate).

Acknowledgment

This work was supported by Nationals Funds from FCT – Fundação para a Ciência e Tecnologia through project PTDC/AAG-MAA/5887/2014; scientific collaboration from FCT, project UID/Multi/50016/2019, is also acknowledged.

References

[1] R. B. R. Mesquita, A. O. S. S. Rangel, Anal. Chim. Acta, 2009, 648, 7-22.

Aplicação de minerais aluminossilicatos em processos foto-Fenton no tratamento de efluentes vinícolas

Ana R. Teixeira[1*], V. Guimarães[1], J. R. Fernandes[1], M. S. Lucas[1], J. A. Peres[1]

[1] *Centro de Química de Vila Real (CQVR), Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5001-801 Vila Real, Portugal*
**e-mail: ritamourateixeira@gmail.com*

As águas residuais vinícolas resultam da mistura, que ocorre ao longo do processo de vinificação, entre perdas inevitáveis de vinho/mosto e a água de lavagem de equipamentos e tubagens. Possuem características específicas como a presença de compostos recalcitrantes, concentrações elevadas de carga orgânica, pH ácido e odores desagradáveis [1]. Tratar este tipo de efluentes torna-se um desafio para os processos biológicos convencionais, como consequência da presença de compostos tóxicos e recalcitrantes. Uma alternativa mais eficaz de tratamento são os Processos de Oxidação Avançados [2]. Os minerais de aluminossilicato são abundantes na crosta terrestre e formados quando átomos de Al substituem alguns dos átomos de Si nos silicatos. Os aluminossilicatos zeolíticos e argilosos são comumente utilizados como filtros e catalisadores moleculares, bem como, para suporte de catalisadores. Como consequência da substituição do Si^{4+} pelo Al^{3+}, ocorre o aumento da carga negativa na estrutura. Aumento esse que é equilibrado pela entrada de um catião para a estrutura [3].

No presente estudo utilizaram-se minerais aluminossilicatos (esmectite e clinoptilolite) como suporte sólido do ferro, com o objetivo de tratar efluentes vinícolas, através da sua aplicação em processos foto-Fenton com UV-C. Avaliou-se a eficiência do processo de tratamento através do valor de COT. Estudou-se a influência das condições experimentais, através da variação das mesmas (massa de catalisador utilizada, pH inicial da reação, concentração de H_2O_2 adicionada), com o intuito de otimizar o processo. Os resultados obtidos (Fig. 1) comprovam que existe atividade por parte dos catalisadores heterogéneos nos processos de foto-Fenton, o que se traduziu em remoções máximas de COT de 90,4 % (Fe-SMT) e 79,9% (Fe-ZEO) após 240 minutos de reação, para 3,00 g e 1,50 de catalisador, respetivamente

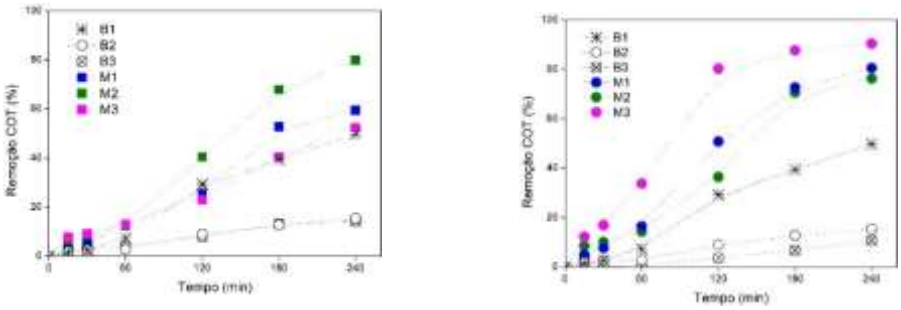


Fig. 4: Processos de oxidação fotocatalítica utilizando diferentes massas de catalisador: A) Fe-SMT; B) Fe-ZEO. Condições experimentais: $V_{efluente}$ = 500 mL; $[COT]_{inicial}$ = 250 mg/L; $[H_2O_2]$ = 97,94 mM; pH= 3,00. Brancos: **B1** = UV-C (254 nm) + 97,94 mg/L H_2O_2; **B2** = UV-C (254 nm); **B3** = UV-C (254 nm) + 1,50 g SMT/ZEO. Ensaios: **M1 -** 0,75 g; **M2 –** 1,50 g; **M3 –** 3,00 g.

Agradecimentos
Os autores agradecem o financiamento da bolsa para mestre no âmbito do Projeto Innovine&Wine NORTE-01-0145-FEDER-000038, co-financiado pelo ERDF através do NORTE 2020 (Programa Operacional Regional do Norte 2014-2020).

Referências
[1] R. Mosteo, P. Ormad, E. Mozas, J. Sarasa, J. L. Ovelleiro, Water Research, 40 (2006), 1561-1568.
[2] M.P. Ormad, R. Mosteo, C. Ibarz, J. L. Ovelleiro, Applied Catalysis B: Environmental, 66 (2006), 58-63.
[3] M. Weller, T. Overton, J. Rourke, F. Armstrong, Química Inorgânica (2014).

Mellora do sistema de xestión de RAEE de Galicia (España) no marco da economía circular

Daniel J. Prieto Vieites[1*], M. Pastora Bello Bugallo[1]
[1]Universidade de Santiago de Compostela, Santiago de Compostela, España
**danieljose.prieto@rai.usc.es*

Os Residuos de Aparellos Eléctricos e Electrónicos (RAEE) son o tipo de residuos que experimentan un maior crecemento na época actual, aumentado de 41,8 millóns de toneladas en 2014 hasta 50 millóns en 2018 [1]. As causas de este crecemento son as rápidas innovacións e o decrecemento no tempo de vida unido a crecente demanda destes produtos [2].

O obxectivo deste traballo é analizar o ciclo de vida dos AEE e RAEE en Galicia (España) e alcanzar unha visión complete da súa situación actual, dende a produción de AEE ata o tratamento dos residuos, incluíndo as fases intermediarias. Ademais, realizar un diagnóstico da situación, sinalando os aspectos principais que necesitan ser mellorados e facer propostas para a mellora dos mesmos que serán feitas dende a perspectiva do marco da economía circular e có obxectivo da sostibilidade.

A realización deste traballo baseouse nunha metodoloxía que inclúe:
- Unha recompilación de datos de diferentes institucións oficiais (a nivel local e europeo) e de estimacións de datos de diferente literatura científica.
-A modelización do sistema con software apropiado, para calcular estimacións de fluxos descoñecidos cando o dato orixinal sexa descoñecido. A modelización foi baseada nun modelo típico de caixas e existencias e inclúe un índice deseñado para medir a calidade das propias estimacións.
-A realización dun inventario das mellores prácticas de xestión e o seu uso para facer as propostas de mellora, seleccionando aquelas máis relevantes.
-Un análise e contextualización da información dispoñible para o diagnóstico apropiado do mesmo e para unhas apropiadas solucións de mellora.

Despois da realización da metodoloxía, chegáronse as seguintes conclusión, nas que se sinalan os principais puntos a mellorar do sistema de xestión en Galicia cun resumo da proposta de mellora:

-O problema principal en Galicia é o baixo nivel de recollida de RAEE. Polo tanto, un dos obxectivos principais do sistema de xestión debe de ser o aumento do índice de colección, xa que é un parámetro clave. Este incremento pode ser logrado co uso de instrumentos económicos e de concienciación social.
-A maioría dos AEE usados en Galicia son importados e a produción e outro factor clave. O cambio necesario no sistema de produción pode ser perseguido mediante o impulso de novos negocios, como os negocios integrados produto-servicio e sistemas de reacondicionamiento/remanufacturación, os cales son compatibles coa produción externa e que poden ser promovidos pola administración local.
-A falta de datos sobre xeración de RAEE e datos que permitan a realización de estimacións é un problema notable. A actualización do sistema de clasificación de RAEE podería ser útil para permitir mellores estimacións. A realización de enquisas a nivel local para o coñecemento do stock actual de AEE dos usuarios pode redundar tamén nunha mellora da calidade das estimacións.

Debido a natureza internacional do problema dos AEE/RAEE, estas propostas poderían ser aplicadas a outras zonas cunha situación ou problemas similares. Ademais, tódalas propostas son solución simples que se espera que poidan ser aplicables coa colaboración conxunta de administración e empresas privadas e que poden axudar a asentar as bases dunha economía circular alargo prazo.

Referencias

[1] Isildar, A., Rene, E.R., van Hullebusch E.D., Lens, P.N.L.: Electronic waste as a secondary source of critical metals: Management and recovery technologies. Resources, Conservation & Recycling nº 135, pp. 296–312. ElSevier (2018).

[2] Zhang, K., Schnoor, J.L., Zeng, E.Y.: E-Waste Recycling: Where Does it Go from Here? Environmental Science & Technology, nº 46, pp. 10861-10867. American Chemical Society (2012)

Three-dimensional reduced graphene/BiOI aerogels for photocatalysis degradation of water pollutants

Julieta Puig[1,2*], Lisandra C. de Castro-Alves[1], Susana Yañez-Vilar[1], Yolanda Piñeiro[1], Cristina E. Hoppe[2], José Rivas[1]
[1]Nanomag Lab, University of Santiago de Compostela, Santiago de Compostela, Spain
[2]INTEMA (Institute of Materials Science and Technology), Mar del Plata, Argentina
**puigjulieta@gmail.com*

Water pollution is a global challenge that has gained increased considerable attention nowadays [1].
Graphene has recently attracted great attention due to its excellent optical, electrical, thermal and mechanical properties. Graphene has large surface area (2630 m^2 g^{-1}) along with high conductivity (3000 W m^{-1} K^{-1}) that make it as a potential support for photocatalysis [2].
BiOX (bismuth oxyhalide; X=Cl, Br and I) compounds exhibit promising visible light photocatalytic performance due to their unique and excellent electrical, optical, magnetic, and photoluminescence properties [3].
In this work, a three-dimensional reduced graphene oxide (rGO) aerogel (Fig.1) is prepared by a simple in situ reduction of graphene oxide with ascorbic acid in presence of BiOI nanoparticles (Fig.1). The photocatalytic performance of the aerogel for degradation of water pollutant is studied.

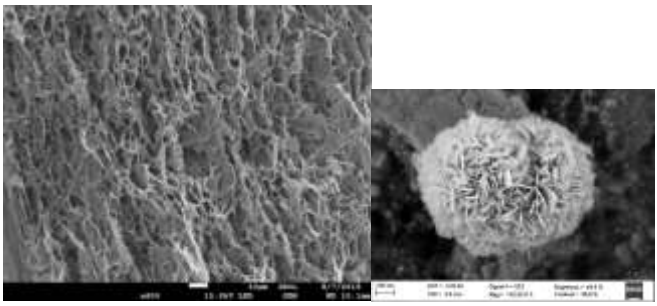


Fig.1. Scanning electron microscopy images of the porous structure of rGO aerogel (left) and the morphology of BiOI nanoparticles (right).

Acknowledgments
This work was supported by the European Commission PANA project (Call H2020-NMP-2015- two-stage, Grant N. 686009) and MADIA project (732678-MADIA-H2020-ICT-2016), the Consellería de Educación Program for the Development of Strategic Grouping in Materials (AEMAT) at the University of Santiago de Compostela (Grant N. ED431E2018/08), and Program for Consolidation of Research Units of Competitive Reference GRC2017(Grant N. ED431C 2017/22), Xunta de Galicia.
J. Puig thanks National Research Council (CONICET, Argentina), the National Agency for the Promotion of Science and Technology (ANPCyT, Argentina) and the University of Mar del Plata.

References

[1] P. Singh, A. Sudhaik, P. Raizada, P. Shandilya, R. Sharma, A. Hosseini-Bandegharaei, Materials Today Chemistry, 12 (2019) 85.
[2] N. Yousefi, M. Elimelech, X. Lu, N. Tufenkji, Nature nanotechnology, 1 (2019).
[3] R. Vinoth, S. Ganesh Babu, R. Ramachandran, B. Neppolian, Applied Surface Science, 418 (2017) 163.

Síntese de *meso*-diarilporfirinas "push-pull" para usar em células solares como sensibilizadores

Melani J.A. Reis[1*], Nuno M.M. Moura[1], Ana M.V.M. Pereira[2], M. Graça P.M.S. Neves[1]

[1] QOPNA & LAQV-REQUIMTE, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal. [2] LEPABE, Departamento de Engenharia Química, Universidade do Porto - Faculdade de Engenharia, 4200-465, Porto, Portugal
* melani@ua.pt

Devido à sua relevância, a procura por fontes de energias mais limpas e renováveis alternativas aos combustíveis fosseis é atualmente um dos principais tópicos de investigação a nível mundial [1].
Presentemente, o mercado das células solares é dominado por painéis à base de silício. No entanto, esta tecnologia exige um elevado grau de pureza por parte do semicondutor e implica elevados custos de fabrico [2]. Em contrapartida, vários estudos têm demonstrado que as células solares sensibilizadas por corante (DSSC, do inglês *dye-sensitised solar cells*) apresentam francas vantagens devido à sua transparência, leveza, flexibilidade e em particular ao funcionamento eficiente quando sujeitas à radiação difusa [2,3], e que permitirá tirar partido de janelas e fachadas de edifícios.
Os macrociclos tetrapirrólicos, nomeadamente as porfirinas, são uma classe de compostos que têm despertado um enorme interesse junto da comunidade científica devido ao seu potencial como catalisadores, sensores, dispositivos eletrónicos, agentes terapêuticos e de teranóstico, e também como corantes para células solares [4]. A versatilidade que apresentam advém do facto de poderem ser funcionalizados seletivamente nas posições *meso* e *beta*-pirrólicas, permitindo, então, a modulação das propriedades fotoquímicas e fotofísicas de acordo com a aplicação alvo [5].
Nesta comunicação, será apresentada a síntese e a caracterização estrutural de *meso*-diarilporfirinas do tipo "push-pull" (Figura 1) com propriedades adequadas com vista à aplicação como sensibilizadores em dispositivos DSSC.

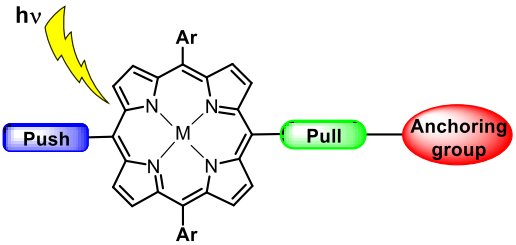


Figura 1. Representação esquemática de uma *meso*-diarilporfirina do tipo "push-pull".

Agradecimentos
Os autores agradecem às Universidade de Aveiro e Universidade do Porto e à FCT/MCTES (PIDDAC) pelo apoio financeiro às Unidades de Investigação QOPNA (UID/QUI/00062/2019) e LEPABE (UID/EQU/00511/2019) e à Rede RMN Portuguesa. Este trabalho foi financiado pelo Projeto FCT POCI-01-0145-FEDER-030357 - "Taylor Made Porphyrinoids for Emerging High Efficient Solar Energy Devices", financiado pelo Fundo Europeu de Desenvolvimento Regional (FEDER), através do COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) e com o apoio financeiro da FCT/MCTES através de fundos nacionais (PIDDAC). M.J.A. Reis, N.M.M. Moura (REF.-048-88-ARH/2018) e A.M.V.M. Pereira agradecem à FCT e ao projeto POCI-01-0145-FEDER-030357 a bolsa de investigação e respetivos contratos.

Referências

[1] M. Ye, X. Wen, M. Weng, J. Iocozzia, N. Zhang, C. Lin, Z. Lin, Mater. Today, 18 (2015) 155.
[2] Carella, F. Borbone, R. Centore, Front. Chem., 6 (2018) 481.
[3] Fakharuddin, R. Jose, T. M. Brown, F. Fabregat-Santiago, J. Bisquer, Energy Environ. Sci., 7 (2014) 3952.
[4] A.F.R. Cerqueira, N.M.M. Moura, V.V. Serra, M.A.F. Faustino, A.C. Tomé, J.A.S. Cavaleiro, M.G.P.M.S. Neves, Molecules, 22 (2017) 1269.
[5] K.M. Kadish, K.M. Smith, R. Guilard, Handbook of Porphyrin Science, World Scientific Publishing Company Co: Singapore, 2010, Vol. 1-12

COMPARISON OF CADMIUM BINDING BY HUMIC AND FULVIC ACIDS EXTRACTED FROM COMPOST SAMPLES OF DIFFERENT FEEDSTOCK

P. Rocha[1], A.C. Silva[1,2], J. Antelo[2], F. Bento[1], P. Bettencourt[1], S. Fiol[2], D. Geraldo[1], R. López[2], F. Macías[2], J.P. Pinheiro[3], M.F. Proença[1], P. Ramísio[4]

[1] Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[2] Instituto de Investigaciones Tecnológicas, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Espanã.
[3] Ecole Nationale Supérieure de Géologie, Université de Lorraine, 54518 Vandœuvre-lès-Nancy, France
[4] Centro de Território, Ambiente e Construção, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal
jprocha@quimica.uminho.pt

Compost is a bio-sustainable material produced by the controlled decomposition of the organic wastes. Composting can be employed for the urban organic waste treatment in alternative to incineration or landfill disposal [1]. The properties of compost are closely related to the presence of humic-like substances (HS). Both fulvic acids (FA) and humic acids (HA) contain a significant amount of carboxylic acids and phenolic groups that are responsible for some of their properties like solubility and ability to complex metal ions [2].

In the scope of the project Res2ValHum [3], composts produced from different feedstock were analysed and compared regarding the ability of the FA and the HA extracts to bind Cd^{2+}. The free cadmium ion concentration was measured using the electroanalytical technique AGNES (absence of gradients and Nernstian equilibrium stripping) [4]. The cadmium binding by FA and HA extracts of two compost samples: compost of algae (CA) and compost of sludge sewage (CSS) is illustrated in Figure 1. Results indicate that the extent of the binding of cadmium by FA is similar despite the nature of the compost. In opposition, the HA extracts from the algae compost exhibit a larger capacity to bind cadmium ion in comparison to the extracted from the sludge sewage compost. These results indicate that the nature of the feedstock seem to affect more the structure of the HA (in comparison to the FA) formed during the composting process. The chemical characterization of these extracts by different analytical techniques are in course in order to fully understand the referred effect.

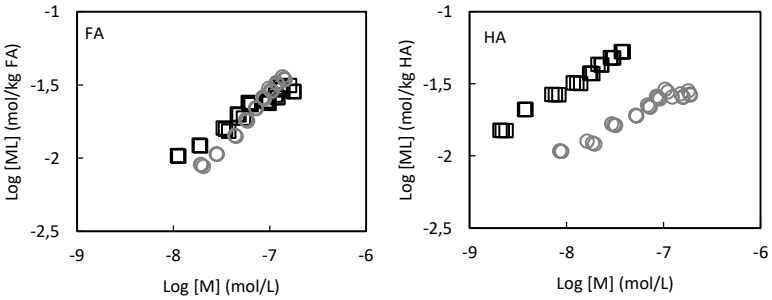


Fig.1. Experimental data obtained by AGNES, for the cadmium binding by fulvic (FA) and humic acids (HA) of two composts: compost of algae (CA, □) and compost of sludge sewage (CSS, ○).

Acknowledgment
This work has been co-financed by the Cooperation Program Interreg V-A Spain-Portugal (POCTEP) 2014-2020 and the European Union through the European Regional Development Fund – FEDER.

References

[1] Cerda, A. Artola, X. Font, R. Barrena, T. Gea, A. Sánchez, Bioresour Technol., 248 (2018) 57.
[2] L.K. Koopal, T. Saito, J.P. Pinheiro, W.H. van Riemsdijk, Colloids and Surfaces A: Physicochem. Eng. Aspects, 265 (2005) 40–54.
[3] Information on http://www.res2valhum.org
[4] E. Companys, J. Puy, J. Galceran, Environ. Chem., 4 (2007) 347–354.

Assessment of the potentialities of siderophores produced by *Rhizobium radiobacter* to cope with iron deficiency in plants grown in calcareous soils

J.Vindeirinho[1,2], C.M.H. Ferreira[1,2,3], C.A. Sousa[1,2,3], E.V. Soares[2,3], H.M.V.M. Soares[1*]

[1]REQUIMTE/LAQV, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2]Bioengineering Laboratory, Chemical Engineering Department, ISEP-School of Engineering of Polytechnic Institute of Porto, rua Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal
[3]CEB-Center of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
**hsoares@fe.up.pt*

Iron is a crucial micro-nutrient for plants, but is insoluble in calcareous soils, which leads to iron deficiency (iron-induced chlorosis), with losses in crops production [1]. In order to overcome the aforementioned problem, a wide range of synthetic organic chelators belonging to the class of aminopolycarboxylic acids (APCAs) have been used to supplement soils due to their ability to form stable and water-soluble chelates with iron at pH values above 7.0 [2]. However, the fate of the referred molecules in the environment conducts to its accumulation in soils and water due to the chemical and biological recalcitrant nature of these compounds [3].
Siderophores are biomolecules naturally produced and released by both plants and bacteria in iron-limited media that possess the capacity to form strong complexes with iron and can be biodegraded. Thus, they can be a good alternative to synthetic APCAs [3]. Some of these molecules can be obtained synthetically but the synthesis is often laborious and originates low yields. The best option to produce siderophores comprises a biotechnological approach using non-pathogenic risk 1 bacterial cultures [3]. *Rhizobium radiobacter* species is a plant growth-promoting bacteria that produces a catecholate-based siderophore, named agrobactin, which structure anticipates a good performance in the complexation of iron in alkaline conditions [3].
The work here developed consisted in: i) a first stage in which *R. radiobacter* DSM 30205 was cultured in a mineral iron deficient culture medium, with subsequent harvest and processing of the culture supernatant to quantify the production of agrobactin, by UV-Vis spectroscopy, at 310-320 nm; ii) a second stage, where the ability of the siderophores to complex iron was evaluated, at pH 9.0, with increasing concentrations of iron added, following the adaptation of a method validated according to the European regulations on fertilizers [4]. The complexation study has shown that all siderophore(s) present in the supernatant was able to complex iron at pH 9.0, in a stoichiometry 1:1.
These results corroborate the potential of *R. radiobacter* agrobactin to be used as a solution to amend iron insolubility and open the door for its utilization in the treatment of iron deficiency induced in plants growing in calcareous soils.

Acknowledgments
This work was financially supported by: Project PTDC-AGR-TEC-0458-2014 - POCI-01-0145-FEDER-016681 - funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES. Carlos H.M. Ferreira would like to thank the support from his grant with reference SFRH/BD/95490/2013 from FCT.

Bibliography
[1] C. M.H. Ferreira, C.A. Sousa, I. Sanchis-Pérez, S. Lopez-Rayo, M.T. Barros, H.M.V.M Soares, J. Lucena, Science of the Total Environment, 647 (2019) 1586-1593.
[2] M. Bucheli-Witschel, T. Egli, FEMS Microbiology reviews, 25(2001) 69-106.
[3] C.M.H. Ferreira, H.M.V.M Soares, E.V. Soares, Science of the Total Environment, 682 (2019) 779-799.
[4] European Committee for Standardization, 2011. EN 15962 Fertilizers. Determination of the complexed micro-nutrient content and of the complexed fraction of micro-nutrients.

PLASTICS IN OUR OCEANS: MANAGEMENT STRATEGIES AND MODELLING

Diego Vázquez Ares[1], Adriana García Rellán[1], Constantino Vázquez Brea[1], Pastora M. Bello Bugallo[1*]

[1]Department of Chemical Engineering, Universidade de Santiago de Compostela, Av. Lope Gómez de Marzoa, s/n, E-15782, Santiago de Compostela, Spain.

[*]*Corresponding author. Tel.: +34 8818 16789; fax +34 8818 16702. E-mail address: pastora.bello.bugallo@usc.es*

Currently, 60-80% of garbage is plastic, and almost 10% ends up in the oceans [1]. Plastics, sometimes suffer from photooxidation, producing microplastics [2]. Microplastics derived from the breakdown of plastics are called secondary microplastics. Cole et al, 2011 [3] are who classify microplastics in Secondary and Primary. Primary microplastics are those that are manufactured to have a microscopic size. The latter are especially used in cosmetics. These particles invisible to the naked eye mix with phytoplankton and simply cannot be extracted from the oceans [4]. Once mixed, they enter the food chain, may have toxic effects [2].

According to Raddadi and Fabio, 2019 [2], the development of plastics management strategies is considered a potential strategy to reduce the impact of plastics. However, synthetic plastics derived from petroleum have been produced and accumulated in the environment for several decades, and there are still gaps in knowledge about their biodegradation rates in terrestrial systems and, in particular, in aquatic systems.

This work analyses the current plastic management strategies in the marine environment. This is developed with the aim of identifying possible needs and improvements from a sustainable point of view, and to define new approaches. Simultaneously a material flows analysis in different media of the marine environment is done. Using system dynamics, a preliminary model of plastics mobilization into the ocean to other media of the marine environment (like sediments and biota) is developed and validated with existing data from the previous steps of the work. The model is use them to analyse different scenarios identified previously.

This analysis permits to contribute to the knowledge of both plastic sources and plastics sinks in the ocean, the plastic and microplastic transformation, and the needs in reference to the plastic management strategies.

References

[1] Avio, C.G.; Gorbi, S.; Regoli, F. Plastics and microplastics in the oceans: From emerging pollutants to emerged threat. Marine Environmental Research, 128 (2017) 2-11.
[2] Raddadi, N.; Fabio, F. Biodegradation of oil-based plastics in the environment: Existing knowledge and needs of research and innovation. Science of The Total Environment, 679, (2019) 148-158.
[3] Cole, M.; Lindeque, P.; Halsband, C.; Galloway, T.S. Microplastics as contaminants in the marine environment: A review. Marine Pollution Bulletin, 62, Issue 12, (2011) 2588-2597
[4] Falkenberg. K. European Commision. Marine Litter: Time To Clean Up Our Act (2010).

AMB41

Avaliação das potencialidades do uso da cinza de carvão para remediar a Drenagem Ácida de Mina. Caso de estudo: Mina de Benga. Moçambique

Autor Principal:
Prof. Esnaider Rodriguez Suárez [a]
Co-Autores:
Eng. Loide Furtado.[b]
Dr[a]. Nelda Come Calbe [c]

[a] Universidade Eduardo Modlane. Facultade de Ciencias. Departamento de Quimica. Secção de Quimica Analitica. Maputo. Moçambique. *(**email:erodriguezsuarez2013@gmail.com**).*
[b] Universidade Eduardo Modlane. Facultade de Ciencias. Departamento de Quimica. Secção de Quimica Analitica. Maputo. Moçambique.*(**email: neldacome@gmail.com**)*
[c] Universidade Eduardo Modlane. Facultade de Ciencias. Departamento de Quimica. Secção de Quimica Analitica. Maputo. Moçambique.

O trabalho de pesquisa teve como local de estudo a Mina de Benga, localizada na Província de Tete- Distrito de Moatize- Região de Benga, onde teve como finalidade avaliar as potencialidades do uso da cinza de carvão obtida a partir do rejeito fino do carvão para remediação da Drenagem Ácida de Mina formada na área de estudo. Para realização da presente monografia, optou-se por usar a metodologia de pesquisa com uma abordagem hipotético-dedutiva auxiliada pela abordagem indutiva, seguindo um objectivo descritivo-explicativo e natureza quantitativa e qualitativa, sendo que a metodologia obedeceu estudo de campo e laboratorial. Para satisfazer os objectivos do trabalho optou-se por determinar a composição físico-química do rejeito de carvão, das cinzas de carvão e do efluente, onde foram avaliados parâmetros físicos (cor, traço, ph, condutividade) e parâmetros químicos (sólidos suspensos e sólidos dissolvidos). Fez-se a caracterização mineralógica do rejeito onde foi verificado a presença de quartzo, caulinita, siderita, paligorsquite, muscovita e dolomita, de carvão, e caracterização geoquímica da cinza de carvão onde destacam-se a presença de Si, Al, Fe, K, Ca, Ti como principais elementos e a presença de Cu, Cr, Zn, Rb, Ir, Mn, As, Y, Pb, Nb, Th como elementos traços, sendo definidos pelo método de Difracção de Raio X e Fluorescência de Raio X. Usou-se ainda os métodos estáticos (Teste fizz; pH da pasta; Balanço acido base; Teste inicial da *British Columbia Research*) que mostrou um alto potencial de neutralização e um baixo potencial de acidez, e os métodos dinâmicos (Estudo da adsorção dos iões H^+) que mostrou o tempo máximo de absorção dos iões H^+ a partir da activação das cinzas no efluente. Obteve-se resultados satisfatórios como a passagem de elementos principais geradores da acidez contidos no rejeito fino para elementos traços após a calcinação (transformação em cinza), constatou-se também a vantagem do pH da cinza ser neutro. Conclui-se que as cinzas de carvão proveniente do rejeito fino de carvão mineral têm potencialidade para remediar a Drenagem Ácida de Mina, tendo como principal vantagem de não precisar de muito tempo de interação para servir como um bom remediador para Drenagem Ácida de Minas.

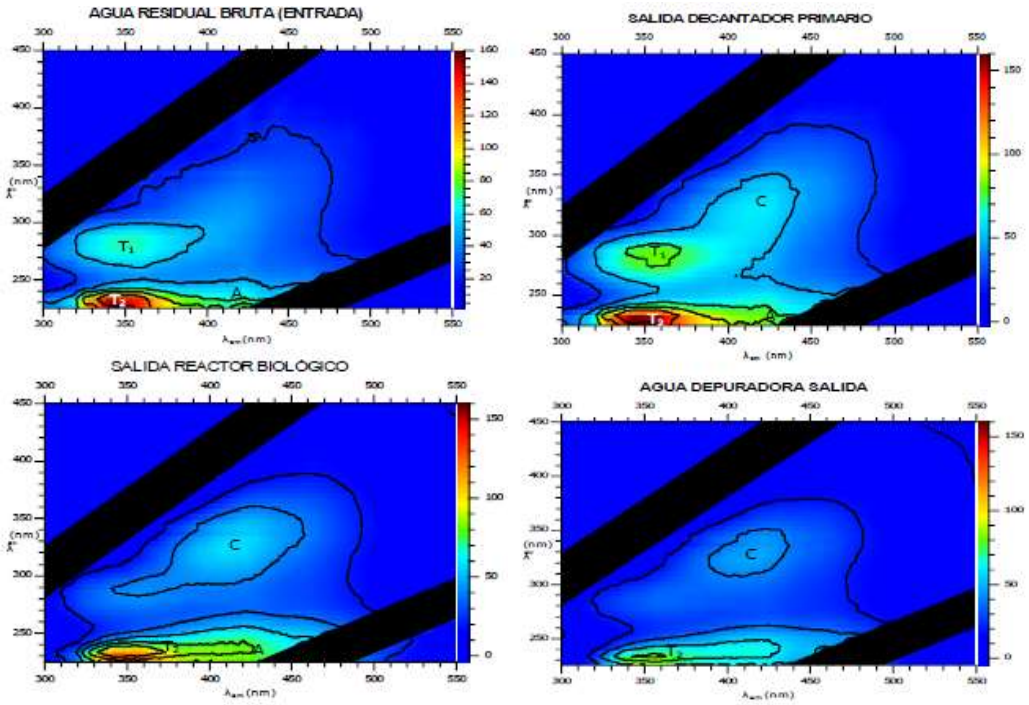
Palavra-chave: Rejeito de carvão fino, Cinza de carvão, Drenagem Ácida de Mina, remediação, Potencialidade, métodos estáticos e dinâmicos.

Seguimiento del tratamiento en una Depuradora de Aguas Residuales Urbanas (EDAR) mediante fluorescencia de matriz de excitación-emisión (fluorescencia EEM)

Rodríguez Vidal - Francisco Javier [1,*], García Valverde - María [2], Ortega Azabache – Beatriz [2]
[1] Universidad de Burgos (Escuela Politécnica Superior), Av. Cantabria s/n, Burgos, España
[2] Universidad de Burgos (Facultad de Ciencias), Av. Cantabria s/n, Burgos, España
* gpvito@ubu.es

En el campo del medio ambiente, concretamente en el análisis de aguas residuales, la fluorescencia de matriz de excitación-emisión (EEM) es una alternativa muy atractiva [1, 2], ya que es una técnica simple (el pretratamiento de la muestra normalmente solo requiere una filtración de la muestra para eliminar sólidos en suspensión y una dilución en caso de aguas muy cargadas en materia orgánica, como los influentes residuales) y rápida (la realización de un espectro EEM suele llevar de 10 a 15 minutos). Mediante fluorescencia EEM se puede hacer el seguimiento de algunos componentes orgánicos de las aguas residuales (proteínas y sustancias húmicas) a través de las distintas etapas de tratamiento de una depuradora urbana (EDAR) [3].

En la Figura 1 se muestran los espectros de fluorescencia EEM para el caso concreto de la EDAR de Burgos, correspondientes a las siguientes etapas de depuración: Influente (agua residual de entrada, sin tratar), Agua decantada (agua de salida del decantador primario), Agua tratada biológicamente (agua de salida del reactor biológico de fangos activados) y Efluente (agua final tratada, salida del decantador secundario).



Referencias
[1] Yu, H. et al, Chemosphere, 121 (2015) 101.
[2] Meng, F. et al, Water Research, 45 (2011) 4661.
[3] Jarusutthirak, C. et al, Water Research, 41 (2007) 2787.

Characterization of chemical composition and sources contribution study of atmospheric particulate matter (PM_{10}) from a Western-Europe coastal city

J. Sánchez-Piñero*, J. Moreda-Piñeiro, M. Fernández-Amado, I. Turnes-Carou, P. López-Mahía, S. Muniategui-Lorenzo

University of A Coruña. Química Analítica Aplicada (QANAP), University Institute of Research in Environmental Studies (IUMA), Centro de Investigaciones Científicas Avanzadas (CICA), Department of Chemistry. Faculty of Sciences. Campus de A Coruña, s/n. 15071 – A Coruña. Spain.
**joel.sanchez@udc.es*

Atmospheric particulate matter (APM) is characterized by wide range of particle type with different composition, sizes, shapes and optical properties, depending on the origin and the physical and chemical transformations that occur during particles transporting into the atmosphere [1]. Several epidemiological studies have shown that chronic environmental exposure to APM have been associated with negative health outcomes and it was classified as carcinogenic to human (group 1) in 2013 by the International Agency for Research in Cancer (IARC). Consequently, some regulations have been carried to address the threat and limit values for PM_{10} concentration and PM_{10}-associated pollutants such as toxic metals (As, Cd, Ni) and polycyclic aromatic hydrocarbons (PAHs) were stablished by the European Environment Agency (EEA) [2].

This work aims to characterize the chemical composition of PM_{10} samples collected on the urban area of de A Coruña city, located at the northwest coast of Spain. PM_{10} mass concentration and PAHs, trace metals, major ions, equivalent black carbon (eBC) and UV-absorbing particulate matter (UVPM) concentrations in PM_{10} samples were studied. A total of 65 PM_{10} samples were selected to carry out the study, covering from January to December 2017. Sampling and filter treatment procedures were according to the European Norm 12341 (EN 12341:2015) [2].

The mass concentration of PM_{10} were determined by gravimetric method, while eBC (indicator of carbonaceous particles) and UVPM (indicator of aromatic organic compounds) in samples were analysed by using a transmissometer. Major inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, K^+, Na^+, Ca^{2+} and Mg^{2+},) were analysed by capillary electrophoresis after sonication–assisted water extraction (aqueous soluble fraction) [3]. Trace metals (Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Rb, Sb, Se, Sn, Sr, V and Zn) and PAHs (naphtalene, acenaphthene, fluorene, phenanthrene , anthracene, fluoranthene, pyrene, chrysene, benzo(e)pyrene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene) were analysed in PM_{10} samples by were analysed by ICP-MS after acid extraction and HPLC-FLD after microwave-assisted extraction (MAE) respectively [4]

Finally, chemical composition of PM_{10} samples were used to explore APM sources by using a statistical analysis (univariate, principal components and cluster analysis) [5].

Acknowledgements

This work was supported by MCIU/AEI/FEDER, UE (RTI2018-101116-B-100) and Xunta de Galicia (ED431C 2017/28-2017-2020). J. Sánchez-Piñero acknowledges the Xunta de Galicia and the European Union (European Social Fund - ESF) for a predoctoral grant (ED481A-2018/164). M. Fernández-Amado appreciates the Ministerio de Ciencia, Innovación y Universidades support (PTA2017-13607-I). The council of A Coruña is acknowledged for its assistance (collaboration agreement between the City of A Coruña and IUMA-UDC). The authors would like to thank P. Esperón (PTA2013-8375-I) for her support.

References

[1] E.S. Galvao, J.M. Santos, A.T. Lima, N.R. Reis, M.T.D. Orlando, R.M. Stuetz. Chemosphere 199 (2018) 546.

[2] Directive 2008/50/EC of the European Parlament and of the Council of 21 May 2008 on Ambient Air Quality and Cleaner Air for Europe.

[3] J. Moreda-Piñeiro, I. Turnes-Carou, E. Alonso-Rodríguez, C. Moscoso-Pérez, G. Blanco-Heras, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríquez. Water, Air, & Soil Pollution 226 (2015) 2240.

[4] M. Piñeiro-Iglesias, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríguez, X. Querol, A. Alastuey. Atmospheric Environment 37 (2003) 4171.

[5] J. Moreda-Piñeiro, L. Dans-Sánchez, J. Sánchez-Piñero, I. Turnes-Carou, S. Muniategui-Lorenzo, P. López- Mahía. Atmospheric Environment 213 (2019) 104.

Evolution of equivalent black carbon concentrations in an urban background site and correlation between on-line and off-line data

J. Sánchez-Piñero*, M. Fernández-Amado, J. Moreda-Piñeiro, M. Piñeiro-Iglesias, S. Muniategui-Lorenzo and P. López-Mahía

Universidade da Coruña, Grupo de Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Centro de Investigaciones Científicas Avanzadas (CICA), Departamento de Química, Facultade de Ciencias, Campus A Zapateira, 15071 A Coruña, Spain
**joel.sanchez@udc.es*

Black carbon (BC) is the fraction of carbonaceous particles that shows a strong absorption of visible light [1]. BC is strongly related to elemental carbon (EC, considered a marker of primary emissions, from biomass burning and mainly from traffic), although this relationship depends on several parameters of the sample and also on the protocol used for analysis [2]. Therefore, monitoring of BC or EC is of great interest. However, their routing monitoring is difficult due to the cost of the required instrumentation for on-line monitoring (an aethalometer for BC or a continuously operated OC/EC analyser for EC) and to the high time consumption for off-line determination of elemental carbon by thermal-optical methods [1].

As BC is a strongly absorbing component of PM, its concentration can be derived from optical absorption measurements, being named as equivalent BC (eBC). This is what an aethalometer does, measuring light absorption on a filter tape loaded with aerosols. But the same approach can be also applied to sampled filters by using a transmissometer. In addition to eBC, data of UV-absorbing particulate matter (UVPM) can be obtained as well. UVPM is an indicator of aromatic organic compounds, proving very useful information as well. The use of a transmissometer has many advantages in addition to the lower cost, being fast and non-destructive and allowing to analyse filters that had been archived for a long time [1]. Using this methodology, our group has recently analysed temporal trends of eBC and UVPM in PM_{10} samples collected over a decade in an urban area [4].

In this work, a SootScan^{TM} OT-21 transmissometer (Magee Scientific) has been used to analyse PM_{10} and $PM_{2.5}$ samples collected in an urban background site, located in the University Institute of Research in Environmental Studies of University of A Coruña. It is about 1 km from the coastline, with significant influence of the Atlantic Ocean air masses, and the main anthropogenic sources are the emissions from traffic and domestic activities. 24h-PM_{10} and $PM_{2.5}$ samples, covering from December 2017 to August 2019 (n=96 for each fraction), were analysed using the transmissometer. Data of an aethalometer AE33 (Magee Scientific) installed in the same sampling site were also recorded.

The obtained data of eBC and UVPM concentrations found in the filters (derived from attenuation at 880 and 370 nm, respectively) have been explored to find temporal trends by using Openair package in R [3]. In addition, the correlation between the data obtained from the sampled filters and the on-line results provided by the aethalometer for the same days has been studied.

Acknowledgements
This work was supported by FEDER-MINECO (UNLC15-DE-3097, financed together (80/20%) with Xunta de Galicia), Xunta de Galicia (GRC2017/28) and MCIU/AEI/FEDER, UE (RTI2018-101116-B-100). M. Fernández-Amado apreciates the Ministerio de Ciencia, Innovación y Unversidades support (PTA2017-13607-I). J. Sánchez-Piñero acknowledges the Xunta de Galicia for a Doctoral grant (ED481A-2018/164). The authors would like to thank P. Esperón (PTA2013-8375-I) for her support.

References

[1] M. Greilinger, L. Drinovec, G. Močnik, A. Kasper-Giebl, Atmospheric Environment, 198 (2019) 1.
[2] H. Moosmüller, R.K. Chakrabarty, W.P. Arnott, Journal of Quantitative Spectroscopy and Radiative Transfer, 110 (2009) 844.
[3] D.C. Carslaw, K. Ropkins, Environmental Modelling & Software, 27-28 (2012) 52.
[4] J. Sánchez-Piñero, M. Fernández-Amado, J. Moreda-Piñeiro, M. Piñeiro-Iglesias, S. Muniategui-Lorenzo, P. López-Mahía, Proc. of 7th Iberian Meeting on Aerosol Science and Technology (RICTA 19), Lisbon, Portugal, 2019, 99.

Characterization, acid-base properties and metal complexation of humic-like substances extracted from organic matter during the composting process

A. C. Silva[1,2,] P. Rocha[1], J. Antelo[2], F. Bento[1], P. Bettencourt[1], P. Ferreira[1], S. Fiol[2], D. Geraldo[1], R. López[2], F. Macías[2], M.C. Paiva[3], J.P. Pinheiro[4], M.F. Proença[1]

[1] Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[2] Instituto de Investigaciones Tecnológicas, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, España
[3] Instituto de Polímeros e Compósitos/I3N, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal
[4] Ecole Nationale Supérieure de Géologie, Université de Lorraine, 54518 Vandœuvre-lès-Nancy, France
**id6274@alunos.uminho.pt*

As an alternative to incineration or disposal in landfills, composting is an environmentally friendly process that can be employed for the treatment of urban organic waste [1]. The chemical and biochemical reactions that occur during composting lead to important changes in the organic material with production of chemical species that are more stable towards degradation. The properties of compost are closely related to the presence of humic-like substances (HS), such as fulvic acids (FA), humic acids (HA) and humin. These substances contain a significant amount of carboxylic and phenolic groups that are responsible for some of their properties like their solubility and ability to complex metal ions [2].

An organic waste (UW_0), the resulting unmatured compost after 15 and 30 days of composting (CUW_{15}, CUW_{30}) and the maturated compost (CUW) were characterized within the scope of the Interreg project Res2ValHum [3]. Humic and fulvic-like acids were obtained following the IHSS protocol for soil humic substances [4]. The characterization of the obtained extracts from the UW_0, CUW_{15}, CUW_{30} and CUW samples was performed by different techniques, namely, Attenuated Total Reflection–Fourier Transform Infra-Red (ATR – FTIR), acid-base potentiometric titrations and the Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) [5].

Although the amount of humic-like and fulvic-like acids extracted from the samples did not change significantly, structural modifications of organic matter during the composting process were observed. To compare these extracts an aromaticity index ($I_{1650/2945}$), calculated from the ratio between peaks at 1650 cm^{-1} (C=O and C=C stretching of aromatic moieties) and 2945 cm^{-1} (C-H stretching of aliphatic moieties) of the ATR-FTIR spectra, was used. The observed increase of the aromaticity index suggests that the organic matter complexity increases as it becomes more stable.

Simultaneously, the concentration of acidic groups, carboxylic and phenolic, and of the protonation constants (obtained from acid-base potentiometric titrations) and the capacity to bind cadmium increased with composting time and maturation.

Acknowledgment
This work has been co-financed by the Cooperation Program Interreg V-A Spain-Portugal (POCTEP) 2014-2020 and the European Union through the European Regional Development Fund - FEDER within the scope of the project «RES2VALHUM (0366_RES2VALHUM_1_P). A.C. Silva acknowledges her PhD grant (UMINHO/BD/40/2016) financed by the Operational Program Norte 2020 (through the Project "NORTE-08-5369-FSE-000033"). Members of the USC are grateful to CRETUS (ED431E 2018/01) cofounded by FEDER and Galician GCR ED431E/12.

References
[1] A. Cerda, A. Artola, X. Font, R. Barrena, T. Gea, A. Sánchez, Bioresour Technol., 248 (2018) 57–67.
[2] L.K. Koopal, T. Saito, J.P. Pinheiro, W.H. van Riemsdijk, Colloids and Surfaces A: Physicochem. Eng. Aspects, 265 (2005) 40–54.
[3] Information on http://www.res2valhum.org
[4] R.S. Swift, in Methods of Soil Analysis, Part 3. Chemical Methods, D.L. Sparks (Ed.), (1996) 1018-1021.
[5] E. Companys, J. Puy, J. Galceran, Environ. Chem., 4 (2007) 347–354.

Concentraciones de actividad de isótopos de uranio en muestras de suelo de la Costa Norte de Galicia (NW España)

José Mª Fernández Solís[1,*], Alberto Otero Pazos[2], Alfonso Calleja García[2], Sonia Casal Romero[2], Jesús Manuel Castro Romero[2], Elena González Soto[1]

Universidad de A Coruña. Departamento de Química. Área Química Analítica.
[1]Escuela Politécnica Superior. Mendizábal, s/n. 15403 Ferrol (A Coruña), España.
[2]Escuela Universitaria Politécnica. Serantes, s/n. 15405 Ferrol (A Coruña), España
**jose.maria.fsolis@udc.es*

La contaminación por radiactividad se debe a la presencia no deseada de sustancias radiactivas en el medio ambiente. El uranio es un elemento radiactivo que se encuentra en rocas y suelos. Su contenido oscila entre 0,5 y 4,7 ppm, con un valor medio de 2,7 ppm, aunque algunas rocas, como las fosfatadas, pueden contener concentraciones mucho mayores. El elemento se encuentra distribuido por todo el planeta, existiendo muchos depósitos fundamentalmente en medios ígneos, metamórficos y sedimentarios.

El uranio natural tiene tres isótopos radiactivos: ^{234}U, ^{235}U y ^{238}U, siendo el más común el ^{238}U que constituye cerca del 99 % del uranio natural. Estos tres isótopos tienen el mismo comportamiento químico pero difieren en sus propiedades radiactivas, siendo el ^{235}U el que presenta una menor actividad.

Puesto que los radionucleidos representan una clase muy importante de contaminantes medioambientales, es necesario disponer de métodos analíticos precisos y fiables para determinar sus concentraciones [1, 2, 3]. En ese sentido, se ha establecido un método radiológico para la determinación isotópica del uranio, empleando un ataque ácido mediante energía de microondas, una extracción con disolventes orgánicos para la eliminación de trazas de hierro, el uso de una resina de intercambio iónico para la retención del uranio, y un proceso de electrodeposición que permite depositar los isótopos de uranio para su posterior medida mediante la técnica de espectrometría alfa.
En este trabajo se ha realizado la determinación isotópica de uranio en 33 muestras de suelo tomadas en la costa norte de Galicia, obteniendo valores de concentración de actividad para ^{234}U, ^{235}U y ^{238}U. En todas las muestras analizadas se encontró que las Actividades Mínimas Detectables son muy bajas.

Referencias

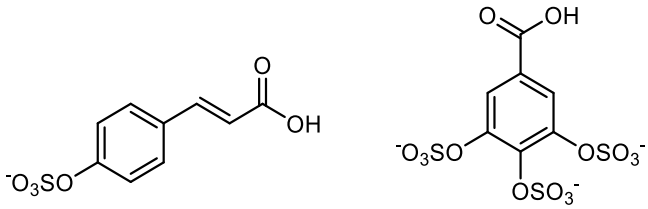
[1] G. Jia, G. Torri, R. Ocone, A. Di Lullo, A. De Angelis, R. Boschetto, Applied Radiation Isotopes, 66 (2008) 1478.
[2] S.H. Lee, J. La Rosa, J. Gastaud, P.P. Povinec, Journal of Radioanalytical and Nuclear Chemistry, 263 (2005) 419.
[3] H. Vandenhove, C. Hurtgen, en "Radionuclides in the Environment" D.A. Atwood (Ed.), Lexington, KY (USA), John Wiley and Sons Ltd., 2010.

Synthesis and antifouling screening of zosteric acid and gallic acid analogues

Ana R. Neves[1,2], Catarina Gonçalves[1,2], Joana R. Almeida[1], Vitor Vasconcelos[1,3], Madalena Pinto[1,2], Emília Sousa[1,2], Marta Correia-da-Silva[1,2*]

[1]CIIMAR/CIMAR - Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Terminal de Cruzeiros do Porto de Leixões Avenida General Norton de Matos, 4450-208 Matosinhos, Portugal.
[2]Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Rua Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal.
[3]Department of Biology, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4069-007 Porto, Portugal.
**m_correiadasilva@ff.up.pt*

In this work, a chemical library of analogues of two promising antifouling sulfated compounds, zosteric acid and gallic acid persulfate, was obtained (**Figure 1**). Zosteric acid is a well-known non-toxic and fully degradable marine natural antifouling compound [1], while gallic acid persulfate is a synthetic compound obtained in our research group, which showed promising antifouling properties with no toxicity to *Artemia salina*, a non-target species [2].



Zosteric acid **Gallic acid persulfate**

Fig.1. Structures of zosteric acid and gallic acid persulfate.

The molecular modifications performed to improve antifouling activity, achieve low toxicity, and high biodegradability included glycosylation, propargylation, amidation and copper (I) catalyzed azide-alkyne cycloaddition reactions (CuAAc). Thirteen compounds were synthesized for the first time and their structures were confirmed using infrared spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance, and high-resolution mass spectrometry.
All the compounds, including the starting materials, were tested using an *in vivo* anti-settlement assay with mussel (*Mytilus galloprovincialis*) plantigrade larvae. Four compounds were active against the settlement of mussel larvae (EC_{50} < 25µg mL^{-1}). Structure-antifouling activity relationships could be observed for these compounds.

Agradecimientos
Support for this work was provided by FCT through UID/Multi/04423/2019 and the European Regional Development Fund (ERDF) in the framework of PT2020 and under the project PTDC/AAG-TEC/0739/2014 (FCT/MCTES and Technology and Higher Education (PIDDAC) and European Regional Development Fund (ERDF) through the COMPETE (POCI-01-0145-FEDER-016793) and RIDTI - Project 9471). A. R. Neves acknowledge FCT for the Grant SFRH/BD/114856/2016.

Referencias

[1] C. Vilas-Boas, E. Sousa, M. M. M. Pinto, M. Correia-da-Silva, Biofouling, 33 (2017) 927.
[2] J.R. Almeida, M. Correia-da-Silva, E. Sousa, J. Antunes, M. Pinto, V. Vasconcelos, I. Cunha, Scientific Reports, 7 (2017) 42424.

Green technologies applied to revalorize agricultural wastes. Case study: *Camellia sinensis*

V.Sanz[1,*], H. Domínguez[1], M.D. Torres[1]
[1]University of Vigo (Campus Ourense), Polytechnic Building, As Lagoas, Ourense, Spain
**matorres@uvigo.es*

One of the best known beverage consumed in the word after water, is tea. Green tea, extracted from the tender leaves from *Camellia sinensis* bushes, is well known for its uses in health, food and beauty industries. It has numerous properties, such as cancer preventive, antioxidant agent, fat burning, improver of the brain function or cardiovascular diseases preventive agent [1][2].

During the pruning season, amounts of plant wastes are generated. Leaves with null commercial interest were dismiss, but, through the use of green technologies (which minimized the use of material, used the lowest possible energy and maximized its efficiency) is possible to recovery compounds of interest of this agricultural raw material. A sequential combination of microwave hydrodiffusion and gravity (MHG) extraction, ultrasound-assisted technique (US) and pressurized hot water extraction (AH) have been used [3][4].

Tea leaves activation was carried out with MHG subjected to irradiation power of 300 W, followed by US system under 80ºC, 80KHz conditions and time range of 15 and 30 minutes. To close the sequence, solid phase was processed through autohydrolisis to 140 and 200ºC. The liquid phases were analysed to quantify bioactive compounds by the Folin-Ciocalteu assay and expressed as Gallic Acid Equivalents (GAE).

Figure 1, shows a remarkable increasing trend of the bioactive compounds when raw material was exposed a higher time in the US bath and lower temperature (140ºC) at AH extraction. The combinations of different technologies guarantee the recovery of bioactive compounds found in the raw material and creating new products that improve the quality of life.

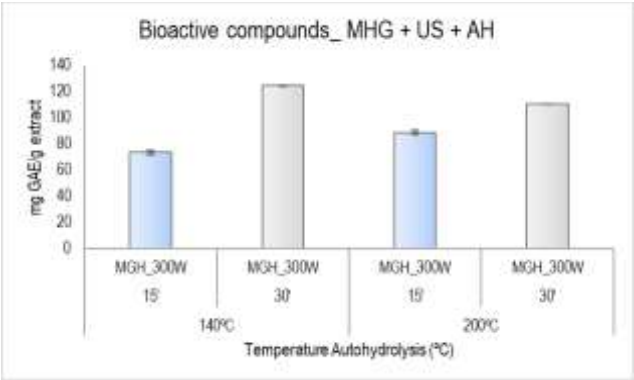


Fig.1. Bioactive properties expressed as mg/g of gallic acid equivalents (GAE) for the optimum conditions using Microwave Hidrodiffusion and Gravity (MHG) at 300W for 15 and 30 minutes in Ultrasound treatment at 140 and 200ºC in the autohydrolysis system.

Acknowledgments
The authors are grateful to Orballo company (Paderne, A Coruña - Spain) for provided the by-products. M.D.T. thanks Spanish Ministry of Economy and Competitiveness for her postdoctoral grant (IJCI-2016-27535).

References
[1] N.T. Zaveri, Life Sciences, 78 (2006) 2073.
[2] Gawron-Gzella, A. Królikowska, M. Pietrzak, Herba Polonica, 64 (2018) 60.
[3] M. Afroz Bakht, M.H. Geesi, Y. Riadi, M. Imran, M. Imtiyaz Ali, M.J. Ahsan, N. Ajmal, Saudi Journal of Biological Sciences, 26 (2019) 1043.
[4] S. Tsubaki, M. Sakamoto, J. Azuma, Food Chemistry, 123 (2010) 1255.

BIOQUÍMICA Y BIOTECNOLOGÍA

Bioactive potential of aqueous extracts from basidiomycete strains

Magda C. Semedo[1*], Sónia Martins[1], Amin Karmali[1]

[1]Centro de Investigação de Engenharia Química e Biotecnologia e Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, IPL, R. Conselheiro Emídio Navarro 1, 1959-007, Lisboa, Portugal;
Centro de Investigação e Tecnologias Agroambientais e Biológicas, Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5001-801, Vila Real, Portugal
* *msemedo@deq.isel.pt*

Biologically active compounds from natural sources such as fungi are again under the spotlight. Due to their impact on human health these products are attracting further attention of researchers from multiple scientific areas such as microbiologists, clinicians and nutritionists [1].

In this work, extractions were performed from mycelia or young fruiting bodies of twelve basidiomycete mushrooms and a multi-step protocol using cold and boiling water, acidic and alkaline conditions, was carried out [2]. Among the bioactive compounds present in mushrooms, β-glucans and phenolics play a significant role due to their antioxidant, anti-inflammatory and antitumor properties, between others. Hence, aqueous fractions were assessed for β-glucans by the Congo Red method [2], total phenolic content by Folin-Ciocalteu method [3] and total flavonoid compounds by aluminum chloride colorimetric assay [4]. Moreover, the antioxidant activity was evaluated by different established *in vitro* methods: chelating effect on ferrous ions assay and DPPH radical and ABTS radical scavenging capacity assays.

Alkaline fractions/KOH presented the highest phenolic concentrations; particularly the ones obtained from the young fruiting bodies of *Auricularia auricula* ($1.87 \pm 7.02\times10^{-2}$ mg GAE/ g biomass) and *Agaricus blazei* ($1.30 \pm 1.17\times10^{-1}$ mg GAE/ g biomass), and from the mycelia of *Ganoderma carnosum* ($1.50 \pm 7.63\times10^{-3}$ mg GAE/g of biomass). Flavonoid contents were detected in all alkaline fractions, being highest in mycelia from *G. carnosum* FKOH ($1.22 \pm 7.00\times10^{-2}$ mg CEQ/ g biomass). Concerning the acidic fractions/HCl, *Hericium erinaceus* results in $1.83 \pm 1.65\times10^{-1}$ mg CEQ/g biomass. Nevertheless, water extractions yielded almost no phenolic contents.

The antioxidant activities of the alkaline fractions/KOH were generally the highest too. All these fractions exhibited iron (II) chelating ability, DPPH and ABTS radical scavenging activities. Moreover these fractions were the ones that revealed the highest content in β-glucans (from $1.97\times10^{-1} \pm 2.67\times10^{-3}$ to $12.66 \pm 6.29\times10^{-1}$ mg/g biomass).

Acknowledgments
This work is supported by National Funds by FCT - Portuguese Foundation for Science and Technology, under the project UID/AGR/04033/2019.

References

[1] L. Barros, R.C. Calhelha, J.A. Vaz, I.C.F.R. Ferreira, P. Baptista, L.M. Estevinho, Eur Food Res Technol, 225 (2007) 151.
[2] M.C. Semedo, A. Karmali, L. Fonseca, J Microbial Biotech, 109 (2015) 140.
[3] F.S. Reis, A. Martins, L. Barros, I.C.F.R. Ferreira, Food Chem Toxicol, 50 (2012) 1201.
[4] J.-Y. Yeh, L.-H. Hsieh, K.-T. Wu, C.-F. Tsai, Molecules, 16 (2011) 3197.

Comparison of methods for extraction of biomolecules from *Phaeodactylum tricornutum*

Soraia Gil[1], Magda C. Semedo[1,2,*], Patrícia D. Barata[1,3], Sónia Martins[1,2], Joana Laranjeira da Silva[4]

[1] Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, IPL, R. Conselheiro Emídio Navarro 1, 1959-007, Lisboa, Portugal
[2] Centro de Investigação e Tecnologias Agroambientais e Biológicas, Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5001-801, Vila Real, Portugal
[3]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal
[4]Allmicroalgae, Av. Eng. Duarte Pacheco 19, 9º piso, 1070-100, Lisboa, Portugal
**msemedo@deq.isel.pt*

Microalgae are a rich source of bioactive compounds such as proteins, polyphenols, polysaccharides, lipids, pigments and vitamins, which have wide range of applications, most particularly in food, animal feed, biofuels, pharmaceuticals, and nutraceuticals [1]. Polysaccharides in general and sulfated polysaccharides in particular, exhibit several biological effects such as antioxidant, anti-inflammatory, antiviral, antitumor and immunomodulating activities [2].

In order to produce these biomolecules, the microalgae *Phaeodactylum tricornutum* was growing under autotrophic conditions with three different concentrations of salinity (25 g/L, 27 g/L and 30 g/L NaCl), over 1 and 3 weeks. For the extraction of the bioactive compounds from *Phaeodactylum tricornutum* biomass, five methods were compared and analysed: conventional Soxhlet extraction (SE), autoclave extraction (AE), multistep extraction (ME) with cold and boiling water, acidic and alkaline conditions, ultrasound-assisted extraction (UAE) and microwave-assisted extraction (MAE). For each method, the process parameters were optimized, such as solvent type, temperature, time, power and/or frequency. With the purpose of monitored these processes, the content in total polysaccharides was estimated by the phenol–sulfuric acid method [3], the sulphate content was determined according to the barium-gelatine method [4] and the protein quantification was performed by Coomassie blue dye-binding method [5].

As showed in Table 1, MAE method revelled to be the most suitable procedure for polysaccharides extraction and the conventional ME led to the highest protein concentration in cellular extracts.

Table 1. Comparison of the extraction methods and optimized parameters for the extraction of polysaccharides and proteins from *Phaeodactylum tricornutum*

Methods	Optimal conditions	Polysaccharides (mg/g biomass)	Sulfates (mg/g biomass)	Proteins (mg/g biomass)
SE	Ethanol 80%; 80ºC; 3h	24.94	248.55	0.14
AE	Water; 121ºC; 1.5h	53.49	153.40	3.62
ME	Water, HCl, KOH; 4.33h	25.04	205.48	37.08
UAE	Water; 62ºC; 20kHz; 90w; 10min	24.30	27.98	0.22
MAE	0.1M KOH; 120ºC; 30min	168.38	158.44	5.23

Acknowledgments
This work is supported by National Funds by FCT - Portuguese Foundation for Science and Technology, under the project UID/AGR/04033/2019 and Project PoliMAlga/IPL/IDI&CA2019.

Referencies

[1] G.L. Bhalamurugan, O. Valerie, L. Mark, Environ Eng Res, 23(2018) 229.
[2] M.F. de Jesus Raposo, A.M.M.B.de Morais, R.M.S.C.de Morais, in Polysaccharides, K. Ramawat, J.M. Mérillon (Eds.), Springer, 2015, 1683.
[3] T. Masuko, A. Minami, N. Iwasaki, T. Majima, S.-I. Nishimura, Y.C. Lee, Anal Biochem, 339(2005) 69.
[4] K.S Dodgson, R.G. Price, Biochem. J., 84(1962) 106.
[5] M.M. Bradford, Anal Biochem, 72(1976) 248.

Bio-hybrid magnetic nanoparticles for the purification of immunoglobulin G

Flávia F. Magalhães[1], Sofia F. Soares[1], Tito Trindade[1], João A.P. Coutinho[1], Ana L. Daniel-da-Silva[1], Ana P. M. Tavares[1], Mara G. Freire[1]

1 CICECO-Aveiro Institute of Materials, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal

flaviamagalhaes@ua.pt

Immunoglobulin G (IgG) is the most widely used antibody (Ab) for biomedical applications such as treatment of cancer, carriers of toxins, and in the treatment of autoimmune diseases [1]. Currently there are several conventional methods available for the purification of Abs, being the most used protein A affinity chromatography [2]. However, the preparation of highly purified Ab is still considered a difficult task, hampering their widespread implementation due to the high manufacturing associated costs.

In this work, hybrid magnetic nanoparticles comprising a magnetite (Fe_3O_4) core encapsulated with a hybrid material of silica and the polysaccharide κ-carrageenan (Fe_3O_4@SiO_2/SiCRG) were investigated for the extraction and purification of IgG from serum rabbit samples using simple magnetically assisted separation. The particles were synthetized and characterised by FTIR spectroscopy and transmission electron microscopy. The conditions for Ab purification, namely contact time, serum concentration and pH were evaluated. At the optimised conditions a purity of 74.9 % and a yield of 54% was observed. The increase in the IgG purity obtained shows the good performance of these new particles to separate target proteins from complex media, for which IgG from serum samples was here used as a proof of concept.

Agradecimientos

This work was developed within the scope of the project CICECO (UID/CTM/50011/2019), financed by national funds through the FCT/MCTES, project POCI-01-0145-FEDER-031268 funded by FEDER, COMPETE2020, POCI and OE. Ana P. M. Tavares acknowledges the FCT Investigator Programme (IF/01634/2015) with financing from the European Social Fund and the Human Potential Operational Programme.

Referencias

[1]. M. Leenaars and C. Hendriksen (2005) ILAR J. 46: 269.

[2]. Shukla, A. A., Hubbard, B., Tressel, T., Guhan, S. and Low, D., Journal of Chromatography, 848, (2007) 28–39.

Isolation and characterization of bioactive compounds from *Phaeodactylum tricornutum*

Soraia Gil[1], Magda C. Semedo[1,2], Sónia Martins[1,2*], Patrícia D. Barata[1,3], Joana Laranjeira da Silva[4]

[1] Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, IPL, R. Conselheiro Emídio Navarro 1, 1959-007, Lisboa, Portugal

[2] Centro de Investigação e Tecnologias Agroambientais e Biológicas, Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5001-801, Vila Real, Portugal

[3]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal

[4]Allmicroalgae, Av. Eng. Duarte Pacheco 19, 9º piso, 1070-100, Lisboa, Portugal

**smartins@deq.isel.pt*

The number of isolated compounds from marine organisms has been growing in the last years, standing out in this context the microalgae. Actually, microalgae are recognized as rich raw materials since they produce different value-added bioactive compounds, namely proteins, vitamins, lipids, pigments and polysaccharides. These biomolecules have demonstrated anticancer, anti-angiogenic, cytotoxic, anti-inflammatory, antioxidant, antimicrobial, immunostimulatory and anti-obesity activities [1,2]. It should be noted that numerous microalgae might also excrete in their environment exopolymers, which are mainly composed by exopolysaccharides (EPS) with several biological activities [3,4].

Aqueous extracts from the microalgae *Phaeodactylum tricornutum* were obtained by using autoclave (water; 121 ºC; 1.5 h), multistep extraction (with cold and boiling water, acidic and alkaline conditions) and microwave-assisted extraction (0.1 M KOH; 120 ºC; 30 min) methods. Their total polysaccharides, β-glucans, total phenolic and total flavonoid contents were investigated, as well as their *in vitro* biological properties (antioxidant activity in different systems). EPS solubilized in culture media were precipitated using alcoholic precipitation method [3] and their contents were also analysed.

The extract obtained by microwave-assisted extraction was fractionated by anion exchange chromatography on DEAE-52. Elution was carried out by stepwise increments in ionic strength of NaCl 0.1-0.5 M, NaOH 0.1-1 M and KCl 2 M at a flow rate of 20 mL/h. Fractions (1.5 mL, each) were collected and analysed by the phenol-sulfuric acid method [5].

Since the biological activities of polysaccharides are correlated with their structure, FT-IR spectroscopy, a powerful technique for the identification of characteristic organic groups in polysaccharides, was used to study the structural features in the aqueous extracts and in the chromatographic fractions.

The studied extracts exhibited a high level of antioxidant activities and antioxidant components, showing that due to their biochemical properties, they have potential to be used in challenging areas, such as biomedical, food science and food engineering.

Acknowledgments

This work is supported by National Funds by FCT - Portuguese Foundation for Science and Technology, under the project UID/AGR/04033/2019 and Project PoliMAlga/IPL/IDI&CA2019.

References

[1] S.P.M. Ventura, B.P. Nobre, F. Ertekin, M. Hayes, M. Garciá-Vaquero, F. Vieira, M. Koc, L. Gouveia, M.R. Aires-Barros, A.M.F. Palavra, in Microalgae-Based Biofuels and Bioproducts - From Feedstock Cultivation to End-Products, C. Gonzalez-Fernandez, R. Muñoz (Eds.), Woodhead Publishing Series in Energy, 2017, 461.

[2] M.I. Khan, J.H. Shin, J.D. Kim, Microb Cell Fact, 17 (2018) 36.

[3] C. Delattre, G. Pierre, C. Laroche, P. Michaud, Biotechnol Adv, 34 (2016) 1159.

[4] R. Xiao, Y. Zheng, Biotechnol Adv, 34 (2016) 1225.

[5] B. Chen, W. You, J. Huang, Y. Yu, W. Chen, World J Microbiol Biotechnol, 26 (2010) 83.

Optimization of ergosterol extraction from *Pleurotus* mushrooms using response surface methodology (RSM)

Oludemi Taofiq[1,*], Ana Rita Silva[1] Cristina Costa[2], Miguel A. Prieto[1,3], Joana Barros[2], Inês Ferreira[2], João Nunes[2], Lillian Barros[1], Isabel C.F.R. Ferreira[1,]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Bragança, Portugal;
[2]Centre Bio R&D Unit, BLC3-Technology and Innovation Campus, Oliveira do Hospital, Portugal
[2]Facultad de Farmacia, CIETUS-IBSAL, Universidad de Salamanca, Spain
[3]Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Spain
*taofiq.oludemi@ipb.pt

Pleurotus genus represents one of the most widely consumed mushrooms in the world with interesting health-promoting benefits, mainly due to their richness in several bioactive compounds [1]. Mushrooms produce ergosterol as one of their main sterols, which has been considered a contributor to their anti-inflammatory, antioxidant, and antitumor properties [2]. Obtaining an ergosterol enriched extract depends on different variables, such as the extraction method, solvent type, temperature, extraction time, and the solid-liquid ratio [2]. Therefore, it is essential to define the main variables and relevant response criteria to maximize the extraction yield and purity, taking into account cost functions.

In the present work, response surface methodology (RSM) was applied to optimize a heat assisted extraction system (HAE), combining time (*t*) and temperature (*T*) effects, and using a circumscribed central composite design (*CCCD*) for the recovery of ergosterol from the fruiting bodies of *P. ostreatus* and *P. eryngii* produced with lignocellulose substrate. Both mushrooms (POG and PEG for *P. ostreatus* and *P. eryngii*) and their by-product (POR and PER for *P. ostreatus* and *P. eryngii*) were used in the present work. The obtained responses were the quantification of ergosterol by HPLC-UV (Y_1: mg of ergosterol per g of extract residue and Y_2: mg of ergosterol per 100 g of dry weight mushroom). The *CCCD* consist of 16 response combinations and 4 centre points. Response surface models were fitted by using the following second order polynomial equation:

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{\substack{i=1 \\ j>i}}^{n-1} \sum_{j=2}^{n} b_{ij} X_i X_j + \sum_{i=1}^{n} b_{ii} X_i^2$$

The obtained results showed that the model successfully explained more than 80% variation in the experimental data (i.e. R^2>8). The global optimum conditions predicted by the model were 10 min, 30°C, and 65.6 min, 30°C for POG and POR, respectively. Under these conditions, the response (Y_1) predicted by the model were 57.61 and 43.72 mg per g of extract for POG and POR respectively. Also, regarding Y_2, the predicted responses were 246.31 and 290.90 mg/100 g dw, for POG and POR respectively. In what concerns *P. eryngii*, the optimum conditions were 150 min, 30°C, and 150 min, 30°C for PEG and PER, respectively. Under these conditions, the response *for* Y_1 was 32.56 and 60.75 mg per g of extract and Y_2 190.41 and 360.60 mg/100 g dw, correspondingly. The values predicted by the model are in close agreement with the experimental observations with very low residual distribution, proving the validity of the applied model. The obtained ergosterol-rich extract can be considered as a bioactive ingredient for food, pharmaceutical and nutraceutical purposes.

Acknowledgements
The authors are grateful to FCT, Portugal and FEDER under Programme PT2020 for financial support to CIMO (UID/AGR/00690/2019); European Regional Development Fund (ERDF) within the scope of project MicoBioExtract (POCI-01-0247-FEDER- 033939); European Agricultural Fund for Rural Development (EAFRD), through the Rural Development Program (PDR2020), within the scope of Project MicoCoating (PDR2020-101-031472); European Structural and Investment Funds (FEEI) through the Regional Operational Program North 2020, within the scope of Project Mobilizador ValorNatural®; L. Barros. thanks the national funding by FCT, P.I., through the institutional scientific employment program-contract for her contract.

References

[1] A.A. Khan, A. Gani, A. Shah, F.A. Masoodi, U. Mushtaq, A. S Naik, Bioactive Carbohydrates and Dietary Fibre, 11 (2017) 67.
[2] S.A. Heleno, M.A. Prieto, L. Barros, A. Rodrigues, M.F. Barreiro, I.C.F.R. Ferreira, Food and Bioproducts Processing, 100 (2016) 25.

Cosmeceutical properties of *p*-hydroxybenzoic acid and use of microencapsulation technique to ensure controlled release

Oludemi Taofiq[1,*], Sandrina A. Heleno[1], Ana Rita Silva [1,2], Ricardo C. Calhelha[1], Isabel P. Fernandes[1], Maria José Alves[1], Ana M. González-Paramás[3], Lillian Barros[1], Maria F. Barreiro[1], Isabel C.F.R. Ferreira[1]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Portugal
[2]Facultad de Farmacia, CIETUS-IBSAL, Universidad de Salamanca, Salamanca, España
[3]GIP- USAL, Unidad de Nutrición y Bromatología, Universidad de Salamanca, Salamanca, España
*taofiq.oludemi@ipb.pt

Topical formulations are designed to exert multifunctional benefits to the skin, and the interest on natural bioactive compounds as cosmeceutical ingredients have recently received increased attention [1]. However, the utilization of natural ingredients can present constraints related to their stability (e.g. against pH and temperature), being microencapsulation a useful strategy to overcome some of these limitations [2].

The present work describes *p*-hydroxybenzoic acids anti-inflammatory, anti-tyrosinase, and antimicrobial activity. The compound was further microencapsulated using the atomization/coagulation method, with sodium alginate coagulated with calcium chloride. The obtained microspheres were characterized in terms of morphology, particle size distribution, and encapsulation efficiency. Free and microencapsulated forms were then incorporated into a semi-solid cosmetic base formulation and HPLC-DAD was used to screen the presence of the compound in the final formulation.

p-Hydroxybenzoic acid showed anti-inflammatory (EC_{50} = 195 ± 9 µg/mL), anti-tyrosinase (EC_{50} = 1.86 ± 0.01 mg/mL), and antimicrobial activity against a panel of Gram positive and Gram negative bacteria, and also *Candida albicans*. The microparticles showed spherical morphology, with various sizes (D_{10}, D_{50} and D_{90} representing 20.5, 74.6, and 206 µm, respectively), little agglomeration, and a unimodal and bimodal particle size distribution (number and volume, respectively). Encapsulation efficiency and yield were 88.3% and 57.8%, respectively. After incorporation, the formulation containing free forms of the compound maintained some of its bioactive properties, while the encapsulated forms preserved the bioactivity showing a slow release profile of the compounds.

In conclusion, the studied compound showed interesting bioactive properties and can be used in the development of multifunctional cosmeceutical formulation. The adopted encapsulation strategy also provides a suitable alternative to prolong retention of bioactive compounds for subsequent release (sustained release), thereby preserving its bioactivity over time.

Acknowledgements

FCT and FEDER under Program PT2020 (POCI-COMPETE2020) for CIMO (UID/AGR/00690/2019) and Associate Laboratory LSRE-LCM (UID/EQU/50020/2019) funded by national funds through FCT/MCTES (PIDDAC). European Structural and Investment Funds (FEEI) through NORTE 2020 (Project Mobilizador ValorNatural®). This work is funded by the European Agricultural Fund for Rural Development (EAFRD), through the Rural Development Program (PDR2020), within the scope of Project MicoCoating (PDR2020-101-031472). L. Barros. R.M. Calhelha and I. Fernandes thank the national funding by FCT, P.I., through the institutional scientific employment program-contract for their contracts, while S. Heleno thanks the national funding by FCT, P.I., through the individual scientific employment program-contract.

References

[1] O. Taofiq, F. Rodrigues, L. Barros, M.F. Barreiro, I.C.F.R. Ferreira, M.B.P.P. Oliveira. Food and Chemical Toxicology 2019, 127, 228–236.

[2] O. Taofiq, S.A. Heleno, R.C. Calhelha, I.P. Fernandes, M.J. Alves, L. Barros, A. M. González-Paramás, I.C.F.R. Ferreira, M.F. Industrial Crops and Products 2018, 124, 44–52.

NANOESTRUCTURAS MAGNÉTICAS PARA LA MEJORA DE TÉCNICAS EN BIOQUÍMICA Y BIOLOGÍA MOLECULAR

Seco-Gudiña R[1,2,3], González-Gómez M A[1], Yáñez-Vilar S[1], Piñeiro Y[1], de la Fuente M[3], López-López R[2], Rivas J[1].

[1]Departamento de física aplicada, Instituto de investigación tecnológica, Laboratorio de nanotecnología y magnetismo—NANOMAG, University of Santiago de Compostela

[2]Grupo de Oncología Médica Traslacional (ONCOMET), Instituto de investigación de Santiago (IDIS); Complexo Hospitalario Universitario de Santiago de Compostela

[3]Unidad de nanooncologia, Instituto de investigación de Santiago (IDIS); Complexo Hospitalario Universitario de Santiago de Compostela

Email: romanseco@hotmail.es

El aislamiento de ciertas poblaciones celulares para realizar un diagnóstico preciso es uno de los grandes retos de la biomedicina, especialmente en el campo de la oncología [1-3]. Gracias al empleo de nanopartículas magnéticas (MNP) ha sido posible una mejora en la selección y manipulación de células tumorales, permitiendo solventar algunos de los inconvenientes que presentan hoy en día las técnicas en bioquímica y biología molecular.

Dada la habilidad de las MNP para ser manipuladas con un campo magnético externo, una serie de avances, entre los cuales podemos destacar la hipertermia, liberación de material genético/fármacos, detección mediante anticuerpos, han sido presentados. En el presente trabajo, se hará especial énfasis en modelos de captación (uptake) por vía activa comparándolos con los métodos tradicionales pasivos. También se hablará de un método de enriquecimiento celular basado en este mencionado uptake activo, el cual resulta muy atractivo si exploramos sus ventajas como la disminución de tiempos de incubación/selección, transfección, conteo celular, etc.

Estos estudios se realizaron sobre la línea celular HeLa (ATCC® CCL-2™). La viabilidad de las partículas para su posterior uso fue testeada mediante ensayos de actividad metabólica (MTT) y la visualización de dichas partículas se realizó mediante observación en microscopía tradicional y confocal. En base a los resultados obtenidos hemos observado que la captación de MNP impulsada magnéticamente por las células es un procedimiento eficiente para la manipulación celular con un estrés mínimo.

Agradecimientos

Este trabajo fue financiado por el Programa de la Consellería de Educación para el Desarrollo de la Agrupación Estratégica de Materiales (AEMAT) en la Universidad de Santiago de Compostela (Beca N. ED431E2018 / 08), y el Programa para la Consolidación de Unidades de Investigación de Referencia Competitiva GRC2017 (Beca N. ED431C 2017/22) de la Xunta de Galicia.

Referencias

[1] MacDonald C, Barbee K, Polyak B. Force dependent internalization of magnetic nanoparticles results in highly loaded endothelial cells for use as potential therapy delivery vectors. Pharm Res. 2012;29(5):1270–1281. doi:10.1007/s11095-011-0663-7.

[2] Lu, Yi Ching & Chang, Fan-Yu & Tu, Shu-Ju & Chen, Jyh-Ping & Ma, Yunn-Hwa. (2016). Cellular Uptake of Magnetite Nanoparticles Enhanced by NdFeB Magnets in Staggered Arrangement. Journal of Magnetism and Magnetic Materials. 427. 10.1016/j.jmmm.2016.11.010.

[3] Plouffe BD, Murthy SK, Lewis LH. Fundamentals and application of magnetic particles in cell isolation and enrichment: a review. Rep Prog Phys. 2014;78(1):016601. doi:10.1088/0034-4885/78/1/016601.

Decolorization of dyes from textile effluents by laccase using ionic liquids

Rui M. F. Bento[1,*], Mafalda R. Almeida[1], Mara G. Freire[1], Ana P. M. Tavares[1]

[1]CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
*ruib@ua.pt

The intensive use of water containing dyes by the textile industry, and consequently the contamination of soils and water, represents serious environmental concerns. Amongst the several processes applied in the treatment of textile effluents, biological-based processes, if designed to be cost-effective and eco-friendly, are promising alternatives to decolorize textile effluents.

In this work we investigate and propose the novel use of ionic liquids (ILs) with surfactant characteristics to improve the degradation of the largely used and highly hydrophobic textile dye indigo carmine by laccase. An initial screening on the activity of laccase in aqueous solutions of twelve surfactant-based ILs from three different families, namely tetraalkylammonium- and imidazolium-based cationic surfactants and cholinium-based anionic surfactants, at different concentrations, was carried out. A high activity of laccase was observed with decyltrimethylammonium bromide, [N10111]Br, and 1-decyl-3-methylimidazolium chloride, [C10mim]Cl, at 75 mM (above the critical micellar concentration of each IL). These ILs were then investigated in aqueous solutions to simultaneously encapsulate laccase and IC for the in situ enzymatic biodegradation of the dye. The use of ILs remarkably increases the degradation rate of the dye and decolorization efficiency; a degradation efficiency of IC of 82% is attained in 0.5 h using aqueous solutions of [N10111]Br, whereas without IL only 6% of IC is degraded. Furthermore, at the end of 24 h, 93% of the dye decolorization was achieved in the presence of 75 mM of [N10111]Br. The overall gathered results show that it is possible to significantly improve the degradation of hydrophobic dyes by enzymes using appropriate surfactant-based ILs, while foreseeing the use of the treated water by the same textile industries in new dyeing steps and thus contributing to a substantial decrease of the economic input and environmental footprint of these industries.

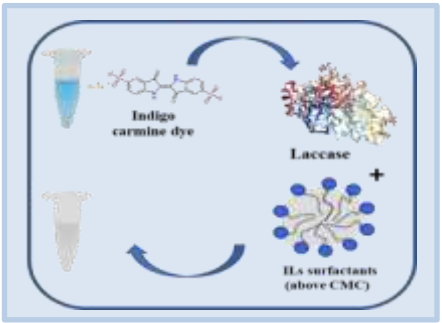


Fig.1. In situ enzymatic biodegradation of the dye.

Acknowledgements
This work was developed within the scope of the project CICECO (UID/CTM/50011/2019), financed by national funds through the FCT/MCTES, project POCI-01-0145-FEDER-031268 funded by FEDER, COMPETE2020, POCI and OE. Ana P. M. Tavares acknowledges the FCT Investigator Programme (IF/01634/2015) with financing from the European Social Fund and the Human Potential Operational Programme.

CATÁLISIS

Funcionalización de superficies mediante nanopartículas de TiO_2

N. Gavieiro[1*], J. Fernandez[2], S. Dosta[3], I. García[3]
[1]Universidad de Barcelona, Facultat de Química, Barcelona, España. [*noemigavieiro@ub.edu]*
[2]Universidad de Barcelona, Facultat de Química, Barcelona, España [*Javier.fernandez@ub.edu]*
[3]Universidad de Barcelona, Facultat de Química, Barcelona, España. [*sdosta@ub.edu]*
[4]Universidad de Barcelona, Facultat de Química, Barcelona, España [*irenegarcia@ub.edu]*

Actualmente existe una gran problemática con los compuestos volátiles como los óxidos nitrosos y CO_2 sobretodo en las grandes ciudades, donde los efectos secundarios en la salud de las personas son muy graves. A día de hoy, se intenta no solo minimizar su exposición sino eliminarlo.

En este proyecto se pretende comparar diferentes substratos para la adhesión de nanoparticulas de dióxido de titanio generadas mediante el método sol-gel. El método sol-gel se puede trasladar fácilmente a nivel industrial, además es el más económico y sencillo a la hora de obtener nanopartículas de dióxido de titanio.

Se pretende estudiar el efecto del disolvente en el tamaño y la forma de las partículas creadas. En la caracterización de estas nanopartículas se estudiará su tamaño, la morfología y la estructura cristalina.

Mediante la modificación del tamaño y la forma de la nanopartícula se pretende optimizar la eficiencia en la eficiencia fotocatalítica de los compuestos orgánicos volátiles generadores de la gran problemática medioambiental.

Este proyecto desea estudiar el efecto de la utilización de un sbstrato poroso y no poroso como soporte de las nanopartículas. Así mismo, los substratos usados provienen de la revalorización de residuos de la industria alimentaria.
Por lo tanto, podemos reutilizar los residuos en la lucha contra los compuestos orgánicos volátiles.

Agradecimientos
Agradezco a Javier Fernandez su apoyo incondicional y al grupo CPT por la confianza depositada en el desarrollo del proyecto.

Referencias
[1] H. Xuebin, C. Yibing, M. Muhammad, S. Xiafei, Y. Qiang, Deposition of TiO2 nanoparticles on porous polylactic acid fibrous substrates and its photocatalytic capability, 20 (2001) 537.
[2] S. F. Li and G. L. Yen, Photocatalytic Degradation of Formaldehyde by TiO2 Nanoparticules Immobilized in Actived Carbon Fibers. Adv. Mater. Res, Vol 482-484. Pp. 2539-2542, 2012.
[3] Fernandez, Ingrid Eliana, J. E. Rodriguez-Páez. Wet-Chemical preparation of TiO2-Nanoestructures Using different solvents: Effect of CTAB Concentration and tentative mechanism of particle formation. Journal of Alloys and Compounds. 2019.

Study of the Performance of Alkaline Ionic Liquids for the Catalysis of Biodiesel Production from Waste Cooking Oil

A. C. Lima[1,2,*], M. C. Gomes[2], P. Brito[1], A. M. Queiroz[1], A. E. Ribeiro[1]
[1]Centro de Investigação de Montanha, Polytechnic Institute of Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]Federal University of Technology of Paraná, Campus Apucarana, Rua Marcílio Dias, Jardim Paraíso, 86812-460 Apucarana, PR - Brazil
** analima.2015@alunos.utfpr.edu.br*

Fossil fuels are a primary energy resource that play a critical role in our daily activities. Currently, the provision of energy relies primarily on fossil fuels such as coal, petroleum and natural gas. Although the fossil-based fuels are satisfying the energy requirements of the world, the depletion of fossil energy reserves, the high demand for fossil fuels and the dependence on it have led researchers to search for sustainable and environmental-friendly energy sources. In this scenario, biodiesel is a sustainable alternative compared to diesel, due to its biodegradability, non-toxicity and low carbon content. Biodiesel can be a blended component in transportation fuels, as it demonstrates similar characteristics to petroleum diesel and has lower greenhouse gas (GHG) emissions [1]. Moreover, there are some concerns related to first-generation biodiesel (derived from food crops), such as the high cost of these oils, which accounts for about 70% of the total value of biodiesel production, as well as the competition with food markets, and the possibility of promoting soil degradation through the uncontrolled stimulation of energy crops [1,2]. Hence, second-generation biodiesel production has a considerable potential to reduce waste residues and GHG emissions by replacing fossil fuels. Waste cooking oils (WCO) are considered a promising alternative in biodiesel synthesis, due to their low cost, high availability and arise as possible alternatives to overcome the disadvantages of the traditional production processes [2].

Therefore, this study focuses on the research of producing biodiesel in a more sustainable way, namely the production of biodiesel from waste oils and the application of an ionic liquid as catalyst. Ionic liquids (ILs) are organic salts composed of cations and anions that can be used in biodiesel catalysis due to their attractive properties, such as good chemical stability, low vapor pressure, ability to be dissolved in a large range of inorganic and organic compounds and simple recovery process [3]. In this work, alkaline ILs, bis-(3-methyl-1-imidazolium-)-ethylene dihydroxide [4] and choline hydroxide [5], were selected for the study of their performance for the catalysis of biodiesel production from WCO samples. The ILs were synthesized, characterised and used for the production of biodiesel batches. Operational parameters such as reaction time, reaction temperature, alcohol/oil molar ratio and catalyst dosage, will be optimized. IL recyclability will be assessed, and kinetic studies will be carried out to determine the activation energy of the transesterification reaction catalysed by the referred ILs.

References

[1] Ambat, I., Srivastava, V., Sillanpää, M., Recent Advancement in Biodiesel Production Methodologies Using Various Feedstock: A Review. *Renewable and Sustainable Energy Reviews*, 90, July 2018, 356–369.

[2] Fonseca, J. M., Teleken, J. G., de Cinque Almeida, V., da Silva, C., Biodiesel from Waste Frying Oils: Methods of Production and Purification. *Energy Conversion and Management*, 184, March 2019, 205–218.

[3] Mohammad Fauzi, A. H., Amin, N. A. S., An Overview of Ionic Liquids as Solvents in Biodiesel Synthesis. *Renewable and Sustainable Energy Reviews*, 16(8), 2012, 5770–5786.

[4] Liang, J., Wang, J., Ren, X., Li, Z., Jinag, M., Preparation of Biodiesel by Transesterification from Cottonseed Oil Using the Basic Dication Ionic Liquids as Catalysts. *Journal of Fuel Chemistry and Technology*, 38(3), 2010, 275–280.

[5] Fan, M., Huang, J., Yang, J., Zhang, P., Biodiesel Production by Transesterification Catalyzed by an Efficient Choline Ionic Liquid Catalyst. *Applied Energy*, 108, 2013, 333–339.

Valorization of used cooking oils through ionic liquid catalyzed biodiesel conversion processes

H. Diniz[1,2],*, D. M. Freitas-Silva[2], A. Queiroz[1], A. Ribeiro[1], P. Brito
1 Centro de Investigação de Montanha, Polytechnic Institute of Bragança, Campus Santa Apolónia, 5300-253 - Bragança, Portugal 2 Centro Federal de Educação Tecnológica de Minas Gerais, Campus I, Av. Amazonas 5253, Nova Suíça, 30421-169 - Belo Horizonte, MG - Brazil
*heloisa27@hotmail.com

The search for alternative technologies to fossil fuel-based energy sources is a recent trend. One possible solution is to use biodiesel as a diesel substitute, reducing environmental impacts such as pollutant emissions. Biodiesel consists of a mixture of long chain fatty acid alkyl esters and is produced by converting vegetable oils or animal fats by transesterification reactions [1].

Due to the high cost of the usual raw material, there is a need to reduce the final price of biodiesel. Thus, oil sources that are not in competition with the food market, such as residual cooking oils, are used. However, these oils show high levels of free fatty acids, which can bring problems to the classic biodiesel production process, alkaline transesterification. To overcome these problems, ionic liquids (IL) can be used as catalysts, since they also promote esterification reactions of free fatty acids to biodiesel. Furthermore, ionic liquids present a few advantages, related to their recoverability and reusability, as well as the environmental and safety perspectives [1].

The objective of this work is to study the production of biodiesel by applying 1-methylimidazolium hydrogen sulfate IL ([HMIM][HSO4]) as a catalyst in esterification/transesterification reactions with methanol in samples of high acidity residual vegetable oils. Additionally, the study of the IL recovery procedure will be carried out, with the evaluation of the maximum number of recovery cycles that can be performed without significant loss of reaction yield.

The following operational conditions were established for each reaction/recovery cycle: reaction time of 4 hours, temperature of 65°C, molar ratio 1:10 of oleic acid/methanol, and 10%wt. of IL charge relating to oleic acid. After the synthesis, the biodiesel acidity and the reaction conversion in terms of acidity decrease were determined by volumetric titration of the light biodiesel organic phase with potassium hydroxide (KOH) solution. Also, the FAME (fatty acid methyl esters) content of the biodiesel sample was quantified by gas chromatography (GC-FID). The IL recovery was done by drying the aqueous heavy phase at 110°C, followed by washing it with distilled water in a 1:3 mass ratio, separation of the IL phase, and a second drying step at 110°C [2]. The assessment of the quality of the recovered IL was done by Fourier Transform Infrared spectroscopy (FTIR), specifically through the measurement of the correlation between the recovered IL and the initial IL spectra.

The results obtained are presented in Table 1. Reaction 1 was performed with the commercial IL and the subsequent reactions were carried out using the IL samples recovered from the previous reaction cycle. Despite the use of the recovered ionic liquid, the conversion remained relatively high, with only a slight decrease. The correlation between the initial IL and the recovered IL was 99,15%, showing that the recovery method is efficient.

Table 1 – Experimental results obtained.

Reaction	Conversion (%)	IL Recovery (%wt.)
1	81,18	73,97
2	79,84	84,16
3	79,45	76,35
4	78,08	74,65

References [1] Z. Ullah, M. A. Bustam, Z. Man, Renewable Energy, 77 (2015) 521-526. [2] A. Baú, G. G. Lenzi, A. Ribeiro, A. Queiroz, P. Brito, Acidic waste cooking oil valorization by biodiesel synthesis catalysed by hydrogen sulfate 1-butyl-3-methylimidazolium, XXIV Encontro Luso-Galego de Química, CAT20, Porto, 21-23 november 2018.

Esterification and transesterification of glycerol to glycerol acetates in the presence of carbon catalysts - synthesis of fuel additives

Karolina Ptaszyńska, Anna Malaika, Mieczysław Kozłowski

Adam Mickiewicz University in Poznań, Faculty of Chemistry
Uniwersytetu Poznańskiego 8
61-614 Poznań, Poland
ptaszynskakarolina@icloud.com

The use of biodiesel is forecast to increase in the coming years. This is mainly because of environmental reasons. First, it is well known that conventional energy sources such as coal, petroleum and natural gas are constatly diminishing. Biodiesel can be a good alternative to replace fossil fuels becouse it can be obtained from renewable sources. Secondly, combustion of biodiesel releases to the atmosphere lower amounts of gaseous and solid pollutants as compared to the combustion of fossil fuels. Currently, biodiesel is obtained in transesterification of vegetable oils or animal fats in the presence of homogeneous catalysts. However, during this synthesis, large amounts of glycerol as a by-product are also formed. Thus, in order to make the production of biodiesel more cost-effective and competitive, it is important to find new ways to upgrade glycerol waste to valuable compounds [1].

One of the possible options for glycerol valorization is obtaining its acetates (mono-, di- and tri-substituted products, MA, DA and TA, respectively). These compounds are valuable for many branches of industry, in particular for the automotive industry where DA and TA are used as important fuel additives [2]. Glycerol acetates can be obtained in the process of esterification or transesterification of glycerol with acetic acid or ethyl acetate, respectively. Usually, in the laboratory scale, these reactions have been carried out in the presence of heterogeneous acid catalysts such as Amberlyst-15. Carbon materials have been applied for this purpose much less frequently. This promped us to study new carbon-type catalysts in the above mentioned processes.
In the present work, the novel acidic carbon materials were obtained in one-step, simple, fast and cheap method based on partial carbonization of selected sugars or glycerol (for the sake of comparison) in the presence of concentrated sulfuric acid. The obtained carbocatalysts were characterized using different techniques, e.g., elemental and textural analyses, SEM or potentiometric titration, and were applied in glycerol esterification and transesterification processes. The esterification of glycerol was carried out with acetic acid at 110°C, using a 1:6 alcohol to acid molar ratio. The glycerol transesterification reaction was performed in the presence of ethyl acetate with a glycerol to ester molar ratio of 1:30 and varying the procesing conditions (e.g. temperature, the type of a reaction system, etc).
Based on the catalytic results, it was found that the prepared materials act effectively in both tested reactions. In the esterification process high glycerol conversion and satisfactory selectivity to DA and TA (most desirable reaction products) were obtained in only 2 hours. The reusability tests confirmed high catalytic stability of these samples in subsequent reaction cycles. On the other hand, glycerol transesterification required the use of excess ethyl acetate to shift the reaction equilibrium towards the formation of products. The process carried out in a system with a condenser showed to be selective mainly to MA, or to a mixture of MA and DA (in similar quantities). Significant improvement of catalytic performance in transesterification results was achieved when the reaction was performed in an autoclave at elevated temperature.

References

[1] J. V. Gerpen, Fuel Processing Technology 2005, 86, 1097–1107.
[2] P.U. Okoye, B.H. Hameed, Renew. Sust. Energ. Rev. 2016, 53, 558-574.

Production and Characterization of Biodiesel obtained by Transesterification Catalyzed by the Ionic Liquid Choline Hydroxide

R. Lima[1,2,*], A.K.C.L Lobato[2], A. Queiroz[1], A. Ribeiro[1], P. Brito[1]

[1] Centro de Investigação de Montanha, Polytechnic Institute of Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2] Salvador University, School of Architecture, Engineering and IT, Salvador, Bahia, Brazil
* *renatalima1306@gmail.com*

Biodiesel is a mixture of alkyl esters derived from vegetable oils or animal fat. It is a biodegradable and renewable fuel and does not contribute to the emission of polluting gases into the atmosphere, but its major disadvantage is its relative high cost usually regarding to production and raw materials costs [1].

Crude oils and fats extracted from plant and animal sources are alternatives to the use of highly polluting fossil fuels. They are composed of triglycerides which can be converted into biofuels through three different paths, cracking, esterification and transesterification, being the last one, the most common method. In transesterification processes, the alcohol most used is methanol due to its low cost and physicochemical properties. The transesterification reaction has glycerol as a byproduct which adds some value to the technology since it shows several potential applications in the industry [2]. The literature describes the alcoholysis of vegetable oils or animal fats in various ways using different types of catalysts: acids, bases and enzymes. Acid catalysis is used when the oil has a high concentration of free fatty acids, but it requires large amounts of alcohol and has a slow reaction velocity. Basic catalysis is about 4,000 times faster than acid catalysis and does not require large amounts of alcohol. The most commonly used basic catalysts are sodium or potassium hydroxide [2, 3]. The use of ionic liquids (IL) in catalytic processes has been studied mainly in the ecological field, as it allows a high recycling efficiency. IL based on the choline's cation (2-hydroxyethyl trimethylammonium) have received much attention in recent years. This fact is due, mainly to its biocompatibility characteristics and potential for various industrial applications, mainly choline hydroxide (ChOH) because of its good catalytic performance due to its good basicity in methanol solution, in addition to its successful reuse [4].

The parameters selected for the study of biodiesel production catalyzed by choline hydroxide IL were: reaction time, reaction temperature, molar ratio oil/methanol, catalyst charge, and catalyst recyclability. In this work, ChOH was synthesized, characterized and used as a catalyst in the production of biodiesel. The preliminary results showed that for a reaction time of 4 h, using a temperature of 60°C, a molar ratio oil/methanol of 1:10 and 10wt% of catalyst, using a waste cooking oil sample, it occurred the transesterification reaction with the synthesis of fatty acid methyl esters (FAME), which was confirmed by gas chromatography (GC-FID).

References

[1] X. Lang, A.K. Dalai, N.N. Bakhshi, M.J. Reany, P.B. Hertz, Preparation and characterization of bio-diesels from various bio-oils. *Bioresource Technology*, 80, pp. 53-62, 2001.

[2] J.D. Rocha, Use of Ionic Liquides in Biodiesel Productions – a review. *Brazillian J. Chem. Eng.*, 29(1), pp. 1-13, 2012.

[3] A. Bessa, Production of biodiesel from residual frying oil using the ionic liquid of choline hydroxide as catalyst. *Master thesis, Universidade Federal do Ceará*, 2015.

[4] M. Fan, J. Huang, J. Yang, P. Zhang, Biodiesel production by transesterification catalyzed by an efficient choline ionic liquid catalyst. *Applied Energy*, Elsevier, 108(C), pp. 333-339, 2013.

Degradation of textile dyes in aqueous solutions using type-Fenton bimetallic zeolite catalysts

Bebiana L.C. Santos[1*], António M. Fonseca[1,2], Isabel C. Neves[1,2]

[1]Center of Chemistry, Chemistry Department, University of Minho, 4710-057 Braga, Portugal
[2]CEB – Center of Biological Engineering, University of Minho, 4710-057 Braga, Portugal

**e-mail del autor de contacto E-mail: id7175@alunos.uminho.pt and ineves@quimica.uminho.pt*

Textile dyes are growing to be a problematic class of pollutants to the environment. The disposal of dyes in water resources has bad aesthetic and health effects, since most of them are carcinogenic and mutagenic [1,2], so it is important to remove them from the environment. Effective and economic treatment by advanced oxidation processes (AOPs) has been attracted great and continuous interest for the degradation of these pollutants [3]. The heterogeneous Fenton-like processes have been paid great attention for its low cost, high efficient and mild conditions among these AOPs processes (20-50°C and atmospheric pressure) [3,4]. Recently, several iron- and copper- based heterogeneous Fenton catalysts have been investigated to be efficient catalytic systems [4]. In this work, in the preparation of type Fentom catalysts, zeolite NaY was used to support Fe, Cu and Mn. The type-Fenton catalysts, mono and bimetallic, were prepared by ion exchange method and the catalysts were tested in degradation of textile dyes in a batch reactor using H_2O_2 at different temperatures and atmospheric pressure. It was observed that iron type-Fenton catalysts are active for the degradation of dyes, but when the reaction is performed with bimetallic type-Fenton zeolite catalysts the degradation becomes faster.

Acknowledgements
This work has been developed under the scope of the projects: BioTecNorte (operation NORTE-01-0145-FEDER-000004), PTDC/AAGTEC/5269/2014, and Centre of Chemistry (UID/QUI/00686/2013 and UID/QUI/0686/2016).

References

[1] M.M.F. Silva, M.M. Oliveira, M.C. Avelino, M.G. Fonseca, R.K.S. Almeida, E.C. S. Filho, Chem. Eng. J., 2012, 203, 259–268.
[2] M.A.M. Salleh, D.K. Mahmoud, W.A.W.A. Karim, A. Idris, Desalination, 2011, 280, 1–13.
[3] M.L. Rache, A.R. García, H.R. Zea, A.M.T. Silva, L.M. Madeira, J.H. Ramírez, Appl. Catal. B: Environ., 2014, 146, 192– 200.
[4] Ch. Zheng, Ch. Yang, X. Cheng, Sh. Xu, Zh. Fan, G. Wang, Sh. Wang, X. Guan, X. Sun, Separation and Purification Technology, 2017, 189, 357–365.

Hybrid nanomaterials for photocatalytic environmental applications

Luísa D. Chiavassa,[1] Olinda C. Monteiro,[1] António J. Silvestre,[2,3] José V. Prata[4,5*]
[1] Centro de Química Estrutural e Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal; [2] Departamento de Física, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal; [3] LSPL and CeFEMA, Departamento de Física, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal; [4] Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal; [5] Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5000-801, Vila Real, Portugal
**jvprata@deq.isel.ipl.pt*

Advanced oxidation processes, for the photodegradation of organic pollutants in air and water media, include methods that join UV-Vis light and semiconductors as photocatalysts. Due to the high optical band gap energy of such neat materials, only part of abundant and cheap energy coming from solar irradiation is available to efficiently produce excited state entities that would trigger photo-induced oxidation processes. To circumvent this and other problems, such as the high recombination rate of excitons in semiconductors upon photoexcitation, hybrid/composite materials were long thought as promising materials for narrowing the band gap allowing for a more effective use of natural energy sources for pollutants degradation.

Herein, studies involving the use of titanate nanotubes (TNT) [1] combined with carbon dots (C-dots), the most recent entry to the class of carbon nanomaterials [2], are described. These will include their synthesis, structural, optical and morphological characterization, and their application as catalysts for the photo-assisted degradation of xanthines, used here as model pollutants. Two synthetic approaches were used. One follows an hydrothermal one-pot procedure were C-dots/TNT hybrid materials (C-dots S/TNT) were simultaneously prepared from suitable precursors and the other (C-dots P/TNT) by post-modification of pre-synthesized TNTs with C-dots obtained from aqueous waste residues [3]. The UV-Vis diffuse reflectance and FTIR attenuated total reflectance spectroscopies indicated, in both cases, the presence of C-dots in TNTs. However, distinct photocatalytic behaviours were observed for the two nanomaterials (see Fig. 1). Moreover, it was found that the photodegradation kinetics were dependent on the excitation source (*e.g.* 450 W Hg lamp *vs*. 500 W Hg-Xe lamp) and on the model pollutant used (caffeine *vs*. theophylline). A discussion of the main reasons underlying such results will be presented.

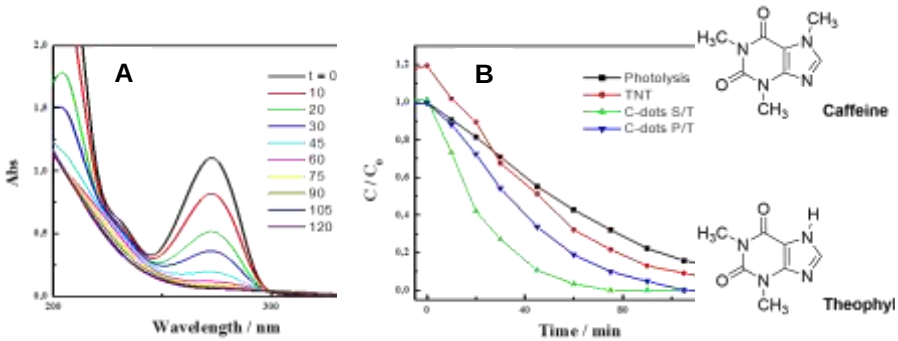


Fig.1. A – UV-Vis absorption data on time-dependency of caffeine (20 ppm) photodegradation in aqueous medium using C-dots S/TNT (20 mg) under irradiation of a 450 W Hg lamp; **B** – Efficiency of photocatalysts (TNT and C-dots/TNT) as compared to photolysis in caffeine degradation.

Acknowledgements
This work has been funded by IPL under the IPL/2018/VLA-NANOC/ISEL research project and partially supported by FCT/MCTES, under PEst–OE/QUI/UI0612/2019, IF/01210/2014, UID/QUI/00616/2019 and UID/CTM/04540/2019 projects.

References

[3] B. Barrocas, A. J. Silvestre, A. G. Rolo, O. C. Monteiro, Phys. Chem. Chem. Phys., 18 (2016) 18081.
[4] P. Zuo, X. Lu, Z. Sun, Y. Guo, H. He, Microchimica Acta, 183 (2016) 519.
[5] D. A. Sousa, A. I. Costa, M. R. Alexandre, J. V. Prata, Sci. Total Environ., 647 (2019) 1097.

ENSEÑANZA DE LA QUÍMICA

Práctica virtual de Laboratorio de Química: Determinación del calor de vaporización del agua

J. M. Fernández Solís[1,*], R. Lourido Rodríguez[1], S. Fernández Alonso[1], E. González Soto[1], J. M. Castro Romero[2]

Departamento de Química, Escolas Politécnica Superior (EPS)[1] y Universitaria Politécnica (EUP)[2], Universidade da Coruña (UDC), Mendizábal s/n, 15403, Ferrol, España
*jose.maria.fsolis@udc.es

La experiencia como docentes nos indica que, debido a la disminución progresiva de las horas asignadas a la asignatura Química en los planes de estudios anteriores y en los de los actuales Grados de Ingeniería, el tiempo que el profesorado dedica a las prácticas de laboratorio es muy pequeño, reduciéndose la presencia física del alumno en el laboratorio a un valor casi testimonial. Consecuentemente, la presentación de videos de carácter descriptivo sobre prácticas virtuales en clase, sin la existencia del condicionante de espacio del laboratorio, permite al profesor impartir con detalle la práctica que corresponda, promoviendo el debate con los estudiantes y favoreciendo una mejor comprensión de los conceptos expuestos.

Las consideraciones anteriores han conducido a llevar a cabo un estudio sobre prácticas virtuales de Química que pudieran complementar a las efectuadas en el laboratorio, sin pretender que lleguen a sustituirlas, ya que se considera totalmente imprescindible que el estudiante adquiera competencias relacionadas con el trabajo experimental a desarrollar en el laboratorio.

Con esa finalidad se realizaron prácticas, en los campos de la Química General y Analítica, relativas a preparación de disoluciones [1,2,3], calor de reacción [2,3], valoraciones ácido-base [1], identificación de iones a partir de sus mezclas en disolución [4] y de metales a la llama, usando el programa virtual ChemLab, General Chemistry Laboratories, v.2.5, anexo al texto de Pearson Educación [5].

La presente comunicación describe una práctica con objeto de determinar el calor de vaporización del agua, mediante los datos obtenidos en un experimento realizado en un laboratorio virtual de Química. El programa informático usado permite elaborar un video, a visualizar por los alumnos, en el que se describen las etapas del experimento, debiendo anotar los valores de los parámetros necesarios para el cálculo de dicho calor de vaporización y obteniendo un resultado que es muy concordante con el valor considerado como referencia [6]. Finalizada la práctica, con el fin de verificar la comprensión y asimilación de los conocimientos expuestos, el profesor propondrá a los estudiantes la resolución, en la misma sesión de la clase, de unas cuestiones sencillas relacionadas con dicha práctica.

Agradecimientos
Queremos expresar nuestro agradecimiento a la Universidad de A Coruña, por la concesión de una Beca de Colaboración en Laboratorios de Docencia a Rodrigo Lourido Rodríguez, y a la Editorial Pearson Educación.

Referencias
[1] R. Casanova, A. Filgueira, J. Fernández, E. Muñoz, en Panorama actual en la docencia universitaria, P. Membiela, N. Casado, M. Cebreiros (Eds.), Ourense, Educación Editora, 2014, 545.
[2] N. Heredia, A. Filgueira, J. Fernández, E. Muñoz, en Nuevos escenarios en la docencia universitaria, P. Membiela, N. Casado, M. Cebreiros (Eds.), Ourense, Educación Editora, 2016, 529.
[3] R. Lourido, J. Fernández, E. González, V. González, E. Alonso, J. Castro, en Nuevos desafíos en la enseñanza superior, P. Membiela, N. Casado, M. Cebreiros, M. Vidal (Eds.), Ourense, Educación Editora, 2018, 95.
[4] S. Fernández, N. Heredia, G. Muñoz, J. Fernández, E. Muñoz, en Libro de resúmenes XXIII Encontro Galego- Portugués de Química, C. Díaz, M. Rodríguez (Eds.), Vigo: Colegio Oficial de Químicos de Galicia, 2017,195.
[5] Laboratorio Virtual de Química General. R. Fuerte, C. Martínez (Eds.), México, Pearson Educación. 2009, 95.
[6] Química, 12ª Ed. M. Rocha, (Ed.), México, McGraw-Hill/Interamericana Editores, S.A. de C.V. 2017, 249.

ExpHerimentando: una propuesta constructivista basada en un enfoque CTS (Ciencia, Tecnología y Sociedad)

Ángel Vidal-Vidal[1,2*]
[1]Departamento de Química Orgánica, Facultade de Química, Universidade de Vigo. Lagoas Marcosende s/n 36310 Vigo, España.
[2]CITACA - Clúster de Investigación y Transferencia Agroalimentaria del Campus Auga, Universidad de Vigo, 32004-Ourense, España.
**a.vidal.vidal@uvigo.es*

ExpHerimentando no es un simple compendio de experimentos de química, ¡es mucho más! ExpHerimentando es una experiencia envolvente nacida en las ferias científicas y llevada a las aulas que te permite adentrarte y profundizar en el mundo científico de manera sencilla y amena gracias a su presentación novedosa, divulgativa y con un toque de humor.
A través de la ciencia oculta en series de televisión y empleando un hilo conductor común (la química ácido-base), se abre un amplio abanico de posibilidades para aprender, analizar y experimentar con diversos contenidos científicos en un contexto cotidiano. La gran adaptabilidad de nivel y extensión en el diseño de los experimentos y las explicaciones permite amoldar las experiencias a cualquier nivel educativo, desde la educación primaria hasta la universidad pasando por la educación secundaria obligatoria y los ciclos formativos. La propuesta se estructura en cuatro bloques diferentes:

- **Cromatismo comestible:** vinculación de la química ácido-base con el color de alimentos y sus usos en la industria alimentaria.
- **Reino pH-lantae:** relación de la química ácido-base con el desarrollo vegetal y el color de las flores.
- **Efervescencias expHlosivas:** conexión de la química ácido-base con el desarrollo de nuevos alimentos y con el cambio climático.
- **Comiciencia:** vinculación de la química ácido-base con la cocina molecular.

Gracias a los experimentos diseñados y a las actividades gamificadas complementarias se podrá comprender tanto la influencia que tiene la química ácido-base en el color de las flores y de los alimentos y cómo usar esos conocimientos en la cocina hasta cómo se forma la lluvia ácida y los efectos nefastos que posee sobre el medio ambiente.

Fig.1. Logo del proyecto ExpHerimentando

QUÍMICA INDUSTRIAL

Pyrolysis of leather wastes from the footwear industry – preliminary results

D. Direito[1], R.M. Pilão[1], A. Crispim[1], A.M. Ribeiro[1,*]
[1] CIETI, Instituto Superior de Engenharia do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal
**asr@isep.ipp.pt*

Most of the leather used by the footwear industry (more than 70%) is produced from skins and hides tanned with chromium sulphate [1]. The production of leather goods, especially shoes, gives rise to wastes that amount to 15 – 20% of the entry leather [2]. As an example, the European footwear industry generates between $1x10^5$ to $2x10^5$ tons per year of leather wastes [1]. In the last few years, various investigations have been carried out in order to find alternatives to the disposal of these residues in landfills. Several processes have been developed to treat the leather residues that include, among others, combustion, pyrolysis, chemical treatment (oxidation and hydrolysis) or direct application of the wastes [2]. Pyrolysis is the thermal degradation of wastes, in the presence of an inert atmosphere, producing a solid phase (biochar), a liquid phase (bio-oil) and a gas phase composed mainly of CO_2, CO, CH_4 and H_2 [3]. Several authors have reported work on the pyrolysis of chromium tanned leather wastes [4, 5, 6].

This work presents preliminary results on the slow pyrolysis of leather wastes from the footwear industry, carried out in a vertical semi-batch reactor with an internal diameter of 9.7 cm. A sample of 95 g of dry finished leather, with particle sizes in the range of 4-5 mm, was pyrolyzed from ambient temperature to 875 °C (inside the reactor), using a heating rate of 20 °C/min. Nitrogen was used as the carrier gas at a flow rate of 0,214 kg/h. After the maximum temperature in the reactor was reached the experiment was extended for an additional 15 min. During each run, several samples of the gas phase evolved were captured in Tedlar bags. At the end of the experiment, the masses of biochar and bio-oil produced were weighed and the gas samples were analysed in a Dani 1000 DPC gas chromatograph. The yields of the various phases obtained were char – 27.9%, bio-oil – 29.0% and gas – 43.1%. The biochar was characterised in terms of its proximate analysis (volatiles – 3.7%, ashes – 21.6%, fixed carbon – 74.7%) and its higher heating value (HHV = 5518 cal/g). The bio-oil had an HHV of 3611 cal/g and a density of 1.1 g/cm^3 at 15 °C. The biochar presented a HHV greater than that of the initial leather waste (4848 cal/g).

The evolution of the volumetric percentage of gas phase produced as a function of the temperature inside the pyrolysis reactor showed that at 100 °C there was the formation of CO_2 (4.01%), CO (1.14%), traces of H_2 and no CH_4. The maximum CO_2 concentration (6.41%) was reached at 202 °C, following which it decreased as the temperature continued to rise. At 518 °C, CO and CH_4 had maximum volumetric percentages of 8.91% and 3.17%, respectively. The most produced gas was H_2, with a maximum of 14.55% at 637 °C. This investigation showed that the pyrolysis of leather wastes can provide products that may be used as fuels or as feedstock for the production of other chemicals.

Acknowledgments
The authors would like to acknowledge ANI for the support of the Project FAMEST 24529 by Portugal 2020 Programme.

References
[1] Valorização de Resíduos de Couro Curtido com Crómio Provenientes da Indústria de Calçado, https://www.ctcp.pt/docs/docmediagaleria/373ca0.pdf, accessed on 24 September 2019.
[2] K. Kolomaznik, M. Adamek, I. Andel, and M. Uhlirova, J. Hazard. Mater, 160 (2008), 514-520.
[3] P. Basu, Biomass Gasification and Pyrolysis – Practical Design and Theory, Burlington, MA, USA, Academic Press, 2010.
[4] O. Yilmaz, I.C. Kantarli, M. Yuksel, M. Saglam, and J. Yanik, Resources, Conservation and Recycling, 49 (2007), 436-448.
[5] H.C. Wells, K.H. Sizeland, R.L. Edmonds, W. Aitkenhead, P. Kappen, C. Glover, B. Johannessen, and R.G. Haverkamp, ACS Sustainable Chemistry Engineering, 2 (2014), 1864-1870.
[6] J. Kluska, M. Ochnio, D. Kardaś, and L. Heda, Waste Management, 88 (2019), 248-256.

ANALYSIS OF THE RELEVANT ASPECTS OF ECODESIGN TO A CIRCULAR ECONOMY: APPLICATION TO GALICIA

Tania Ferreira Anta[1], Alexandra Del Castillo Llamosas[1], Pastora M. Bello Bugallo[1*]

[1]School of Engineering, Universidad de Santiago de Compostela, Av. Lope Gómez Marzoa, s/n, E-15782, Santiago de Compostela, Spain

**pastora.bello.bugallo@usc.es*

In a context of lack and fluctuation in raw material costs, CE contributes to security of supplying as well as to the reindustrialization of the territory. This is possible because waste from ones becomes resources for others, extending the life cycle of products, paradigm of a future system [1]. Related to production and consumption, it is important to have a framework providing the appropriate signals to producers and consumers as to promote resources efficiency and CE [2,3,4].

However, the transition to an CE presents various barriers and challenges. For this reason, governments, in different areas, are working on policies oriented towards this new challenge which involves CE. In addition, it seems logical to incorporate ecodesign measures, that is, the product must be designed to be deconstructed [2,3,4]. Before the incorporation of these policies, it become necessary to analyse specific challenges and opportunities in the area of implementation.

Therefore, the objective of this work is to identify challenges and opportunities in addition to provide possible actions for their incorporation into a strategy adapted to this region towards CE. This goal is carried out by identifying the current eco-design situation in Galicia. The "hot spots" present in the ecodesign system taking care of the processes and products, are identified. Thus, defining actions in Galicia in CE and ecodesign matters helps the region to achieve a social, economic and environmental development towards sustainability.

References

[1] European Commission, 2015. Communication from the Commission on ‘Closing the loop — An EU action plan for the Circular Economy. COM (2015) 614

[2] Bundgaard, A. M., Mosgaard, M. A., & Remmen, A. (2017). From energy efficiency towards resource efficiency within the Ecodesign Directive. Journal of cleaner production, 144, 358-374.

[3] Directive 2009/125/Ec of the European Parliament and of the Council of 21 October 2009 establishing a framework for the setting of eco-design requirements for energy-related products.

[4] Karlsson, R., & Luttropp, C. (2006). EcoDesign: what's happening? An overview of the subject area of EcoDesign and of the papers in this special issue. Journal of Cleaner Production, 14(15-16), 1291-1298.

Modified carbon nanotubes for the purification of immunoglobulin G

Daniel F. de Castro[1], Márcia C. Neves, João A. P. Coutinho[1], Joaquim L. Faria[2], Mara G. Freire[1], Cláudia G. Silva[2] and Ana P. M. Tavares[1]

[1]CICECO – Aveiro Institute of Materials, Chemistry Department, University of Aveiro, Aveiro, Portugal.
[2]Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal.
**E-mail:danielfcastro@ua.pt*

Antibodies (Ab's) are molecules with high specificity for binding and inactivation of antigens, such as bacteria and viruses. Ab's, such as immunoglobulin G (IgG)s have been the subject of extensive research for the treatment of infectious diseases, immunodeficiencies and as new therapies for cancer. Currently, IgG is the most commercially available Ab type being usually obtained from small mammals or by cell cultures. However, Ab's are among the most expensive therapeutic options because of the lack of a cost-effective and efficient purification method. The most common method for the purification of IgG uses protein A affinity chromatography, which is expensive. Thus, there is an urgent need for new purification technologies for IgG production. In this work, the main objective was to determine the best operation conditions for purifying IgG from rabbit serum. The selective extraction of IgG was carried out using functionalized carbon nanotubes (CNTs). Experimental conditions, such as pH and material/serum ratio and IgG concentration were optimized. All materials were characterized by TEM, FTIR and N2 adsorption-desorption isotherms at 77 K.

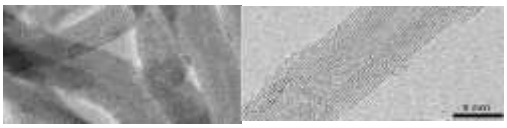


Fig.1. TEM images of pristine CNT 10-20 nm.

Tabla 1. Characterization of CNT with different external diameters

CNT diameter range (nm)	S_{BET} (m^2 g^{-1})	d_p(nm)	V_p (cm^3 g^{-1})
10-20	73	3.6	0.242
20-40	67	3.8	0.269
60-100	35	4.0	0.081

[a] The results presented in Tabla 1 show that the surface area increases with the decrease in CNT external diameter. The surface areas of modified 10-20 nm CNT, determined by the BET method, revealed that the oxidation treatment led to an increase in the surface area of the resulting material [1]. Figure 1 shows TEM analysis where the sidewalls of CNT could be observed.

Agradecimientos
This work was developed within the scope of the project CICECO (UID/CTM/50011/2019), financed by national funds through the FCT/MCTES, project POCI-01-0145-FEDER-031268 and POCI-01-0145-FEDER-006984 - funded by FEDER, COMPETE2020, POCI and OE. Ana P. M. Tavares and Cláudia G. Silva acknowledge the FCT Investigator Programme (IF/01634/2015 and IF/00514/2014, respectively) with financing from the European Social Fund and the Human Potential Operational Programme.

Referencias

[1] C. G. Silva, A. P. Tavares, G. Dražić, A. M. Silva, J. M. Loureiro, J. L. Faria, ChemPlusChem (2014) 1116-1122

Extraction of the bioactive compounds from the solid residue obtained by microwave extraction using *Mastocarpus stellatus* red seaweed as raw material

N. Flórez-Fernández[1*], M. Barral[1], M. Álvarez-Viñas[1], M.D. Torres[1], H. Domínguez[1]

[1]Dept. Chemical Engineering, Faculty of Sciences, University of Vigo, As Lagoas s/n, 32004 Ourense, Spain

**noelia.florez@uvigo.es*

Mastocarpus stellatus is a red seaweed widely distributed in the Atlantic coast, mainly in the north west of the Iberian Peninsula. Its main polysaccharide is kappa/iota hybrid carrageenan, which in the last years gained attention by the scientific community. Their structures have been classified basically in three types designed by Greek letters: kappa-, iota- and lambda. Red seaweeds are very valuable because they can present different combinations of types of carrageenans, these hybrid structures can offer a broad range of bioactive and gelling characteristics. This compound has a great importance in the food and cosmetic industry for its potential applications as gelling or thickening agent [1]. In this context, in order to extract bioactive compounds, an ecofriendly technology was proposed. A first pretreatment using microwave assisted extraction (MAE) [2] followed by a second step using water as a solvent were carried out. The aim of this work was to extract bioactive compounds from the red seaweed *Mastocarpus stellatus* using a green extraction processing in two stages from the solid residue pretreated by microwave assisted extraction.

The raw material, *Mastocarpus stellatus*, was kindly provided by Portomuíños enterprise (A Coruña, Spain). The extraction was performed in a microwave by hydrogravity with different power and time conditions. Five fractions were obtained, which were employed in a second water extraction stage to extract the bioactive compounds. The extraction was carried out using water as a solvent consisting in heating the mixture (seaweed + water) with a RLS 65 at 90°C for 2 hours in a water bath. After this heating, the mixture was cooling until room temperature (25 °C). Then, a centrifugation step was required to separate the liquid and solid phases. The hybrid carrageenan was precipitated with ethanol [3]. Antioxidant activity and phloroglucinol content were assessed in the carrageenan free liquid phase.

The results exhibited an increase in the bioactive properties directly related with the extraction conditions, thus with the composition of the raw material after the first extraction done. Maximum of the antioxidant activity and phloroglucinol content were identified at the maximum power (500 W) studied. The obtained outcomes suggested that MHG pretreatment is an interesting step to enhance the recovery of bioactive compounds from the tested red seaweed, which could be useful for other seaweeds. Overall, these seaweeds seem to have a great potential to applicate their bioactive and biopolymers compounds in the cosmetic, food and pharmaceutical industry.

Fig. 1. Image of a *Mastocarpus stellatus* sample

Acknowledgements

Authors acknowledges the financial support to the Ministry of Science, Innovation and Universities of Spain (RTI2018-096376-B-I00). M.D.T. also thanks Spanish Ministry of Science, Innovation and Universities for her postdoctoral grant (IJCI-2016-27535), and N.F.F. acknowledges Xunta de Galicia for her postdoctoral grant (ED481B 2018/071).

References

[1] E. Gómez-Ordóñez, A. Jiménez-Escrig, P. Rupérez, Bioactive Carbohydrates and Dietary Fibre, 3 (2014) 29-40.

[2] P. Rodríguez Seoane, N. Flórez-Fernández, E. Conde Piñeiro, H. Dominguez González, in Water extraction of bioactive compounds from plants to drug development, H. Dominguez González, M.J. González Muñoz (Eds.), Amsterdam, Elsevier, 2018, 6.

[3] M.D. Torres, N., Flórez-Fernández, H., Domínguez, Food Hydrocolloids, 84 (2018). 321-329

Alternativas para el tratamiento de madera de pino azulada

Julia González-Álvarez[1,*], Cristina Galiñanes[1], Antonio Magán[2]
[1]Universidade de Santiago de Compostela, Departamento de Ingeniería Química, c/ Lope Gómez de Marzoa s/n, 15782 Santiago de Compostela, España
[2]SEISTAG INNOVACIÓN, S.L., c/ Rueiro 17 bajo, 15220 Bertamiráns, España
**julia.gonzalez@usc.es*

La aparición de manchas de azulado en la madera está provocada por el ataque de hongos cromógenos o hongos del azulado, siendo el predominante *Ceratocystis pilífera* [1]. Estas manchas azules no influyen en las propiedades físico-mecánicas de la madera [2], pero su valoración sí que disminuye significativamente en aquellas aplicaciones en las que el aspecto estético es importante.

Con el fin de prevenir el azulado de la madera de pino (*Pinus pinaster*) en el aserradero de la empresa SEISTAG INNOVACIÓN (Gres, Pontevedra), la madera verde se somete a un tratamiento protector por inmersión en un producto antiazulado comercial. No obstante, en la época estival en la que la temperatura ambiental es más alta, el tiempo que transcurre desde que el árbol es cortado en el monte hasta que las tablas aserradas son sometidas al tratamiento antiazulado en el aserradero, es en ocasiones suficiente para que los hongos cromógenos ataquen la madera. Por tanto, el objetivo de este trabajo es analizar la posibilidad de tratar las tablas de madera que han sido atacadas con el fin de eliminar las manchas del azulado y recuperar el valor del material.

En una primera etapa se han seleccionado diferentes tratamientos [3] que se han aplicado a madera de pino azulada previamente secada (~12% b.s.), manteniendo contantes el tiempo de tratamiento por inmersión (45 min/tratamiento) y la temperatura (ambiente, ~20ºC): 1) disolución acuosa de hipoclorito sódico al 10% (en volumen); 2) disolución acuosa de hipoclorito sódico al 10% (en volumen) e hidróxido sódico al 5% (en peso), seguido de disolución acuosa de peróxido de hidrógeno al 30% (en volumen); 3) disolución acuosa de peróxido de hidrógeno al 30% (en volumen) y ácido acético al 10% (en volumen) y 4) disolución acuosa de peróxido de hidrógeno al 30% (en volumen). Tras cada tratamiento las muestras se dejaron secar al aire y se midió la diferencia cromática total (ΔE^*) con respecto a la madera azulada de partida (colorímetro Minolta CR-400/410). Todos los tratamientos se ensayaron al menos por duplicado y las medidas de color se realizaron al menos en dos caras de la probeta de ensayo por triplicado. El tratamiento 1) con hipoclorito sódico fue el que condujo a una mayor eliminación del azulado (mayor $\Delta E^*=5{,}12\pm0{,}94$) seguido por el 4) realizado con peróxido de hidrógeno al 30% ($\Delta E^*=4{,}64\pm1{,}60$) y ya a mayor distancia los tratamientos 2) ($\Delta E^*=3{,}83\pm0{,}73$) y 3) ($\Delta E^*=2{,}12\pm0{,}54$). Seleccionado el tratamiento con hipoclorito sódico, en una segunda etapa se estudió la influencia de las variables implicadas: concentración (2, 6 y 10%), temperatura (ambiente, 40 y 60ºC) y tiempo (5,15, 45 min). El mayor grado de eliminación de la mancha de azulado se consiguió tras un tratamiento con hipoclorito sódico al 10% durante 15 min a 40ºC.

Finalmente, se comparó el color de la madera tras la eliminación de la mancha del azulado con el color de la madera de pino natural no atacada por el hongo del azulado. Este análisis demostró que la diferencia de color es bastante significativa, es decir, el tratamiento elimina la mancha del azulado, pero cambia el color de la madera, que adquiere una tonalidad más clara y menos rojiza. Esto significa que, en aquellas aplicaciones en las que se no se permita un color diferente a la tonalidad natural de la madera de pino, será necesario realizar un tratamiento a mayores para recuperar ese color lo que aumentaría el coste global del proceso. Por otro lado, existe la posibilidad de destinar estas tablas de pino a la industria del mueble, en la que en la mayoría de los casos la madera se pinta mediante pigmentos incorporados en la formulación de los barnices y donde un color más claro podría significar una clara ventaja en cuanto a consumo de pigmentos y calidad final del producto.

Agradecimientos
Este trabajo fue parcialmente financiado por la Xunta de Galicia (PROGRAMA INNOVA PEME 2017).

Referencias

[1] M. Osorio, Bosque, *6*(2) (1985) 116.
[2] K. A. Seifert, in Ceratocystis and Ophiostoma: Taxonomy, Ecology, and Pathogenicity, M. J. Wingfield, K. A. Seifert, J. F. Webber (Eds.), St Paul, APS Press, 1993, 141.
[3] P. D. Evans, G. Palmer, M. Chowdhury, Holz Roh-Werkstoff, 65 (2007) 485.

Natural creams formulated with green extracts from wild *Acacia dealbata* Link flowers and thermal spring waters

L. López-Hortas[1,*], E. Falqué[2], H. Domínguez[1], M.D. Torres[1]
[1]Dept. Chemical Engineering, Faculty of Sciences, University of Vigo, As Lagoas s/n, 32004 Ourense, Spain
[2]Dept. Analytical Chemistry, Faculty of Sciences, University of Vigo, As Lagoas s/n, 32004 Ourense, Spain
*luclopez@uvigo.es

The utilization of extracts from valuable plant species is thoroughly widespread in the development of personal care products. Frequently, the traditional knowledge of the use of these resources is supported by their chemical composition, so their employment in cosmetology industry is backed up. This circumstance occurs with *Acacia dealbata* Link, since their pollen can be employed with facial beauty purposes [1], in part due to the phenolic content and antioxidant capacity of their flowers [2]. Furthermore, the use of thermal spring waters in the formulation of cosmetic products enriches the properties of these systems contributing with their healthy features. Therefore, the combination of these two elements can have a potential use in the improvement of natural products as skin care creams [3]. Nowadays, emerging eco-friendly processes promote the extraction of phytochemicals more efficiently than traditional extraction methods. In this context, microwave hydrodiffusion and gravity (MHG) system could be an alternative procedure, since this innovative green technology can recovery bioactive compounds using limited energy, time and resource costs at atmospheric pressure without added solvent [4]. The aim of this study was the enrichment of moisturizing creams based on different thermal spring waters with *A. dealbata* extracts, their characterization and stability evaluation.

The emulsion (oil/water, O/W) formulation of the moisturizing creams was prepared in duplicate following the cosmetic preparation indicated by Balboa *et al.* [5]. This cosmetic model was elaborated with three thermal spring waters (TSW1-3) from the Ourense region, whereas control samples were made with distilled water without added extracts. Commercial antioxidants were used for comparative purposes against extracts by MHG at 75 W (optimized in a previous work) and distilled fraction derived of steam distillation without cohobation from wild *A. dealbata* flowers. These creams were submitted at physicochemical tests (pH, total solid content and colour by CIEL*a*b* system). Their solar protector factor (SPF) and thiobarbituric acid reactive substances (TBARS) were also determined. The sensorial properties and rheology features of these topical cosmetic products were evaluated as well as their physicochemical stability during an accelerated oxidation test at 50 ± 2 ºC during 15 days. Above analyses were made in triplicate.

Overall, the outcomes indicated that the skin care creams did not differ with each other from the point of view of the physicochemical or mechanical characteristics. For example, the values of pH fluctuated between 5.27 and 6.24, while their TBARS content varied over the range 11.98 - 26.71 nmol malonaldehyde/g sun cream dry weight. The L*, a* and b* coordinates varied on the range of 89.05 - 94.25, -5.85 - -5.42 and 6.03 -7.50, respectively.

In conclusion, extracts by MHG technology from renewable flowers of *A. dealbata* can be considered as a potential bioactive ingredient for the development of personal care products.

Acknowledgements
The authors are grateful to the Ministry of Economy and Competitiveness of Spain (CTM2015-68503-R) and FEDER for the financial support. L. López-Hortas thanks the Xunta de Galicia for her pre-doctoral grant (2014/2020 European Social Fund). M.D. Torres acknowledges the Ministry of Economy, Industry and Competitiveness for her post-doctoral grant (IJCI-2016-27535).

References
[1] A. Moteetee, R.O. Moffett, L. Sleteng-Kose, South African Journal of Botany, 122 (2018) 21.
[2] M.P. Casas, E. Conde, D. Ribeiro, E. Fernandes, H. Domínguez, M.D. Torres, Waste and Biomass Valorization, *In press* (2019).
[3] F.R. Lupi, L. Gentile, D. Gabriele, S. Maxxulla, N. Baldino, B. De Cindio, Journal of Colloid and Interface Science, 459 (2015) 70.
[4] M.K. Khan, K. Ahmad, S. Hassan, M. Imran, N. Ahmad, C. Xu, 45 (2018) 361.
[5] E.M. Balboa, M.L. Soto, D.R. Nogueira, N. González-López, E. Conde, A. Moure, M.P. Vinardell, M. Mitjans, H. Domínguez, Industrial Crops and Products, 58 (2014) 104.

Obtención de fertilizantes líquidos a partir de material bioestabilizado

C. Llorente Pérez[1,*], M. Fernández-Delgado[1], E. del Amo[1], M. Coca[1,2], S. Lucas[1,2] y M.T. García-Cubero[1,2]

[1]Dpto. de Ingeniería Química y Tecnología del Medio Ambiente, Escuela de Ingenierías Industriales, Universidad de Valladolid, C/Dr. Mergelina s/n, 47011, Valladolid, España

[2]Instituto de Procesos Sostenibles, Universidad de Valladolid, C/Dr. Mergelina s/n, 47011, Valladolid, España

**cristina.llorente.perez@uva.es*

Cada año se producen entre 118 y 138 millones de toneladas de biorresiduos en la UE, de los que casi 88 millones de toneladas son desechos urbanos. Se prevé que esta cifra aumente un 10% hasta 2020[1], lo que pone de manifiesto la necesidad de llevar a cabo procesos de tratamiento de los biorresiduos evitando que sean depositados en vertederos. La Directiva Europea 2008/98/CE sobre los residuos, insta a los Estados miembros a recoger y reciclar los biorresiduos de forma separada de acuerdo con la jerarquía de residuos. La recogida separada de biorresiduos permite que la materia orgánica presente en los mismos pueda ser compostada, obteniéndose compost de alta calidad que puede ser usado en la agricultura [2]. Sin embargo, el uso de la fracción orgánica de los RSU, obtenida mediante triaje en plantas de tratamiento mecánico-biológico que tratan mezclas de residuos domésticos, produce un material bioestabilizado (MB) de baja calidad cuya aplicación agrícola ha sido considerablemente restringida.

El objetivo de este trabajo es recuperar, mediante un proceso de extracción y concentración, los nutrientes presentes en el MB (materia orgánica, nitrógeno, fósforo y potasio) para obtener fertilizantes líquidos que cumplan con los requerimientos legales. Se pretende comparar dos alternativas de proceso basadas en extracción con KOH y extracción con agua desde el punto de vista económico y ambiental, aplicando para ello las métricas de sostenibilidad publicadas por el ICHEME.

Una vez realizada la etapa experimental y los estudios correspondientes, se puede concluir que, para el caso de extracción alcalina, solamente es necesario llevar a cabo una etapa de extracción para obtener un líquido que cumpla con la legislación europea. Sin embargo, cuando se utiliza agua como solvente, el extracto no alcanza las concentraciones mínimas de nutrientes exigidas para ser considerado fertilizante líquido y es necesario realizar una etapa de concentración posterior mediante evaporación a vacío. La resolución de los balances de materia, para una planta con una capacidad de tratamiento de 300 kg/h de MB que opera 8000 h/año cuando se utiliza disolución de KOH como solvente, da una corriente de líquido rico en nutrientes de 473 kg/h en las condiciones más adecuadas de operación (relación S/L 40%, disolvente KOH 1M, 48h y 45ºC). Para una planta con la misma capacidad y tiempo de operación, cuando se utiliza agua como solvente, se obtiene una corriente de líquido rico en nutrientes de 46 kg/h en las condiciones más adecuadas de operación (relación S/L 40%, 24h y 45ºC). Desde un punto de vista económico, los resultados indican que los costes de producción anual son superiores en el proceso de extracción con disolución KOH (2 millones € frente a 917.000 €, aprox.). Sin embargo, teniendo en cuenta estos costes de producción anual y la capacidad de producción de fertilizante de la planta en cada caso (casi 3 millones l/año para el KOH frente a 441.000 l/año con agua) se tiene que el coste de producción por litro de fertilizante es menor cuando se usa KOH (0,7 €/l con KOH frente a 2,5 €/l con agua). Desde el punto de vista ambiental, se observa que la extracción con KOH requiere de un consumo de agua inferior al de la extracción con agua (2300 kg/h frente a 16250 kg/h, respectivamente). Del mismo modo, la demanda de energía en el proceso de extracción con KOH es menor que en el del agua (300 kW frente a 670kW, respectivamente).

Agradecimientos

Este trabajo ha sido financiado por el programa de cooperación INTERREG V-A España-Portugal (POCTEC) 2014-2020 y FEDER (Proyecto 0119_VALORCOMP_2_P "Valorización de compost y otros desechos procedentes de la fracción orgánica de los residuos municipales).

Referencias

[1] COM(2010)235 final. Próximas medidas de gestión de los biorresiduos en la UE.

[2] Lin, Long, Fuqing Xu, Xumeng Ge, and Yebo Li. "Improving the Sustainability of Organic Waste Management Practices in the Food-Energy-Water Nexus: A Comparative Review of Anaerobic Digestion and Composting."

Poly(ionic liquid)-based materials for CO_2 capture

Mónica M. Lopes[1,*], Marcileia Zanatta[1], Marta C. Corvo[1]

[1]LabNMR Cenimat, i3N|Cenimat, Department of Materials Science, School of Science and Technology, NOVA University of Lisbon, 2829-516 Caparica, Portugal

**mam.lopes@campus.fct.unl.pt*

Carbon dioxide (CO_2) is considered the largest anthropogenic greenhouse gas source and, from an environmental perspective, is vital to reduce the atmospheric concentrations. Nowadays, the conventional CO_2 capture (CC) methods mostly used at an industrial level are performed by aqueous alkanolamines solutions. Nevertheless, these methodologies require high energy consumption, produce corrosive by-products and suffer from decreased performance in the presence of impurities. Even with all the investigation on CC, the development of nontoxic and easy recyclable sorbents remains a challenge. Ionic liquids (ILs) are organic compounds composed exclusively of ions with a melting point of less than 100 ºC and a negligible vapor pressure, most of them are also non-volatile and recyclable. ILs are being used in order to replace amine solutions, due to their high CO_2 solubility. Furthermore, it is possible to tailor ILs physical and chemical properties by modifying the cation-anion combination or by functionalizing the alkyl chain [1,2]. Similarly, poly(ionic liquid)s (PILs) are a new class of functional materials derived from the polymerization of monomeric ILs. These compounds combine ILs characteristics with polymers macromolecular structures that enrich the properties and applications of PILs.

Employing Nuclear Magnetic Resonance (NMR) spectroscopy, our group demonstrated the site and the strength of CO_2-IL interactions, the water effect in the IL CO_2 sorption capacity and the effect of IL anions in the sorption mechanism. We also developed NMR protocols for CC in high-pressure (HP-NMR) and near atmospheric pressure, that allowed a direct measurement of CO_2 solubility and intermolecular interactions. Currently, we are working on the development of new materials based on PIL/IL mixtures, focusing on different NMR techniques that enable the study of PIL-IL-CO_2 interactions. Our NMR methodologies allow the interpretation of the solvation mechanism, quantification of sorption and consequently the tailoring of new materials for CC applications. An ideal combination of PIL/IL demonstrated promising CO_2 sorption capacities and is the focus of our current investigation [2-6].

Acknowledgment

This work was supported by Portuguese funding through FCT – Fundação da Ciência e Tecnologia, Portugal (PTDC/QUI-Q-FI/31508/2017, ROTEIRO/0031/2013, PINFRA722161/2016), co-financed by FEDER, European funds, through COMPETE 2020, POCI, and PORL and FCT through PIDDAC (POCI-01-0145-FEDER-007688; UID/CTM/50025/2019).

References

[1] M. E. Boot-Handford, J. C. Abanades, E. J. Anthony, et al. Energy and Environ. Sci., 7 (2014) 130-189.
[2] M. C. Corvo, J. Sardinha, T. Casemiro, G. Marin, M. Seferin, et al. ChemSusChem, 8 (2015) 1935-1946.
[3] M. Zanatta, N. M. Simon, F. P. dos Santos, M. C. Corvo, et al., Angew. Chem. Int. Ed., 58 (2019) 382-385.
[4] N. M. Simon, M. Zanatta, J. Neumann, A. Girard, G. Marin, et al., ChemPhysChem, 19 (2018) 2879-2884.
[5] N. M. Simon, M. Zanatta, F. P. dos Santos, M. C. Corvo, et al., ChemSusChem, 10 (2017) 4927-4933
[6] M. C. Corvo, J. Sardinha, S. C. Menezes, S. Einloft, et al., Angw. Chem. Int Ed., 52 (2013) 13024-13027

Pyrolysis of leather wastes from the footwear industry – preliminary results

D. Direito[1], R.M. Pilão[1], A. Crispim[1], A.M. Ribeiro[1,*]
[1] CIETI, Instituto Superior de Engenharia do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal
**asr@isep.ipp.pt*

Most of the leather used by the footwear industry (more than 70%) is produced from skins and hides tanned with chromium sulphate [1]. The production of leather goods, especially shoes, gives rise to wastes that amount to 15 – 20% of the entry leather [2]. As an example, the European footwear industry generates between $1x10^5$ to $2x10^5$ tons per year of leather wastes [1]. In the last few years, various investigations have been carried out in order to find alternatives to the disposal of these residues in landfills. Several processes have been developed to treat the leather residues that include, among others, combustion, pyrolysis, chemical treatment (oxidation and hydrolysis) or direct application of the wastes [2]. Pyrolysis is the thermal degradation of wastes, in the presence of an inert atmosphere, producing a solid phase (biochar), a liquid phase (bio-oil) and a gas phase composed mainly of CO_2, CO, CH_4 and H_2 [3]. Several authors have reported work on the pyrolysis of chromium tanned leather wastes [4, 5, 6].

This work presents preliminary results on the slow pyrolysis of leather wastes from the footwear industry, carried out in a vertical semi-batch reactor with an internal diameter of 9.7 cm. A sample of 95 g of dry finished leather, with particle sizes in the range of 4-5 mm, was pyrolyzed from ambient temperature to 875 °C (inside the reactor), using a heating rate of 20 °C/min. Nitrogen was used as the carrier gas at a flow rate of 0,214 kg/h. After the maximum temperature in the reactor was reached the experiment was extended for an additional 15 min. During each run, several samples of the gas phase evolved were captured in Tedlar bags. At the end of the experiment, the masses of biochar and bio-oil produced were weighed and the gas samples were analysed in a Dani 1000 DPC gas chromatograph. The yields of the various phases obtained were char – 27.9%, bio-oil – 29.0% and gas – 43.1%. The biochar was characterised in terms of its proximate analysis (volatiles – 3.7%, ashes – 21.6%, fixed carbon – 74.7%) and its higher heating value (HHV = 5518 cal/g). The bio-oil had an HHV of 3611 cal/g and a density of 1.1 g/cm^3 at 15 °C. The biochar presented a HHV greater than that of the initial leather waste (4848 cal/g).

The evolution of the volumetric percentage of gas phase produced as a function of the temperature inside the pyrolysis reactor showed that at 100 °C there was the formation of CO_2 (4.01%), CO (1.14%), traces of H_2 and no CH_4. The maximum CO_2 concentration (6.41%) was reached at 202 °C, following which it decreased as the temperature continued to rise. At 518 °C, CO and CH_4 had maximum volumetric percentages of 8.91% and 3.17%, respectively. The most produced gas was H_2, with a maximum of 14.55% at 637 °C. This investigation showed that the pyrolysis of leather wastes can provide products that may be used as fuels or as feedstock for the production of other chemicals.

Acknowledgments
The authors would like to acknowledge ANI for the support of the Project FAMEST 24529 by Portugal 2020 Programme.

References
[1] Valorização de Resíduos de Couro Curtido com Crómio Provenientes da Indústria de Calçado, https://www.ctcp.pt/docs/docmediagaleria/373ca0.pdf, accessed on 24 September 2019.
[2] K. Kolomaznik, M. Adamek, I. Andel, and M. Uhlirova, J. Hazard. Mater, 160 (2008), 514-520.
[3] P. Basu, Biomass Gasification and Pyrolysis – Practical Design and Theory, Burlington, MA, USA, Academic Press, 2010.
[4] O. Yilmaz, I.C. Kantarli, M. Yuksel, M. Saglam, and J. Yanik, Resources, Conservation and Recycling, 49 (2007), 436-448.
[5] H.C. Wells, K.H. Sizeland, R.L. Edmonds, W. Aitkenhead, P. Kappen, C. Glover, B. Johannessen, and R.G. Haverkamp, ACS Sustainable Chemistry Engineering, 2 (2014), 1864-1870.
[6] J. Kluska, M. Ochnio, D. Kardaś, and L. Heda, Waste Management, 88 (2019), 248-256.

Optimization and characterization of the products obtained from *Eucalyptus globulus* wood in sequential hydrothermal stages

Mar López[1*], Valentín Santos[1], Juan C. Parajó[1]

[1]University of Vigo (Campus Ourense), Chemical Engineering Department, Polytechnical Building, 32004 Ourense, Spain
**e-mail: marlopezr@uvigo.es*

Autohydrolysis, a hydrothermal process which employs hot and compressed water, has been widely used for hemicellulose solubilization, being considered as a fractionation method. Among its advantages it can be highlighted its "green" character (no acids are externally added to the process, being water the only solvent employed for wood processing), as well as its ability to extensively remove hemicelluloses from the solid phase with high yield and selectivity.

The main drawback of this method is that the liquid phase obtained directly from autohydrolysis (enriched in hemicellulose-derived saccharides: basically xylooligosaccharides (XOs)) presents limited concentrations of these products for a number of applications, if it is used as collected. This is due to the low hemicellulose content of lignocellulosic materials (LCMs), in comparison with its other main components: cellulose and lignin. In order to get a richer stream in these products, autohydrolysis liquors need to be concentrated. The most commonly used technologies are evaporation or membrane processing [1]. Another approach for increasing product concentration consists on coupling autohydrolysis stages. This last strategy not only increases the target products but also the degradation products, as in subsequent stages the acetic acid present in the reaction media gradually increases the concentration of hydronium ions, which act as a catalyst, thus affecting the kinetics of the reaction, which go faster.

The target products here obtained, XOs, are sugar oligomers derived from the hemicellulosic fraction (mainly composed of xylan) of lignocellulosic materials. They have applications based on their biological properties, being suitable for their use as prebiotics.

In this study, an experimental assessment has been carried by coupling sequential autohydrolysis stages with the aim of increasing the concentration of XOs present in the liquid phase. The optimal operational conditions (defined as those which lead to maximum concentrations of XOs and minimal of degradation products) were determined for each one of the three reaction stages considered using *Eucalyptus globulus* wood as starting material. The solid phases obtained in every stage were characterized (compositional data, FTIR) as well as the liquid phases (HPLC, HPSEC, HPAEC-PAD, MALDI-TOF, FTIR, TGA, Total Phenolic Content and Trolox Equivalent Antioxidant Capacity), in order to assess their suitability to be used as prebiotics.

Acknowledgements
The authors are grateful to the Spanish Ministry of Economy and Competitivity for supporting this study in the framework of the research project "Modified aqueous media for wood biorefineries" (reference CTQ2017-82962-R), partially funded by the FEDER program of the European Union. Ms. Mar López thanks for her predoctoral grant (reference ED481A-2017/316) with financial support from the "Xunta de Galicia" and the European Union (European Social Fund – ESF).

References
[1] P. Gullón, M.J. González-Muñoz, H. Domínguez, J.C. Parajó, Journal of Food Engineering, 87:2 (2008) 257.

Green extraction for the recovery of high valuable compounds from model red seaweeds

M.D. Torres[1,*], M. Barral[1], N. Flórez-Fernández[1], H. Domínguez[1]
[1]Dept. Chemical Engineering, Faculty of Sciences, University of Vigo, As Lagoas s/n, 32004 Ourense, Spain
**matorres@uvigo.es*

Carrageenophyte algae as *Mastocarpus stellatus* are highly demanded to obtain biopolymers with specific functionalities [1]. Particularly, this model red seaweed belonging to the *Gigartinales*, Rhodophyta species, is geographically distributed in the Atlantic Iberean Peninsula coast (Galicia and north Portugal) [2]. The gelling properties of these hybrid carrageenans exhibits interesting rheological features to be used as matrices in the development of new gelled products. The use of green technologies for the extraction of these biopolymers could help to alleviate the growing market demand.In this context, the main aim of this work is to recover kappa/iota-hybrid carrageenans from *Mastocarpus stellatus* red seaweed using microwave hydrodiffusion and gravity (MHG) at different experimental conditions, as well as the corresponding mechanical characterization to select the most adequate biopolymers for the formulation of carrageenan-based gelled systems with a broad range of potential applications.

The red seaweed employed as raw material was gently supplied by Portomuíños company (A Coruña, Spain). Samples were pre-treated by microwave hydrodiffusion and gravity using different time and power conditions in order to optimize the seaweeds drying prior to the kappa/iota-hybrid carrageenan extraction. A modified green protocol based on the conditions previously proposed for the conventional carrageenan isolation [3], but using only water as extraction solvent was carried out. A number of kappa/iota-hybrid carrageenan gels formulated at different biopolymer content in the presence of Ca^{2+} and Mg^{2+} were developed and rheologically characterized. Mixtures of commercial kappa and iota carrageenan at comparable experimental conditions were also used to the development of the gels with comparative purposes. The sol-gel diagrams of aforementioned systems were also carefully prepared and analysed.

The rheological results indicated that kappa/iota-hybrid carrageenans extracted from *Mastocarpus stellatus* after a pre-treatment with microwave hydrodiffusion and gravity exhibited improved yields and mechanical properties when compared with those obtained by the conventional method, saving extraction time (about three times). At the same time, the obtained biopolymers also presented enhanced viscoelastic features when compared with the corresponding mixtures of commercial kappa and iota carrageenans. The study of the sol-gel diagrams indicated that the pre-treatment of the algae by MHG at different powers allowed the obtaining of kappa/iota-hybrid carrageenans with gelling capacities at low concentrations and low ionic forces, expanding the range of gels with respect to conventional extraction methods. Moreover, kappa/iota-hybrid carrageenan gels formulated in the presence of tested counterions showed rheological properties comparable to those of other commercial biopolymers [4].

To conclude, it can be stated that with an environmentally friendly technology as microwave hydrodiffusion and gravity, it is possible to effectively extract high added value compounds from the tested model red seaweed with adequate mechanical properties and potential applications in the food and non-food fields, which could be extrapolated to other algae.

Acknowledgements
Authors acknowledges the financial support to the Ministry of Science, Innovation and Universities of Spain (RTI2018-096376-B-I00). M.D.T. also thanks Spanish Ministry of Science, Innovation and Universities for her postdoctoral grant (IJCI-2016-27535), and N.F.F. thanks Xunta de Galicia for her postdoctoral grant (ED481B 2018/071).

References

[1] G. Azevedo, L. Hilliou, G. Bernardo, I. Sousa-Pinto, R.W. Adams, M. Nilsson, R.D. Villanueva, Food Hydrocolloids, 31 (2013) 94.
[2] J. Wang, M. Zhang, Z. Fang, Trends in Food Science and Technology, 88 (2019) 251.
[3] G. Azevedo, M.D. Torres, I. Sousa-Pinto, L. Hilliou, Food Hydrocolloids, 50 (2015) 150.
[4] F. Van de Velde, Food Hydrocolloids, 22 (2008) 727.

Pressurized ethanolic extraction of polyphenols from maqui (*Aristotelia chilensis Stuntz*) leaves

P.R. Rivera[1,*], M.D. Torres[2], J.R. Pérez[1], H. Domínguez[2]
[1]Department of Chemical Engineering and Bioprocess, Pontificia Universidad Católica de Chile, Vicuña Mackenna 4860, Santiago, Chile
[2]Department of Chemical Engineering, Faculty of Sciences, University of Vigo, Edificio Politecnico, As Lagoas s/n, 32004 Ourense, Spain.
**matorres@uvigo.es*

Abstract. The intake of polyphenols is related to prevention and slowdown of the development of chronic, degenerative and cardiovascular diseases. In recent years, the production, processing and exportation of maqui (Chilean berries) have increased due to their high Total Polyphenols Content (TPC) and high Antioxidant Capacity (AC). However, the leaves of these berries are agro industrial discards that present even higher TPC and AC values [1, 2]. The aim of this research work was to optimize the extraction of leaves of maqui looking to maximize TPC (mg gallic acid equivalent/ g leaves in dry weight) and AC (mg trolox equivalent/g leaves in dry weight) and also include purity as a restriction of the multi-response cost function using Response Surface Methodology.

Methods. Extraction was performed in an Accelerated Solvent Extraction System ASE 200 (Dionex Corporation, Sunnyvale, CA, USA) using different ethanol solutions as solvents. Dried leaves sample (1 g dry weight) was mixed with 0.75 g of diatomaceous earth and placed into a 5 mL volume extraction cell. The fixed operating conditions were: 5 minutes to static extraction time, 70% of flush volume, 60 seconds of purge and 1500 psi (10 MPa) of pressure. Extraction temperature, ethanol concentration and number of cycle values varied in each experiments in the intervals [80 – 200] ºC, [5 – 80] % v/v and [1 - 5] respectively. The extract was protected from light and stored at -20ºC until analysis. Optimization was carried out in three steps, applying the response surface methodology (RSM) in each of three experimental regions, two of which were defined according to Box-Behnken experimental design and the last one combinatory of all experiments.

Results and discussion. Two ethanolic liquors from maqui leaves were obtained using the response surface methodology and multi-response optimization (table 1). One of them focused on maximization the TPC and AC, presenting a reduction in liquor's purity. The second liquor was optimized including purity as one of the responses. Both liquors reach 2.9 and 1.7 times more TPC than the liquor obtained by traditional extraction (room temperature, 50% ethanol v/v) [3]. The application of each one will depend on the existence of a subsequent purification stage (e.g. liquid column chromatography).

Table 1. Optimization achieve with methods of desirability functions and superimposition contours methods.

Optimization objetive	Independent variables			Teorical responses[a]		
	T (°C)	EtOH (%)	ciclos	mg GAE/g (dw)	mg TE/g (dw)	Purity (%)
TPC and AC	200	22.7	3	200.7	814.43	n.a.
TPC, AC and purity	122	5	2	120.5	419.83	35.1

[a] These values were verified where the experimental values presented an average error of 2%
n.a. Not analyzed

Acknowledgments
Financial support from the Scholarship: Scholarship Instructor and Stay abroad for doctoral students granted by the Vicerrectoría de Investigación de la Pontificia Universidad Católica de Chile. Operational and logistical support of the laboratory of the Department of Chemical Engineering of the University of Vigo, Faculty of Sciences of Ourense.

References
[1] P.R. Rivera, M.S. Mariotti, J.R. Pérez, Mini-Reviews in Organic Chemistry, 16, 3 (2019) 261-276.
[2] J.E. Brauch, M. Buchweitz, R.M. Schweiggert, R. Carle, Food Chemistry, 190 (2016) 308-316.
[3] M. Rubilar, C. Jara, Y. Poo, F. Acevedo, C. Gutierrez, J. Sineiro, C. Shene, Journal of Agricultural and Food chemistry, 59 (2011) 1630-1637.

TOWARDS THE CIRCULARITY OF PRODUCTS: THE CASE OF A WASTE INTERMEDIATE PLANT

David Viruega Sevilla[1], Mariana Romero Esquivel[1]
Alexandra Del Castillo Llamosas[1], Pastora M. Bello Bugallo[1,*]

[1]School of Engineering, Universidade de Santiago de Compostela, Av. Lope Gómez de Marzoa, s/n, E-15782, Santiago de Compostela, Spain

**pastora.bello.bugallo@usc.es*

In recent years, end-of-waste criteria has emerged to fight against continuous increase of waste production, boosting the use of secondary raw materials (SRMs) to achieve the objectives of the Circular Economy Action Plan [1-2]. The way we design, produce, use, distribute and discard products has a strong impact on the economy, society and environment [3]. Products and processes designed in a circular way can minimise resource use and foster materials' reuse, recovery and recyclability down the road. This also means that adapting actual industrial processes including Small and Medium-Sized Enterprises (SMEs), is essential in the core of the transition [2].

This work presents a redesign plan for a waste intermediate management plant, covering all management activities (both off an in-site), including, among others, collection, transport and treatment. The waste management hierarchy is modified or amplified considering the original definition [4] together with the circular economy focus. This includes the optimisation of collection and shipping routes, the improvement of existing processes and/or the design of new sustainable processes from waste to energy and useful materials. Different focus (eco-design, life cycle thinking, system dynamics, industrial ecology, circular economy, integrated pollution prevention and control, green engineering, gaming, transport logistics) and tools (LCT tools, flows and stocks models, material and energy flow analysis, industrial symbiosis, Best Available Techniques analysis, process simulation, simulation games, geographical information systems) [5]. These tools help us to improve the sustainability of the transport system, the waste to energy and useful materials processes and the industrial park symbiotic behaviour.

The application of this methodology to the case study shows the real possibility to achieve the circularity of products, transforming the waste sector into a productive one, producing their own products. Meanwhile, it contributes to the extinction of the traditional concept of waste.

Acknowledgements
The authors would like to thank Galiza Verde S.L. for their support and enthusiasm in this work, especially the administrator, Francisco Conde Cabanas, for his guidance, ideas and advice as well as for his financial collaboration.

References

[1] European Commission: COM (2015) 614- Communication from the Commission to the European Parliament,the council, the European economic and social committee and the committee of the regions, Closing the loop - An EU action plan for the Circular Economy.
[2] European Commission: COM (2019) 190 final- Report from the commission to the European Parliament, the council, the European economic and social committee and the committee of the regions on the implementation of the Circular Economy Action Plan.
[3] European Commission: SWD (2019) 92 final- Commission staff working, Sustainable Products in a Circular Economy - Towards an EU Product Policy Framework contributing to the Circular Economy.
[4] Government of Spain: Law 22/2011, of July 28, on contaminated waste and soil. Official Bulletin of State
[5] BOE-A-2011-13046.
[6] L. Cristobal Andrade, M.A Bernal Papín, M.C Taboada Gómez, P.M Bello Bugallo, Optimization of Improvable Flows by combining BAT Analysis and process simulation, Chemical Engineering Research and Design, Volume 92, Issue 10, October 2014, Pages 1976-1987.

Optimización de la planta de lavado de pasta cruda de celulosa para la excelencia ambiental

F. Rincón*, R. Makoto, M. Reza
Ence, Energía y Celulosa, Pontevedra, España
*frincon@ence.es

El lavado de la pasta tras la cocción Kraft tiene los siguientes objetivos: 1) Retirar extractos y otros compuestos orgánicos e inorgánicos que interferirían en las etapas siguientes y afectarían a la calidad, 2) Recuperar los productos químicos gastados [1, 2].

Un lavado eficiente supone una mejora en la recuperación de sales, reduce el consumo de químicos en el blanqueo y reduce la carga en el efluente. La eficiencia depende del factor de dilución y de la configuración de la planta [2]. Por otro lado, un bajo factor de dilución es clave para la eficiencia energética en la planta de evaporación [3]. Todos los equipos lavadores aplican todas o algunas de las cinco operaciones básicas del lavado: dilución, mezclado, espesado, difusión y desplazamiento.

Esta comunicación resume las mejoras en lavado aplicadas en los últimos años en la biofábrica de Ence en Pontevedra, que se fundamentan en la mejora de los lazos de control e instrumentación, implantación de un sistema PI y estudios de diferentes escenarios analizados el simulador WinGEMS. Los resultados, separados por fases, son los siguientes:

1. Control completamente automatizado del factor de dilución (nov 2017): Supuso la reducción de la variabilidad de la concentración del licor débil
2. Sustitución prensa lavado post O: Mejora de la consistencia (espesado) del 26 al 32%; reducción de la DQO a blanqueo (32%); reducción make-up de químicos (17%), reducción carga efluente (14%); incremento capacidad de producción (7%)
3. Sustitución de los filtros de vacío existentes: reducción carga DQO a preblanqueo con oxígeno (13%) e incremento de la eficiencia de esta etapa (3%).

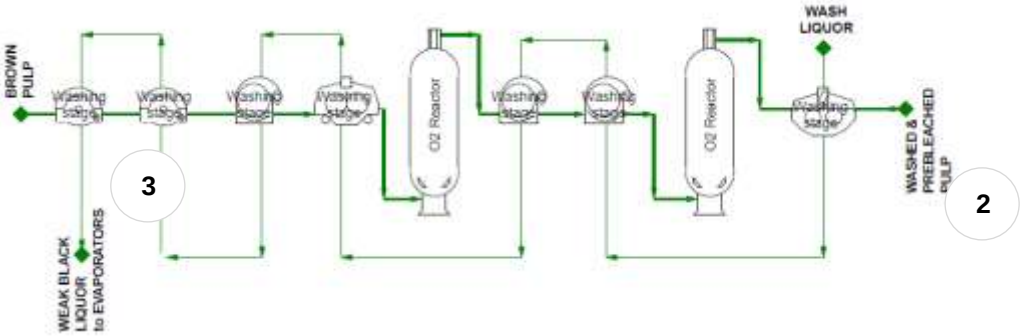


Fig.1. Secuencia Lavado de pasta y Deslignificación con Oxígeno

Referencias
[1] M. Sillanpää, Studies on washing in kraft pulp bleaching. Tesis U. Oulu (2005).
[2] P. Hart. Washing. Tappi Brown stock washing course (2005)
[3] R. Compton. Economic analysis of brown stock washing. Tappi Brown stock washing course (2005)
[4] https://www.valmet.com/pulp/automation-for-pulp/apc-advanced-process-controls/valmet-wingems/

Use of nettle leaves (*Urtica dioica* L.) extracts as cosmetic agent in topical cream formulation based on thermal spring waters

L. López-Hortas[1,*], C. Le Juge[2,3], E. Falqué[3], H. Domínguez[1], M.D. Torres[1]
[1]Dept. Chemical Engineering, Faculty of Sciences, University of Vigo, As Lagoas s/n, 32004 Ourense, Spain
[2]IUT Quimper, University of Bretagne Occidentale, Rue de l'Université 2, 29334 Quimper, France
[3]Dept. Analytical Chemistry, Faculty of Sciences, University of Vigo, As Lagoas s/n, 32004 Ourense, Spain
*luclopez@uvigo.es

Nowadays, the concern for personal care and the demand for natural cosmetic products is constantly growing. In this context, *Urtica dioica* L. presents a great potential as cosmetic agent for their incorporation into skin care products, since the significant antioxidant properties of this plant could be of interest to counter the oxidative stress that accelerates skin deterioration [1]. The utilization of extracts from this renewable resource in skin care creams based on thermal spring waters combines the healthy features of this raw material and the positive therapeutic effects of this type of water [2]. In parallel, the cosmetic industry is in continuous renovation looking for novel sustainable extraction processes with less environmental impact in order to respond the increasing attention of consumers about this item of health-care products [3]. In this sense, microwave hydrodiffusion and gravity (MHG) is an eco-friendly extraction method that provides aqueous extracts at atmospheric pressure without added solvent with less time extraction requirements consuming limited energy supplies and productive costs in comparison with traditional techniques [4]. In this work, the enrichment with nettle leaves extract of moisturizing creams based on distinct thermal spring waters was evaluated so that the principal characteristics and stability study of these cosmetic emulsions were defined.

The analysed cream models were prepared following the instructions that Balboa *et al.* reported [5] using tree thermal spring waters (TSW1-3) from the Ourense region and adding extracts obtained by MHG at 100 W and by distilled fraction derived of steam distillation without cohobation from *U. dioica* leaves. These topical cosmetic products were compared with an equivalent formulation which instead of extracts and thermal spring waters contained commercial antioxidants or distilled water, respectively. Their main physicochemical properties were determined, as pH, total solid content, colour, solar protector factor (SPF), thiobarbituric acid reactive substances (TBARS) content and rheological parameters. A sensory evaluation of the different products was also realized. The moisturizing creams were submitted at an accelerated oxidation evaluation at 50 ± 2 ºC during 15 days in order to evaluate their physicochemical stability.

The obtained outcomes indicated that the evaluated topical preparations exhibited similar values of the analysed features. For instance, the pH values of the emulsion (oil/water, O/W) creams varied on the range of 5.27 and 6.32. It was also noteworthy that their TBARS concentration varied between 12.14 and 26.71 nmol malonaldehyde/g sun cream dry weight whereas their colour magnitudes were also comparable among which (the data of hue angle, Chroma and saturation was around 129.70º, 8.84 and 0.10, respectively). Overall, the results revealed that extracts from *U. dioica* by MHG can be a potential candidate for integrate the formulation of innovative moisturizing products with incorporated natural ingredients.

Acknowledgements
The authors are grateful to the Ministry of Economy and Competitiveness of Spain (CTM2015-68503-R) and FEDER for the financial support. L. López-Hortas thanks the Xunta de Galicia for her pre-doctoral grant (2014/2020 European Social Fund). M.D. Torres acknowledges the Ministry of Economy, Industry and Competitiveness for her post-doctoral grant (IJCI-2016-27535).

References

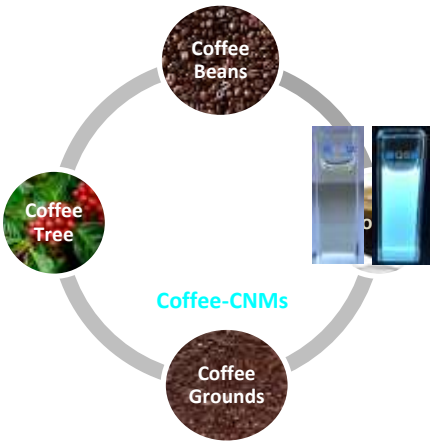
[1] C. Bourgeois, E.A. Leclerc, C. Corbin, J. Doussot, V. Serrano, J.-R. Vanier, J.-M. Seigneuret, D. Augin, C. Pichon, É. Lainé, C. Hano, Comptes Rendus Chimie, 19 (2016) 1090.
[2] S. Seite, D. Moyal, Journal of the American Academy of Dermatology, 76 (2017) AB403.
[3] J.V. Tarazona. P. Wexler (Ed.), London, Academic Press, 2014.
[4] F. Chemat, M. Abert-Vian, A.S. Fabiano-Tixier, J. Strube, L. Uhlenbrock, V. Gunjevic, G. Cravotto, TrAC Trends in Analytical Chemistry, 118 (2019) 248.
[5] E.M. Balboa, M.L. Soto, D.R. Nogueira, N. González-López, E. Conde, A. Moure, M.P. Vinardell, M. Mitjans, H. Domínguez, Industrial Crops and Products, 58 (2014) 104.

NANOQUÍMICA Y NANOTECNOLOGÍA

Coffee Grounds of Vending Machines: A Sustainable Route for Synthesis of Luminescent Carbon Nanomaterials

Alexandra I. Costa[1,2*], Bianca Moraes[1], José V. Prata[1,2]
[1]Área Departamental de Engenharia Química, ISEL - Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Lisboa, Portugal
[2]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal
*acosta@deq.isel.ipl.pt

Carbon nanomaterials have an important place in nanoscience due to their numerous potential applications in optoelectronic devices, composite materials, sensors, biological labelling and biomedicine [1-4]. Coffee waste is a qualified carbon raw material for production of valuable carbon materials because it is available in huge amounts, and it is an environmentally friendly renewable resource [5].
Herein we report our most recent outcomes concerning the coffee-carbon nanomaterials (Coffee-CNMs) synthesis from the coffee grounds of vending machines by a one-step hydrothermal green process, during 4h, under a variety of conditions. Several procedure variables (e.g. reaction temperature (200º-300ºC), amount/nature of additives (*viz*. ethylene diamine and melamine), under a nitrogen atmosphere/air-equilibrated conditions) were evaluated, leading the establishment of certain processing-structure-property correlations.
The structural characteristics of the luminescent Coffee-CNMs were studied by FTIR and $^{1}H/^{13}C$ NMR and their luminescent properties investigated by means of steady- and time-resolved fluorescence and ground-state absorption. The Coffee-CNMs show blue-green fluorescence ($\lambda_{em\ max}$ = 462 nm upon excitation at 380 nm), exhibiting moderate quantum efficiencies ($Ø_F$ = 0.04-0.14) and an excited-state lifetime of 5.02 ns. High photostability were observed when continuously irradiated for 5h at 380 nm and reversible pH-responsive photoluminescence (pH 1-12).
The characteristics of Coffee-CNMs obtained, as well as to their easy and sustainable synthesis, carbon source affordability and excellent dispersion in aqueous solutions, prospectively pointing to their valorization in several technological applications.



Acknowledgments
We are grateful to IPL (Project IPL/2017/NANOCHIRAL/ISEL) and to Fundação para a Ciência e a Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior (FCT/MCTES) for financial support (UID/QUI/00616/2019) of this work.

References
[1] a) P. Zuo, X. Lu, Z. Sun, Y. Guo, H. He, Microchim. Acta, 183, (2016), 519; b) S. Y. Lim, W. Shen, Z. Gao, Chem. Soc. Rev., 44, (2015), 362.
[2] P. Miao, K. Han, Y. Tang, B. Wang, T. Lin, W. Cheng, Nanoscale, 7, (2015), 1586.
[3] Y. Dong, J. Cai, X. You, Y. Chi, Analyst, 140, 2015, 7468.
[4] V. Sharma, P. Tiwari, S. M. Mobin, J. Mater. Chem. B, 5, (2017), 8904.
[5] T. Tokimoto, N. Kawasaki, T. Nakamura, J. Akutagawa, S. Tanada, J. Colloid Interface Sci., 281 (2005), 56.

Water-in-oil nanoemulsions based in natural extracts with antimicrobial and antioxidant properties

Colucci, G.[1,2], Rezende, S.C[1], Silva, S. C.[1], Sipoli, C. C.[3], Fernandes, I.P. [1], Barreiro, M. F. [1,*]

[1]Mountain Research Centre (CIMO) and Laboratory of Reaction and Separation Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Polytechnic Institute of Bragança, Bragança, Portugal
[2]PPGEQ, Federal Technological University of Paraná, Apucarana, Brazil
*barreiro@ipb.pt

Nanoemulsions are biphasic systems characterized by droplets in the nanometer size range, which gives to these systems several advantages, such as excellent bioavailability and bioefficacy during the release of functionalities incorporated therein [1,2]. The development of nanoemulsions from natural compounds may confer to the final product bioactive properties. In this context, the present work aimed to develop water-in-oil (W/O) nanoemulsions based on sweet almond oil and cinnamon aqueous extract to produce a moisturizing product with antimicrobial and antioxidant properties. For this purpose, a base nanoemulsion and nanoemulsions with different cinnamon extract concentrations (1.25%; 2.5%; 3.75%; 5%, w/v - water base) were prepared. The W/O ratio was 40/60 and Span 80/Tween 80 mixture (54/46 ratio, v/v) was used as the emulsifier system. The production was made by preparing a coarse emulsion using a mechanical homogenizer (11000 rpm, 5 min). Then, the droplet size was reduced using a high-pressure homogenizer (HPH) during 12 cycles of homogenization. These systems were evaluated by Confocal Laser Scanning Microscopy (CLSM), antioxidant activity (DPPH radical-scavenging activity method), and antimicrobial activity (agar diffusion test with the microorganisms *P. aeruginosa* ATCC 9027, *E. coli* AATCC 10536 and *S. aureus* ATCC 19213). Formulation stability was evaluated by visual inspection during storage at room temperature. As results, the CLSM analysis confirmed the nature of the W/O system, in addition to revealing a change in the microstructure of the emulsion with the increase of cinnamon extract concentration. The formulations with cinnamon extract showed antioxidant and antimicrobial activities, revealing the effect of the cinnamon presence. Regarding the antimicrobial analysis, the formulations with cinnamon have a prolonged effect against *E. coli* and *S. aureus* bacteria, maintaining the same zone of inhibition (9 mm) after 96 hours of incubation. Regarding the antioxidant analysis, the increase in cinnamon extract resulted in a relevant increase of the antioxidant activity. The Fig. 1. shows the (a): antioxidant results, and the antimicrobial assay for sample with 2.5% cinnamon against (b): *S. aureus* and (c): *E.coli* after 96 hours of incubation. The formulations revealed macroscopic stability, since no instability phenomena was detected during this study (more than 1 month). The formulations developed with cinnamon extract presented antimicrobial and antioxidant properties besides macroscopic stability, making them of great interest for applications like cosmetics and pharmaceutics.

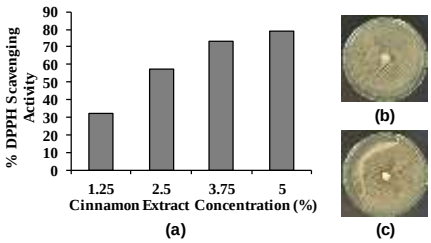


Fig. 1 (a) Antioxidant analysis; (b) and (c) Antimicrobial test

Acknowledgements

Associate Laboratory LSRE-LCM (UID/EQU/50020/2019) funded by national funds through FCT/MCTES (PIDDAC) and FCT, and CIMO (UID/AGR/00690/2019) trough FEDER under Program PT2020. To the national funding by FCT, P.I., through the institutional scientific employment program-contract for I.P. Fernandes contract.

References

[1] Mcclements, D. J., Rao, J. Critical Reviews in Food Science and Nutrition, 51 (2011).
[2] Setya, S., Talegaonkar, S., Razdan, B. K. World Journal of Pharmacy and Pharmaceutical Sciences, 3 (2014).

Influence of the starch dissolution approach in the green synthesis of starch-capped silver nanoparticles

Magda Fonseca[1,*], Ana L. Teixeira [2], Francisca Dias[2,3], Mariana Morais [2,3], Vera Machado [2], Rui Medeiros [2,3,4,5,6], João A. V. Prior[1]

[1] LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[2] Molecular Oncology and Viral Pathology Group, IPO-Porto Research Center (CI-IPOP), Portuguese Oncology Institute of Porto
[3] ICBAS, Abel Salazar Institute for the Biomedical Sciences, University of Porto
[4] Research Department, LPCC-Portuguese League Against Cancer (NRNorte)
[5] FMUP, Faculty of Medicine, University of Porto
[6] CEBIMED, Faculty of Health Sciences, Fernando Pessoa University

**mfonseca@ff.up.pt*

Recent studies suggest that silver nanoparticles (AgNPs) have promising biological activity and their synthesis by green chemistry processes has advantages over conventional chemistry. The main goal of this work was to optimize the synthesis of silver nanoparticles using $AgNO_3$ as silver source, glucose as reducing agent for silver and soluble starch as capping and core stabilizer of the nanoparticles.

Some preliminary syntheses were performed using mass ratios of Ag+/starch 1.0:1.3 and molar ratio for Ag+/glucose 1.0:1.5, through microwave radiation and fixing the reaction temperature at 150 ° C for 4.5 minutes. The obtained suspension of nanoparticles was analysed by TEM and revealed that the nanoparticles size was in average 3 nm. The UV-Vis spectrophotometry analysis suggested a surface plasmon resonance band at approximately 408 nm, indicating metallic silver nanoparticles formation.

In the literature one can find works revealing that starch granules subjected to aqueous solubilization with the aid of heat can originate different molecular structures of the solubilized starch [1]. Considering the dependence of the synthesis of silver nanoparticles by the starch structure [2], some assays to study the influence of starch in the synthesis were performed. Following, the reagent for capping was prepared by different techniques by varying the temperature and rate of aqueous dissolution of starch, through conventional heating or by microwave radiation. The UV-Vis spectrophotometric and DLS analysis revealed different spectra profile and hydrodynamic sizes of AgNPs, respectively, indicating that the procedure adopted for the starch aqueous dissolution influences the physical-chemical properties of AgNPs. The obtained results were of outmost importance considering that the application of silver nanoparticles, for example, in cellular assays or bio-imaging, is highly dependent on the capping of the nanoparticles.

Further optimization assays of starch capping design and other parameters affecting the AgNPs synthesis will be performed, as valuable variables that should be taken into account when designing silver nanoparticles for specific purposes.

Acknowledgements
The work was supported by UID/QUI/50006/2019 with funding from FCT/MCTES through national funds. This work received financial support from National Funds (FCT, Fundação para a Ciência e Tecnologia) through project PTDC/ MED-QUI/29800/2017.

References
[1]Liu, C.Z., et al., Preparation and characterization of starch nanoparticles via self-assembly at moderate temperature. International Journal of Biological Macromolecules, 2016. 84: p. 354-360.
[2]Khan, Z., Encapsulation of silver nanoparticles into the helix of water soluble starch and their sensing properties. International Journal of Biological Macromolecules, 2019. 136: p. 165-176.

INFLUENCIA DEL TAMAÑO DE PARTÍCULA SOBRE LAS PROPIEDADES MAGNÉTICAS DE NANOPARTÍCULAS DE Fe_3O_4

Pelayo García Acevedo[1,*], Manuel González Gomez[1], Susana Yañez Vilar[1], Yolanda Piñeiro[1], José Rivas[1]

[1]Departamento de Física Aplicada, Laboratorio NANOMAG, Instituto de Investigación Tecnológica, Universidad de Santiago de Compostela (USC), Santiago de Compostela, España
**pelayo.garcia.acevedo@usc.es*

En los últimos años, el creciente desarrollo de los materiales nanoestructurados y de la nanotecnología ha generado un elevado interés en los óxidos de hierro, en particular sobre las nanopartículas de magnetita, debido a sus interesantes propiedades magnéticas y su baja toxicidad. [1]
En la actualidad, existen diferentes métodos de síntesis para la preparación de nanopartículas de magnetita (coprecipitación, microemulsión, solvotermal, etc). Sin embargo, la baja cristalinidad y elevada polidispersidad de las nanopartículas obtenidas afecta considerablemente a las propiedades magnéticas de las mismas. [1] Debido a esto, se observan diferentes comportamientos magnéticos que pueden llevar a una gran cantidad de errores intrínsecos en la determinación de las propiedades físicas. [2]
En este trabajo, presentaremos el estudio de la influencia del tamaño de partícula sobre las propiedades magnéticas de nanopartículas de magnetita bien cristalizadas y con baja polidispersidad (Fig.1).

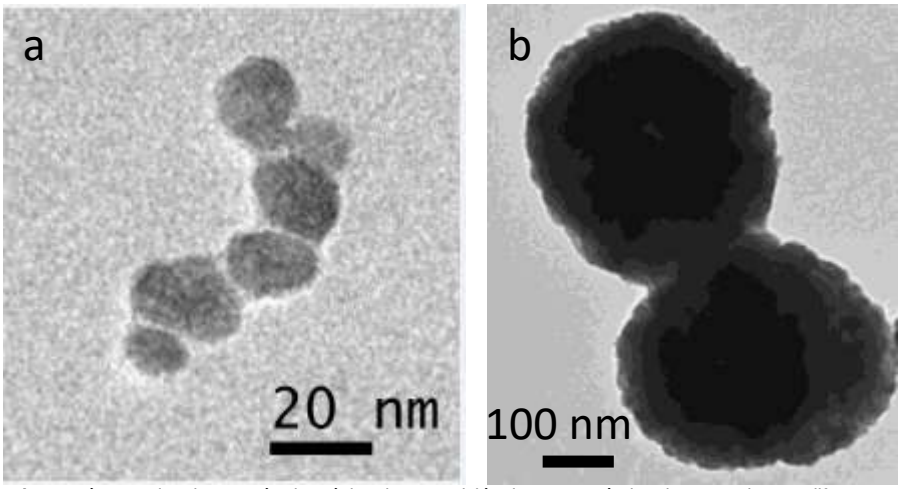


Fig.1. Imágenes de microscopía electrónica de transmisión de nanopartículas de magnetita con diferentes tamaños de partícula.

Agradecimientos
Este trabajo ha sido financiado por el proyecto MADIA de la Comisión Europea **(**732678-MADIA-H2020-ICT-2016), el Programa para el Desarrollo del Grupo Estratégico de Materiales (AEMAT) de la Universidad de Santiago de Compostela (N. ED431E2018/08) y el Programa para Consolidación de Grupos de Referencia Competitiva GRC2017 (N. ED431C 2017/22) de la Xunta de Galicia.

Referencias

[1] Leyu Wang, Jie Bao, Lun Wang, Fang Zhang, Yadong Li, Chemistry-A European Journal, 12 (2006) 6341-6347.
[2] The Physical Principles of Magnetism, Allan H.Morris, Wiley, Series on Science and Technology of Materials, 2001.

Silica-based aerogels reinforced with aramid fibers for thermal insulation at extreme temperatures

Mariana Emilia Ghica*, **Cláudio M.R. Almeida, Luisa Durães**
[1]CIEPQPF, Department of Chemical Engineering, University of Coimbra,
3030-790, Coimbra, Portugal
**meghica@eq.uc.pt*

Silica aerogels belong to a class of highly porous materials (> 90%), obtained by sol-gel technology, which exhibit unique properties, such as low thermal conductivity (< 20 mW m^{-1} K^{-1}), low density (< 150 kg m^{-3}) and high surface area (500-1200 m^2 g^{-1}) [1,2]. Due to their specific properties, these aerogels present a wide range of applications in: thermal insulators, battery electrodes, catalysts, humidity sensors, adsorbents for pollutants, as well as optical, acoustic insulators and dielectric devices [1,2]. Despite their excellent and unique properties, pure silica aerogels present some drawbacks, like fragility and hydrophilic behaviour, which limit their application on a large-scale. Nevertheless, silica aerogels present high versatility for surface modification and allow easy incorporation in their structure of various compounds, such fibers, particles and polymers, for improving their mechanical, optical and thermal properties [1,3]. The proper selection of silica precursors also permits to obtain more durable aerogels with higher strength. Among the organic reinforcement materials, aramids are very promising materials due to their excellent mechanical behaviour and dimensional/thermal stability in harsh environments [4].

This project focuses on the development of fiber-reinforced silica-based aerogel nanocomposites for high-performance thermal insulation at extreme temperature/vibration conditions imposed to Space devices, especially in launch/re-entry operations and at cryogenic propulsion stages. For the aerogels preparation, different silica co-precursors in various ratios and reinforcement with different para/meta aramid fibers were tested. The aerogels´s characterization was performed in order to investigate their morphology, structure, chemical composition and thermal resistance. The most promising architecture exhibited low bulk density value (~200 kg m^{-3}), as well as low thermal conductivity (< 30 mW m^{-1} K^{-1}) and hydrophobic behaviour (Fig.1). Globally, the prepared aerogel composites presented high thermal stability up to 550-600 ºC and integrity.

(a) (b)

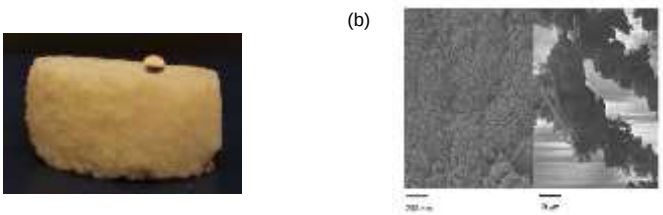


Fig.1. (a) Contact angle and (b) SEM image of aramid-silica aerogel nanocomposites

Acknowledgments
This work was developed by University of Coimbra under the project AeroXTreme (CENTRO-01-0145-FEDER-029533) - "High-performance silica aerogel nanocomposites for insulation under extreme temperature Space environments", co-funded by Foundation for Science and Technology (FCT) and by the European Regional Development Fund (FEDER), through Centro 2020 - Regional Operational Program of the Centre of Portugal.

References

[1] H. Maleki, L. Durães, A. Portugal, Journal of Non-Crystalline Solids 385 (2014) 55-74.
[2] R.B. Torres, J.P. Vareda, A. Lamy-Mendes, L. Durães, The Journal of Supercritical Fluids 147 (2019) 81-89.
[3] Lamy-Mendes, R.F. Silva, L. Durães, Journal of Materials Chemistry A 6 (2018) 1340-1369.
[4] Z. Li, L. Gong, C. Li, Y. Pan, Y. Huang, X. Cheng, Journal of Non-Crystalline Solids 454 (2016) 1-7.

Biocompatible and macrophage-targeting mannosylated lipid nanoparticles for the treatment of tuberculosis

Marina Pinheiro[1,2*], Joana Magalhães[1], Barbara Drasler[3], Dedy Septiadi[3], Alke Petri-Fink[3], Susana G. Santos[4,5], Barbara Rothen-Rutishauser[3], Salette Reis[1]

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal
[2]Faculdade de Medicina, Universidade do Porto, Portugal
[3]Adolphe Merkle Institute, University of Fribourg, Fribourg, Switzerland
[4]i3S - Instituto de Investigação e Inovação em Saúde, INEB - Instituto de Engenharia Biomédica, Universidade do Porto, Porto, Portugal.
[5]ICBAS - Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Porto, Portugal.

**mpinheiro@ff.up.pt*

Macrophages are important targets for drug delivery in diseases where they host persistent pathogens, such as Mycobacterium tuberculosis. Lipid nanoparticles, namely nanostructured lipid carriers (NLCs), represent promising alternatives for the pulmonary delivery of antibiotics, which has particular interest in tuberculosis (TB) treatment since the lungs are the primary sites of infection. Thus, this work aims to optimize the design of macrophage-targeted NLCs and also to assess their biocompatible profile as pulmonary drug delivery systems. For that purpose, NLCs were designed to facilitate drug delivery to infected areas by exploiting the macrophage mannose receptor. Non-mannosylated and mannosylated NLCs were characterized in terms of size, polydispersity, surface charge and morphology. Cell viability, uptake and pro-inflammatory response activation studies were performed in monocultures of primary human macrophages (MDMs) and in a 3D lung model mimicking the alveolar epithelial tissue barrier. Results revealed formulations with proper size for deep lung deposition and high absolute ζ-potential values. TEM analyses showed spherical formulations, uniform in shape and diameter, with no visible aggregation. Upon NLCs exposure, no morphological changes or toxicity in MDMs viability were observed. Imaging flow cytometry results showed that MDMs efficiently internalized NLCs with more mannosylated than non-mannosylated NLCs being internalized. Moreover, in the 3D lung model, the cell layer integrity was maintained and MDMs and alveolar epitelial cells were able to internalize mannosylated and non-mannosylated NLCs without evidence of cytotoxic or pro-inflammatory responses. Overall, this study describes the design of macrophage-targeted biocompatible carriers, providing new directions for the treatment of TB.

Agradecimientos

MP thanks FCT (Fundação para a Ciência e Tecnologia) for funding through program DL 57/2016 – Norma transitória. JM thanks FCT and POPH (Programa Operacional Potencial Humano) for the PhD grant SFRH/BD/110683/2015. This work was also supported by FCT through the FCT PhD Programs, specifically by the BiotechHealth Program. BD was supported by the Peter und Traudl Engelhorn foundation. The authors also thank the European Union (FEDER funds POCI/01/0145/ FEDER/007265, and POCI/01/0145 FEDER/30624) and Portuguese National Funds under the Partnership Agreement PT2020 UID/QUI/50006/2013. In addition, the Adolphe Merkle Foundation is acknowledged.

Referencias

Costa A, Pinheiro M, Magalhaes J, Ribeiro R, Seabra V, Reis S, et al, Advanced drug delivery reviews, 102 (2016) 102-15.

Lapatinib-loaded nanostructured lipid carriers for breast cancer therapy

Andreia Granja[1], Marina Pinheiro[1], Célia T. Sousa[2] and Salette Reis[1]*

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, R. Jorge de Viterbo Ferreira 228, 4050-313, Porto, Portugal.
[2]IFIMUP-IN and Dep. Física e Astronomia, Faculdade de Ciências, Universidade do Porto, Rua Campo Alegre 687, 4169 - 007 Porto, Portugal
**shreis@ff.up.pt.com*

Lapatinib is an oral dual tyrosine kinase inhibitor targeting the epidermal growth factor receptor-2 (HER2) currently approved by FDA for treatment of HER-2 positive breast cancer. Despite being an effective treatment option, the clinical use of lapatinib is limited by its poor aqueous solubility, low oral bioavailability, high binding affinity to blood proteins and toxicity induced by its administration at high daily doses [1]. Entrapment of this drug into an adequate delivery vehicle is a promising approach to increase its efficacy and accumulation in tumor tissues and reduce the administered doses and associated toxicity [1].

In this work, nanostructured lipid carriers (NLC) were designed, optimized and characterized for loading of lapatinib. The NLC developed appeared homogeneous with a spherical morphology, presented adequate size for oral administration and highly negative surface charge, suggesting good stability. Furthermore, a high encapsulation efficiency of the drug was obtained. A controlled release profile was obtained, with higher release of the drug at acidic pH, characteristic of the tumoral environment. Taken together, these results suggest that the developed NLC is a suitable delivery vehicle for the oral administration of lapatinib and can be further explored as a promising therapy for breast cancer.

Acknowledgments
This work received financial support from the European Union (FEDER funds) and National Funds (FCT/MEC, Fundação para a Ciência e Tecnologia and Ministério da Educação e Ciência) under the Partnership Agreement PT2020 UID/QUI/50006/2013 - POCI/01/0145/FEDER/007265. This work was also supported by FCT through the FCT PhD Programmes and by Programa Operacional de Capital Humano (POCH), specifically by the BiotechHealth Programme (Doctoral Programme on Cellular and Molecular Biotechnology Applied to Health Sciences). The authors thanks FCT for the grants SFRH/BPD/99124/2013 and SFRH/BD/130147/2017.

References
[1] G.V. Bonde, S.K. Yadav, S. Chauhan, P. Mittal, G. Ajmal, S. Thokala, B. Mishra, Lapatinib nano-delivery systems: a promising future for breast cancer treatment, Expert opinion on drug delivery, 15 (2018) 495-507.

QUÍMICA DE POLÍMEROS

Study of the degradation mechanisms of PVC insulation on electrical wires

Sandra Matos[1,*], Ana Vera Machado[1], Luís Domingues[2], Leonardo Gonçalves[3]

[1]Universidade do Minho, Campus de Azurém, Guimarães, Portugal
[2]JLD Unip. Lda, Tapada das Mercês, Mem Martins, Portugal
[3] Instituto Politécnico de Setúbal, Campus do IPS - Estefanilha, 2910-761 Setúbal

e-mail: matos.sandra.c@gmail.com

PVC is the second most widely used thermoplastic in the world and the most widely used material for the insulation of electrical wires. Due to the need for it's resin to be formulated by incorporating additives, it is a very versatile polymer in which its characteristics are changed according to the need for use. Thus, PVC can be rigid or extremely flexible depending on end use.

The development of PVC resins began in the 19th century, when the vinyl chloride monomer was found. By incorporation of plasticizers on the production process PVC became even more versatile due to its high flexibility and rubber-like characteristics.

The problem of low heat stability was further solved with the development of organometallic compounds and salts based mainly on lead, cadmium, barium, zinc and tin (some already eliminated due to their toxicity), with stabilizing properties of the intermediates responsible for the degradation reactions (thermal stabilizers).

The use of additives, like plasticizers, stabilizers, etc., in the insulation of electrical conductors has no impact on the final characteristics of the product, but when wires are used in subsequent processes where a small variation on the characteristics affect the process it demands un understand of insulation behaviour.

For that reason a study was conducted to understand the degradation mechanisms of PVC that may affect the product on processes used afterwards.

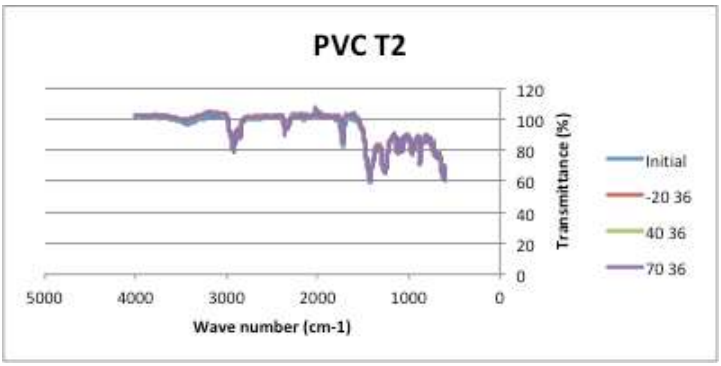


Fig.1. FTIR analysis

REFERENCES

[1] Lacabanne, C.; Thermally stimulated creep for the study of ageing insulating polymers under electrical field (IEEE International Symposium on Electrical Insulation, Baltimore, MD USA, pp. 62-65 – June 1992)

[2] DIN EN 60811-1-1; Common test methods for insulating and sheathing materials of electric cables and optical cables - Methods for general application - Measurement of thickness and overall dimensions - Tests for determining the mechanical properties; Revision date 27.05.2002

[3] Rodolfo Jr., A.; I. Mei. L. H. - Mecanismos de degradação e estabilização térmica do PVC; Centro de Tecnologia e Inovação - Vinílicos, Braskem S/A; Faculdade de Engenharia Química, UNICAMP

[4] Gunzler, H., Gremlich H.; IR Spectroscopy an introduction, Wiley-VCH, Weinheim, 2002, pg.171-253

[5] Paiva, M. C.; Espectroscopia de Infravermelho, Universidade do Minho, 2006

Synthesis and Sensing Ability of New Fluorescent Oxacyclophane-Calix[4]arene-based Polymer

Alexandra I. Costa[1,2*], **Carlos M. Teixeira**[1,3], **José V. Prata**[1,2]
[1]Área Departamental de Engenharia Química, ISEL - Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Lisboa, Portugal
[2]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal
[3]Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisboa, Portugal
*acosta@deq.isel.ipl.pt

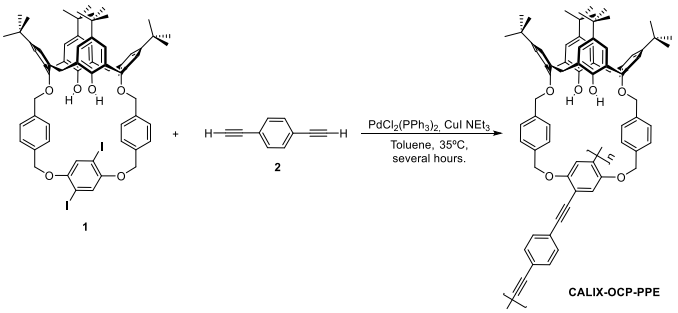
Fluorescent conjugated polymers have received a great deal of recent interest due to their ability to act as chemosensors to detect various chemical species in both environmental and biological systems with sensitivity and selectivity [1-6]. Our recent work in the field has been focused on the synthesis and application of several calix[4]arene architectures as chemosensors, either as single-standing molecules or incorporated in conjugated polymer systems, having nitroaromatic explosives, explosive taggants and pollutants as target analytes [3-6].

Herein we present our recent findings in that regard using a novel conjugated polymer incorporating an oxacyclophane-calix[4]arene receptor into the main chain as solid-state fluorescent chemical sensor.

The novelty of such system is the close proximity of the molecular receptor to the transduction site (main chain) which is expected to improve the sensing abilities of this material. The synthetic strategy is outlined in Scheme 1.

The polymer was isolated in high yield and characterized by FTIR and $^{1}H/^{13}C$/HSQC NMR techniques and GPC analysis. The photophysical properties of the synthesized material were evaluated in fluid-phase and in solid-state by UV/Vis and fluorescence spectroscopy. The polymer exhibits high quantum yield ($Ø_F$ = 0.55, $CHCl_3$) and a longer-than-usual excited-state lifetime (1.80 ns).

Its ability for detection of nitroaromatics and nitroanilines in vapour phase was evaluated in solid-state (thin-films). A high selectivity and sensitivity were attained for both classes of analytes.



Scheme 1 - Synthesis of **CALIX-OCP-PPE** with narrow rim 1,3-oxacyclophane tethered calix[4]arene derivative **1** and its Sonogashira-type cross-coupling polymerization with 1,4-diethynylbenzene (**2**).

Acknowledgments
We are grateful to IPL (Project IPL/2018/INCALIX/ISEL) and to Fundação para a Ciência e a Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior (FCT/MCTES) for financial support (UID/QUI/00616/2019) of this work.
We also thank Prof. M. N. Berberan-Santos for providing access to fluorescence lifetime equipment and Dr. A. Fedorov for his assistance in the measurements.

References
[1] X. Sun, Y. Wang, Y. Lei, Chem. Soc. Rev., 44 (2015) 8019.
[2] U. H. F. Bunz, Chem. Rev., 100 (2000) 1605.
[3] C. M. Teixeira, A. I. Costa, J. V. Prata, Tetrahedron Lett., 54 (2013) 6602.
[4] A. I. Costa, J. V. Prata, Sensors and Actuators B, 161 (2012) 251.
[5] A. I. Costa, H. D. Pinto, L.F.V. Ferreira, J.V. Prata, Sensors and Actuators B, 161 (2012) 702.
[6] P. D. Barata, J. V. Prata, Supramol. Chem., 25 (2013) 782.

Materiais de base poliuretano com resistência incrementada à fadiga térmica para calçado de segurança

Diana F. Cuma[1], Helder M. Rafael[1], Isabel P. Fernandes[1], Helder T. Gomes[1], Vera Pinto[2], Maria J. Ferreira[2], Maria F. Barreiro[1*]

[1]Mountain Research Centre (CIMO) and Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Polytechnic Institute of Bragança, Campus de Santa Apolonia - 5300-253 Bragança, Portugal (barreiro@ipb.pt).

[2]Centro Tecnológico do Calçado de Portugal (CTCP), Rua de Fundões - Devesa Velha, 3700-121 S. João da Madeira, Portugal

*barreiro@ipb.pt

A perda de propriedades ao longo do tempo de vida útil do calçado está relacionada com a variação térmica e esforço mecânico ocorrido em condições de utilização; o calçado pode ser utilizado de forma intercalada a temperaturas elevadas e a temperaturas baixas (p.exe. o calçado usado por militares que operam no deserto). Os materiais de base poliuretano (PUs), nomeadamente os microcelulares, são convencionalmente aplicados na construção de calçado sendo associados a boas propriedades de conforto. Devido às exigências dos consumidores quanto a produtos de elevado desempenho, o desenvolvimento de novos PUs microcelulares com resistência incrementada à fadiga térmica é um tópico de elevado interesse industrial. Assim, o presente trabalho está focado no desenvolvimento de PUs microcelulares resistentes à fadiga térmica, partindo de uma formulação e de um sistema químico de base poliéster típico para a produção de entressolas para calçado, e onde o incremento desta propriedade é realizado pela aditivação do PU com nanocargas inorgânicas. Produziram-se PUs moldados correspondentes à formulação base e a formulações modificadas com o aditivo inorgânico nano-A (tamanho médio de partícula<10 µm) através da incorporação de 1, 3, 5, 7 e 10% (m/m) (Fig.1 (1a)). Os PUs produzidos foram caracterizados quanto à estrutura celular por microscopia ótica (MO) (Fig.1 (2a)) e *Scanning Electron Microscopy* (SEM), servindo também esta última técnica para verificar a distribuição das cargas nas células (Fig. 1 (3a)). As propriedades térmicas foram avaliadas por *Differential Scanning Calorimetry* (DSC). Para avaliar o efeito da fadiga térmica nas propriedades dos PUs, desenvolveu-se um teste laboratorial que consistiu em colocar as amostras numa estufa a 60ºC durante 12 horas, seguido de um período a 4 ºC (frigorífico) durante 12 horas. Este procedimento foi repetido durante 5 ciclos, seguindo-se a análise por DSC de forma a avaliar o efeito nas propriedades térmicas. Os resultados obtidos por MO permitiram observar que a introdução do aditivo originou distribuições de tamanho de células mais homogéneas, e que esta característica melhorou com o aumento do teor de 1 para 10%. A análise por DSC das amostras após produção evidenciou que a incorporação do aditivo incrementou o valor de Tm de 292.1 (PUbase) para 311.7 °C (PU10nano-A), enquanto após o teste de fadiga térmica os valores de Tm variaram entre 292.7 (PUbase) e 314.7 °C (PU10nano-A). Este resultado aponta para um efeito positivo da utilização deste tipo de cargas no aumento da resistência do PU a temperaturas elevadas.

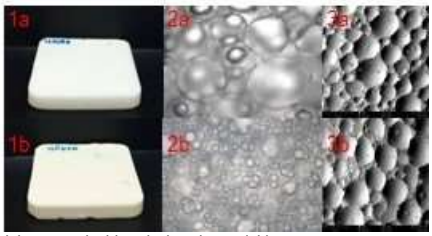


Fig.1. Amostras dos PUs microcelulares produzidos: (1a) PUbase; (1b) PU5nano-A. Imagens de MO (ampliação 100x): (2a) PUbase, e (2b) PU5nano-A; e imagens SEM (ampliação 300x): (3a) PUbase e (3b) PU5nano-A.

Agradecimentos

SHOE@FUTURE – Soluções tecnológicas para calçado profissional (projeto SI I&DT - Projetos em Co-Promoção Nº 33835) cofinanciado pelo Fundo Europeu de Desenvolvimento Regional (FEDER), através do Programa Operacional Competitividade e Internacionalização (COMPETE 2020). Laboratório Associado LSRE-LCM (UID/EQU/50020/2019) financiado por fundos nacionais através da FCT/MCTES (PIDDAC) e FCT, e CIMO (UID/AGR/00690/2019) através do FEDER no âmbito do Programa PT2020. Ao financiamento nacional da FCT, P.I., através do contrato de programa institucional de emprego científico de I.P. Fernandes.

Analysis of the effect of temperature on durability of polymers used in the coating of electrical conductors

Sandra Matos[1,*], Luís Domingues[2],

[1]Universidade do Minho, Campus de Azurém, Guimarães, Portugal
[2]JLD Unip. Lda, Tapada das Mercês, Mem Martins, Portugal

**e-mail: matos.sandra.c@gmail.com*

In normal operation, the coated electric wires are subjected to various types of stress, which can be electric (voltage and operating frequency), heat (room and operating temperature), mechanical (vibration, torsion) and environmental (moisture and contamination by chemical agents).

Stress accelerates the aging process which can cause irreversible changes in the material damaging the required performance. In advanced cases of aging or from the manufacturing process defects, begins the process of deterioration which can lead to rupture of the coating.

The materials used in the various areas of the vehicles are properly studied in order to satisfy the customer, but if the processes that they are subject from manufacture to use are not properly maintained, the end result may be catastrophic. According to customer standards, usage temperature of finished coated conductors should not be lower than 20 degrees Celsius negative and do not exceed 40 degrees Celsius, but with climatic changes, nowadays is quite difficult to accomplish with this specifications when moving material among regions. Based on that a study was carried out to determine the impact of temperature on the durability of polymers used in the coating of electrical conductors.

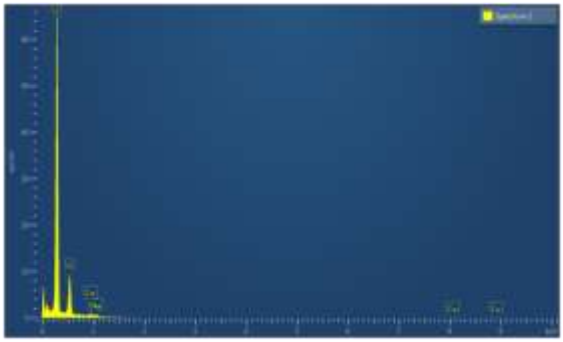


Fig.1. EDX analysis

Table 1. coating characterization

Element	Weight %
C	84,42
O	10,95
Na	1,76
Cu	2,87
TOTAL	**100**

REFERENCES

[1] Lacabanne, C.; Thermally stimulated creep for the study of ageing insulating polymers under electrical field (IEEE International Symposium on Electrical Insulation, Baltimore, MD USA, pp. 62-65 – June 1992)

[2] DIN EN 60811-1-1; Common test methods for insulating and sheathing materials of electric cables and optical cables - Methods for general application - Measurement of thickness and overall dimensions - Tests for determining the mechanical properties; Revision date 27.05.2002

[3] Rodolfo Jr., A.; I. Mei. L. H. - Mecanismos de degradação e estabilização térmica do PVC; Centro de Tecnologia e Inovação - Vinílicos, Braskem S/A; Faculdade de Engenharia Química, UNICAMP

[4] Hyvönen, P. - prediction of insulation degradation of distribution power cables based on chemical analysis and electrical measurements; Doctoral Dissertation; Helsinki University of Technology; Faculty of Electronics, Communications and Automation; Department of Electrical Engineering; 2008

Lignina: ¿es posible garantizar su calidad?

P. A. Calvo[1,*], J. Labidi[2], M.ª M. Castro[3]

[1]ENCE Energía y Celulosa, c/ Lourizán, s/n. 36153 – Pontevedra. España.
[2] Dpto. Ing. Química y Medioambiental, UPV-EHU, pl. Europa 1, 20018 San Sebastián. España.
[3] CETIM, Parque empresarial de Alvedro, c/ H 20, 15180- Culleredo (Coruña). España

**pcalvo@ence.es*

La lignina varía en composición según la especie vegetal [1] y, dentro de la especie, según el período de crecimiento [2]. Los procesos de obtención de celulosa, que varían en cuanto a condiciones de procesado (T, P, t, reactivos químicos, etc.) añaden una nueva variación a la lignina obtenida. Esta variabilidad dificulta su uso, ya que hace necesario verificar con cada nueva lignina los procesos de transformación (química y/o física) previamente realizados y asegurar su repetibilidad.

ENCE, en su biofábrica de Pontevedra, ha producido (en planta piloto) lignina a partir del licor gastado de proceso y ha verificado la constancia físico-química de la misma; lo que permite su uso en procesos de transformación.

Se presentan resultados de ligninas obtenidas en la planta piloto y de ligninas obtenidas por variación diferencial de pH y ultracentrifugación.

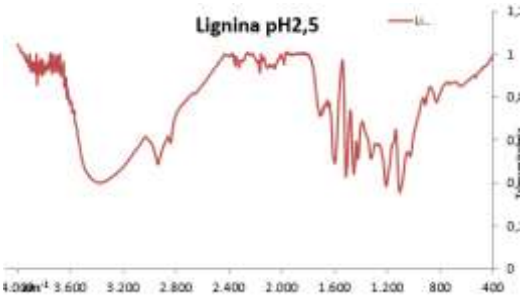


Fig.1. Espectro FTIR de lignina obtenida precipitando a pH 2,5.

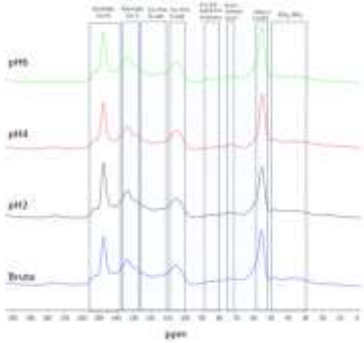


Fig.2. Espectro RMN-^{13}C de ligninas obtenidas a distintos pH.

Agradecimientos
Agradecemos a CDTI la ayuda recibida para la realización de los proyectos “Revalorización de lignina proveniente de licores negros del sector papelero en nuevos productos competitivos y mediambientalmente sostenibles. LIGNOSPREAD” y “Procesos de biorrefino para la obtención de productos de alto valor añadido a partir de lignina – LIGNOPRIZED”.

Referencias

[1] GÓMEZ, E.A. et al.; Información tecnológica, 23(6) (2012), p. 73-86.
[2] TREVIÑO, J.-GONZÁLEZ, G.- ZAERA, E.; Anuario de estadística agraria, 1974. Ministerio de agricultura

QUÍMICA ANALÍTICA

Exploiting flow-based systems for monitoring persistent inorganic pollutants (PIPs) in recreational waters

António O. S. S. Rangel*, **Raquel B. R. Mesquita**

Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327, 4169-005 Porto, Portugal

**arangel@porto.ucp.pt*

Recreational waters, both coastal and inland, are stressed by anthropological activities, with consequent contamination by inorganic and organic persistent pollutants. The economic impact to Portugal, and any coastal country, of recreational waters as leisure, touristic and commercial areas, makes it essential to invest in the sustainability of these water bodies. In this scenario, we propose to develop automatic flow-based methods for real-time monitoring of persistent pollutants. The methods will hopefully present advantages over existing ones in terms of cost, reagent consumption, portability and speciation of analytes.

The target analytes are heavy and transition metals (cadmium, lead, copper, chromium, nickel and zinc) as persistent inorganic pollutants, PIPs, and iron, due to is environmental relevance. These parameters are related to activity of maritime traffic, namely refueling, cleaning, maintenance and navigation. To assess the PIPs content, spectrophotometric sequential injection methods are being developed. Flow-based methodologies, namely sequential injection (SI) analysis, present advantageous characteristics such as automation, robustness, and versatility make them a quite suitable choice. Additionally, the potential of SI manifolds to be coupled to miniaturized detectors and pre-treatment units, namely clean-up/pre-concentration columns, is also explored.

In this communication, the methods developed in this context for the determination of zinc, copper, iron, and chromium will be discussed.

Acknowledgment

This work was supported by Nationals Funds from FCT – Fundação para a Ciência e Tecnologia through project POCI-01-0145-FEDER-031522 – Programa Operacional Competitividade e Internacionalização; scientific collaboration from FCT, project UID/Multi/50016/2019, is also acknowledged.

Correlación entre métodos espectrofotométricos y electroquímicos para la determinación de la capacidad antioxidante en frutos silvestres.

Aravena Sanhueza F.[1]; Pérez Rivera M.[1]; Peña–Farfal C.[1]
[1]*POLECTRO, Facultad de Ciencias Químicas, Universidad de Concepción, Concepción, CHILE.*
Felaravena@udec.cl

Una de las grandes preocupaciones de la sociedad actual es la alimentación de la población, principalmente por el ritmo de vida acelerado que esta, llevando al consumo de alimentos con altos contenido en grasas, conservantes y azucares, ante esta problemática es que se recomienda que la dieta la compongan alimentos de origen natural y en especial alimentos con altos contenidos en antioxidantes, contribuyendo a la inhibición y retraso del daño celular oxidativo conducente a varios tipos de enfermedades.

En este trabajo se desarrolló un método electroquímico a partir de técnicas voltamperométricas para la determinación de la capacidad antioxidante total en frutos silvestres y estudiar su correlación con metodologías espectrofotométricas, en particular con ensayos tradicionales de determinación de capacidad antioxidante como el ensayo ORAC (capacidad de absorción de radicales oxigeno)[1], resultados expresados en equivalentes de trolox, para así evaluar la posibilidad de ser un ensayo alternativo o sustituto a estos ensayos a nivel de screening o cribado.

Los frutos silvestres estudiados son: *Greigia sphacelata* conocida como chupón, fruto originario de Chile que crece al pie de árboles en bosques nativos y al fondo de quebradas [2]. *Ribes grossularia* conocida como grosella espinosa, fruto originario y cultivado en Europa, una baya principalmente encontrada de color verde con pequeñas espinas o vellos en su superficie [3]. *Smilax aspera* comúnmente conocida como zarzaparrilla, arbusto originario de Europa pero encontrado en muchos países de América, que presenta una baya de color rojo que otorga abundantes beneficios a la salud [4].

Las determinaciones realizadas al estandar de referencia Trolox mediante el ensayo ORAC a partir de una curva de calibrado de 50 µmol/L de Trolox a 600 µmol/L de Trolox, presenta una correlacion de 0,9876 con las determinaciones realizadas mediante voltamperometría cíclica del estándar que presentan un potencial de oxidación de 430 mV vs Ag/AgCl.

Los ensayos realizados mediante el ensayo ORAC en los frutos presentan concentraciones de 105 µmol/L eq Trolox y de 8125 µmol/L eq Trolox para el Jugo y semilla de *Greigia sphacelata respectivamente, 15394* µmol/L eq de Trolox para *Ribes grossularia,* y 21330 µmol/L eq de Trolox en *Smilax aspera,* presentando correlación de 0,9898 con las determinaciones mediante Voltamperometría cíclica.

Referencias

[1] Apak, R., Capanoglu, E., & Shahidi, F. (Eds.). (2017). *Measurement of Antioxidant Activity and Capacity: Recent Trends and Applications*. John Wiley & Sons

[2] Will, B., & Zizka, G. (1999). A review of the genus Greigia Regel (Bromeliaceae) in Chile. *Harvard Papers in Botany*, 225-239.

[3] Hempfling, K., Fastowski, O., Kopp, M., Pour Nikfardjam, M., & Engel, K. H. (2013). Analysis and sensory evaluation of gooseberry (Ribes uva crispa L.) volatiles. *Journal of agricultural and food chemistry*, *61*(26), 6240-6249.

[4] Longo, L., & Vasapollo, G. (2006). Extraction and identification of anthocyanins from Smilax aspera L. berries. *Food Chemistry*, *94*(2), 226-231.

Determinación de plomo en plásticos (LDPE) mediante el análisis de emulsiones por ETAAS

N. Cañás-Carro[1*], H. Case[2], R.M. Soto-Ferreiro[1], A. Carlosena[1], E. Alonso-Rodríguez[1], S. Muniategui[1]

[1]Universidade da Coruña, Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Centro de Investigaciones Científicas Avanzadas (CICA), Departamento de Química, A Coruña, Spain

[2]University of Surrey. Department of Chemistry. Faculty Engineering and Physical Science, United Kingdom

**nerea.canas@udc.es*

Los plásticos representan un peligro potencial para el medio ambiente y la biota y además pueden actuar como vectores de contaminación tanto por lixiviación de sus aditivos como de contaminantes que hayan adsorbido. En este sentido, la evaluación del contenido metálico en plásticos es de gran interés. La mayoría de las metodologías para la determinación de elementos metálicos en este tipo de muestras se basan en su análisis directo mediante técnicas de espectrometría de rayos X o sometiendo a la muestra a una digestión previa para poder emplear técnicas de mayor sensibilidad como son ETAAS o ICP-MS. Esto implica el uso de cantidades relativamente grandes de reactivos tóxicos y/o peligrosos así como un incremento del tiempo de análisis. El objetivo de este trabajo es el desarrollo de un método para la determinación de plomo en plástico (LDPE, polietileno de baja densidad), en concordancia con la Química Analítica Verde, basado en la preparación de emulsiones a partir del plástico disuelto en tolueno [1,2]. La emulsión se prepara directamente en el cubilete del automuestreador mediante una sonda de ultrasonidos, que se acopla a la técnica de espectrometría de absorción atómica con atomización electrotérmica (US-ETAAS).

Para establecer las condiciones de preparación de la emulsión se realizó un estudio multivariante aplicando el diseño de experiencias de Plackett-Burman, siendo las variables críticas la masa de plástico disuelta y el volumen de HNO_3. Se estudió la etapa de medida por ETAAS en ausencia y presencia de modificador químico, resultando imprescindible la utilización de dihidrogenofosfato amónico para obtener valores de absorbancia satisfactorios y reproducibles.

Se llevó a cabo la validación del método analítico mediante la evaluación de los parámetros de desempeño. Se comprobó la influencia de la matriz en la cuantificación del analito, siendo necesario el uso del método de adiciones estándar. Se obtuvieron resultados satisfactorios del estudio de la sensibilidad, precisión y exactitud del método (LOD = 1,25 µg/g; 9,5 % RSD; 116 % de recuperación, con respecto al valor certificado del material de LDPE ERM®-EC681m).

Agradecimientos

Este trabajo fue financiado por el proyecto JPI-Oceans BASEMAN y el Ministerio de Economía y Competitividad de España - financiado parcialmente con fondos FEDER-FEDER- (Subvenciones: PCIN-2015-170-C02-01 y CTM2016-77945-C3-3-R, ARPA-ACUA). La Xunta de Galicia es reconocida por su apoyo al Grupo QANAP (Programa de Consolidación y Estructuración de Unidades de Investigación Competitiva). Ref. ED431C 2017/28), con fondos FEDER-FEDER.

Referencias

[1] S. Carballo, J. Terán, R.M. Soto, A. Carlosena, J.M. Andrade, D. Prada, Microchemical Journal, 108 (2013) 74-80.

[2] Y.B. Zhao, X.D. Lv, H.G. Ni, Chemosphere, 209 (2018) 707-720.

Direct determination of lead in mussels, microalgae and microplastics by ultrasonic slurry sampling-ETAAS

H. Case[2], N. Cañás-Carro[1*], A. Carlosena[1], E. Alonso-Rodríguez[1], R.M. Soto-Ferreiro[1], S. Muniategui[1]

[1]Universidade da Coruña, Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Centro de Investigaciones Científicas Avanzadas (CICA), Departamento de Química, A Coruña, Spain

[2]University of Surrey. Department of Chemistry. Faculty Engineering and Physical Science, United Kingdom

**nerea.canas@udc.es*

Marine pollution is a major environmental concern requiring monitoring programs to establish the link between chemical pollution and harmful effects on organisms, to guide conservation, protection and sustainable ecosystem management. In this study, lead in bivalves, microalgae and microplastics was determined by ultrasonic slurry sampling and electrothermal atomic absorption spectroscopy (USS-ETAAS), with a focus on green analytical chemistry techniques [1]. Minimising sample manipulation and achieving low detection limits were paramount due to the expected low analyte concentrations, matrix complexity and sample availability.

Pb was chosen as a model pollutant due to its environmental relevance, given its toxicity and non-essentiality. The matrices were selected considering that mussels are well-known marine pollutant biomarkers, microalgae are filter fed by bivalves with an absorbed exposure pathway of metals, and microplastics are vectors for pollutants that are in the marine environment and transferred to bivalves from accidental consumption.

To ensure sample compatibility of each of the matrices with the analysis technique, samples underwent particle size reduction and drying. The mussel flesh was removed from the shell, freeze-dried and ground; marine microalgae (*T-ISO)* was cleaned, by displacing the salt using 1 % ammonium formate, and centrifuged, then dried and ground with an agate pestle and mortar [3]; plastic (Low Density Polyethylene, LDPE) required grinding using cryogenic mill to get a particle size lower than 200 µm.

For each matrix, slurry preparation and measurement procedure were optimised individually. Sample masses were weighed directly into 1 mL autosampler cups to which nitric acid and Triton X-100® were added. Slurry aliquots were injected after ultrasonic agitation and analysed using the optimized furnace programme. Each sample matrix required different ultrasonic slurry sampling approaches. Mussels were directly analysed as slurries without the use of a chemical modifier; however, when the method was validated for materials with Pb content lower than 0.50 µg/g, a slurry-extract procedure was established using palladium as chemical modifier. Microalgae were successfully analysed as slurries using palladium as chemical modifier. Slurries of LDPE microplastics showed low reproducibility, requiring further investigation.

Agradecimientos

This work was supported by the JPI-Oceans BASEMAN project and the Spanish Ministry of Economy and Competitiveness -partially financed by the ERDF-FEDER funds- (Grants: PCIN-2015-170-C02-01 and CTM2016-77945-C3-3-R, ARPA-ACUA). The Galician Government ("Xunta of Galicia") is acknowledged for its support to the QANAP group (Programa de Consolidación y Estructuración de Unidades de Investigación Competitiva. Ref. ED431C 2017/28), with ERDF-FEDER funds

References

[1] M.J. Cal-Prieto, A. Carlosena, J.M. Andrade, S. Muniategui, P. Lopez-Mahía, E. Fernández, D. Prada, Journal of Analytical Atomic Spectroscopy, 15 (1999) 707.

[2] R. Beiras, Marine Pollution: Sources, Fate and Effects of Pollutants in Coastal Ecosystems. Elsevier, 2018.

[3] Z. Yi-Bo, L Xu-Dong, N Hong-Gang, Chemosphere, 209 (2018) 707-720.

Prediction of methane and propane in natural gas using mid-IR spectrometry and PLS

B. Ferreiro*[1], J.M. Andrade[1], C. Paz-Quintáns[1], P. López-Mahía[1], S. Muniategui[1], C. Vázquez-Padín[2], M. Rey-Garrote[2], C. Vales[2]

[1] Grupo de Química Analítica Aplicada, Departamento de Química, Universidade da Coruña, Campus da Zapateira, 15071, A Coruña, España.

[2] REGANOSA (Regasificadora del Noroeste, S.A.). Punta Promontoiro, s/n. 15620. Mugardos, A Coruña, Spain.

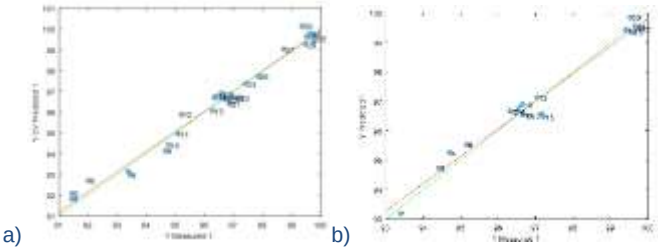
** borja.fferreiro@udc.es*

Gas chromatography (GC) is the reference analytical technique for the quantitative analysis of the composition of natural gas samples [1]. It allows the separation, identification and quantitation of the most important compounds in the samples. However, in-line systems are still difficult to control and maintain. A faster and cheaper alternative consist of combining spectrometric and multivariate chemometric techniques.

Despite the complexity of the IR spectra, which difficults its complete interpretation, the chemometric tools extract the most relevant information from them [2] so that the development of satisfactory predictive models is possible. Partial Least Squares (PLS) is a reference tool for this purpose [3], so it will be applied here.

In this work, a major (methane, 90-99 %) and a minor (propane, 0.2-1 %) component of natural gas were selected to evaluate whether it is possible to estimate their concentrations, with predictive errors lower than the reproducibility of the reference chromatographic method. Figure 1 (a) shows the predictions obtained for the calibration set whereas Figure 1 (b) presents the validation predictions, with a satisfactory root mean square error of prediction (RMSEP) of 0.34 %, lower than the GC reproducibility (~1 %). For propane the RMSEP was 0.05%. As a conclusion, which compares well with the GC reproducibility (~10% for propane). This study shows a reliable alternative to predict the concentration of the most relevant components of natural gas with the use of PLS regression.

Fig.1. Measured reference methane values versus the predicted ones (a) Calibration (n=31) (b) validation (n=20).



a) b)

Data preprocessing:
1. Baseline correction
2. Normalization
3. Mean Center

Acknowledgments

Reganosa, Naturgy and Mestrelab are acknowledged by their financial support to the QANAP-UDC group. This work was developed partly under the framework of the EURAMET EMPIR 16ENG09 LNG III Project (*Metrological support for LNG and LBG as transport fuel*), which is acknowledged.

Thanks are given to the Galician Government ("Xunta of Galicia") by Grant ED431C 2017/28 (Programa de Consolidación y Estructuración de Unidades de Investigación Competitiva.), partially financed by FEDER (RDEF funds).

References

[1] AENOR. Gas natural. Determinación de la composición y de la incertidumbre asociada por cromatografía de gases. Parte 2: Cálculos de la incertidumbre. UNE-EN ISO 6974-2. Madrid: AENOR, 2013

[2] R. Bro, Analytica Chimica Acta, 500, (2003), 185

[3] S. Wold, M. Sjöström, L. Eriksson, Chemometrics and Intelligent Laboratory Systems, 58, (2001), 109

Differentiation of microplastic polymers by reflectance FT-mid IR spectrometry and principal components analysis (PCA)

B. Ferreiro*, **C. Paz-Quintáns, J.M. Andrade, P. Lopez-Mahia, S. Muniategui**
Grupo de Química Analítica Aplicada, Departamento de Química, Universidade da Coruña, Campus da Zapateira, 15071, A Coruña, España

**borja.fferreiro@udc.es*

Nowadays, one of the most extended anthropogenic contaminants are plastic materials, especially on aquatic environments. The large amount of plastics produced for very different applications, along with their longevity due to their scarce degradation makes them very hard to eliminate from the environment. Besides, the photodegradation and mechanical abrasion of bigger fragments yield microplastics (MPs). In this form, they can enter the trophic chain [1] and it is common to find microplastics in the digestive system of aquatic species. That, combined with their capacity to adsorb other contaminants may have detrimental effects on living species [2].

Being plastics a large family of quite different materials, it is important to be able to identify which polymer constitutes the plastic fragment under study. This can be done using different analytical techniques, being the most used one infrared (IR) spectrometry. Its speed, high selectivity, and low demand of sample quantity makes it a suitable technique to study MPs.

However, identifying the polymer that constitutes the MP can be a difficult task. The large amount of spectral bands and the weathering of the plastic can difficult the interpretation of the spectra. To mitigate this problem it is possible to use unsupervised chemometric models, like Principal Components Analysis (PCA). **Figure 1** shows a graphic representation of the scores of a model, in the PC1-PC3 subspace, where a separation between 9 different plastics was possible considering their IR spectra, in reflectance mode. Their preprocessing involved a baseline correction at fixed points and 1st derivative.

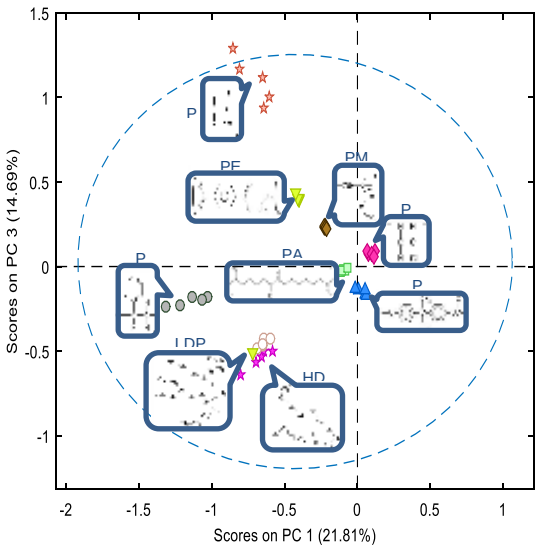


Fig.1. *Scores of a collection of aged samples of 9 different polymers.*

Acknowledgments
This work was supported through the JPI-Oceans BASEMAN project, by the Spanish Ministry of Economy and Competitiveness - partially financed by the ERDF-FEDER funds- (Grants: PCIN-2015-170-C02-01 and CTM2016-77945-C3-3-R, ARPA-ACUA). The Galician Government ("Xunta of Galicia") is acknowledged for its support to the QANAP group (Programa de Consolidación y Estructuración de Unidades de Investigación Competitiva. Ref. ED431C 2017/28) partially financed by RDEF-FEDER funds.

References

[1] M. R. Gregory, Philosophical Transactions of the Royal Society B: Biological Sciences, 364, (2009) 2013.
[2] E. Diamanti-Kandarakis, *Endocrine Reviews*, 30, (2009) 293.

Exploiting solid phase extraction in a sequential injection system for phosphate determination in fertilized soil leachates

Francisca T. S. M. Ferreira, Letícia S. Mesquita, Raquel B. R. Mesquita*, António O. S. S. Rangel

Universidade Católica Portuguesa, CBQF – Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Rua Diogo Botelho 1327, 4169-005 Porto, Portugal
**rmesquita@porto.ucp.pt*

The soil structure is a fundamental property of soil use and management and it has impact in the storage and movement of water, gas and both macronutrients and micronutrients [1]. The soil leaching process has a huge impact on the quality of surface and ground waters; therefore, the monitoring of nutrients and contaminants is an essential procedure in environmental and agricultural studies [2].

In the last few decades, fertilizers have been intensively used in agricultural activities and the inorganic phosphate compounds derived from them are often found in excess in ground waters. Phosphate is a well-known contaminant and its concentration is an indicator of water quality, so it is important to have an efficient monitorization method of the soil leaching process. Most methods for phosphate determination in water are based on the molybdenum blue chemical reaction in which there is a formation of phosphomolybdate and consequent reduction to molybdenum blue [3].

In this work, the main goal is the development of an automatic, low cost flow analysis method, capable of real-time monitoring of the soil leaching processes using spectrophotometric detection. The developed system (Fig. 1) has a solid phase extraction (SPE) step, incorporated in a sequential injection (SI) system, for phosphate determination.

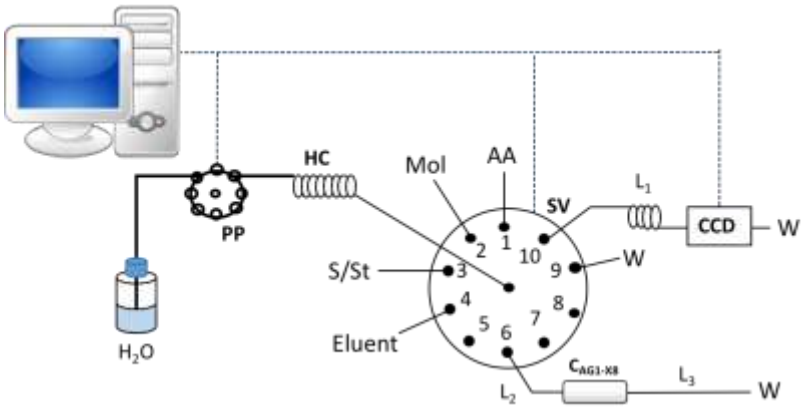


Fig.1. Sequential injection manifold for the determination of phosphate; SV, selection valve; PP, peristaltic pump; HC, holding coil, 200 cm; AA, ascorbic acid 30 g/L; Mol, molibdate reagent (16 g/L $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 0.1 g/L $C_4H_4KO_7Sb$, 7.5 g/L $C_4H_6O_6$ and 0.78 M H_2SO_4); S/St, sample/phosphate standard; Eluent, NaCl 0.5 M; L_1, reaction coil 120 cm; CCD, detector (λ=710 nm); L_i, connections (L_2 - 3 cm; L_3 - 20 cm); $C_{AG1\text{-}X8}$, column packed with AG1-X8 anionic exchange resin; W, waste.

Agradecimientos
F. T. S. M. Ferreira thanks Fundação para a Ciência e a Tecnologia (FCT) for the grant PTDC/AAG-MAA/5887/2014_BI_4. This work was supported by National Funds from FCT through project PTDC/AAG-MAA/5887/2014. Scientific collaboration from FCT project UID/Multi/50016/2019 is also acknowledged.

Referencias
[1] H. Zhou, H. Fang, S. J. Mooney, and X. Peng, Geoderma, vol. 266, pp. 66–74, 2016.
[2] A. B. Cundy, L. Hopkinson, and R. L. D. Whitby, Science of the Total Environment, vol. 400, no. 1–3, pp. 42–51, 2008.
[3] E. A. Nagul, I. D. Mckelvie, P. Worsfold, and S. D. Kolev, Analytica Chimica Acta, vol. 890, pp. 60–82, 2015.

Caracterização de Pigmentos de Algas da Galiza

C. Lourenço-Lopes[1], P.G. Oliveira[1], C. Jiménez-López[1], A.G. Pereira [1], M.A. Prieto[1,2], J. Simal-Gandara[1]*

1 Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain.

2 Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.

**jsimal@uvigo.es*

Os oceanos cobrem cerca de 71% da superfície terrestre e mais de 90% da biomassa viva da Terra se pode encontrar aí, por isso é de grande interesse encontrar matérias-primas que possam ter valor no referido meio. Nos ecossistemas aquáticos, podemos encontrar algas, que são plantas fotossintéticas com características muito heterogéneas [1].

As algas são um recurso vegetativo realmente interessante para o estudo de novos ingredientes naturais. Essas plantas marinhas tiveram um desenvolvimento significativo nos últimos anos e estão sendo introduzidas nas indústrias alimentar, farmacêutica e cosmética, tendo um interesse público crescente no uso desse recurso natural para a produção de ingredientes úteis que possam melhorar a saúde e o bem-estar gerais. Extractos de várias algas marinhas demonstram uma grande variedade de bioactividades como antioxidante, antibacteriana, anti-inflamatória, antifúngica, antiviral, cito toxicidade, entre outras [2].

De todos os compostos que se encontram na composição das algas os pigmentos são sem dúvida alguns dos mais relevantes, e têm vindo a ser utilizados em várias aplicações, no entanto a procura de pigmentos por parte da indústria ainda é maioritariamente respondida pelos fabricantes de microalgas. No entanto, com o aumento da demanda industrial de produtos naturais, a exploração de novas fontes de pigmentos é necessária e considerando que as macroalgas são encontradas em abundância por toda a costa ibérica torna-se relevante o aproveitamento destas matrizes.[3]

Tabela 1. Espécies de algas comestíveis utilizadas para este estudo

Nome comum local	Nome científico
Wakame	*Undaria pinnafitida*
Espagueti de mar	*Himanthalia elongata*
Pelvetia	*Pelvetia canaliculata*
Carrapicho de mar	*Mastocarpus stellatus*
Algatinado	*Gigartina pistillata*
Kombu real	*Saccharina latissima*
Musgo de Irlanda	*Chondrus crispus*
Alga percebe	*Codium tomentosum*
Bifurcaria	*Bifurcaria bifurcata*

Como tal este estudo teve como objectivo caracterizar e quantificar os diferentes pigmentos presentes em cada espécie, para futuramente serem estudadas as suas bioactividades e aplicabilidades nas indústrias acima referidas.
As algas utilizadas foram recolhidas nas costas da Galiza, liofilizadas e trituradas e os extractos foram obtidos utilizando etanol como solvente.

Após extracção foram evaporados e resuspendidos em Etanol/Água 80:20 e analisados por HPLC-MS

Agradecimentos

À AlgaMar pelo material de algas fornecido (www.algamar.com). Ao MICINN pelo apoio financeiro Ramón & Cajal dado ao investigador M.A. Prieto. Á Xunta de Galicia e Universidade de Vigo pelo apoio financeiro aos investigadores de pré-doutorado A.G. Pereira, P.G. Oliveira e C. Jiménez López. Á Xunta de Galicia pelo "Programa de axudas à etapa pré-doutoral da Xunta de Galicia" para os investigadores de pré-doutorado de A.G. Pereira e P. G. Oliveira. Á Xunta de Galicia pelo apoio financeiro de Axudas Conecta Peme ao Projecto IN852A 2018/58 NeuroFood. Os autores agradecem ainda ao Interreg Espanha - Portugal pelo apoio financeiro através do projecto 0377_Iberphenol_6_E.

Referencias

1 Rosa, D., Mª, C., Fuente, D., Linde, D. & Fernández, E. Macroalgas g marinas invasoras en el litoral de Andalucía. 4 (2004).

2 Bedoux, G., Hardouin, K. & Burlot, A. S. Bioactive Components from Seaweeds : Cosmetic Applications and Future Development. in *Advances in Botanical Research* 346–369 (Elsevier, 2014). doi:10.1016/B978-0-12-408062-1.00012-3

3 Haryatfrehni, R., Dewi, S. C., Meilianda, A., Rahmawati, S. & Sari, I. Z. R. Preliminary Study the Potency of Macroalgae in Yogyakarta: Extraction and Analysis of Algal Pigments from Common Gunungkidul Seaweeds. *Procedia Chem.* (2015). doi:10.1016/j.proche.2015.03.051

Ranitidine selective electrode based on curcubit[6]uril for pharmaceutical quality control

A. Mantovani, R.L. Gil, A.N. Araújo, M.C.B.S.M. Montenegro, C.G. Amorim*

LAQV-REQUIMTE/Departamento de Ciências Químicas,
Faculdade de Farmácia – Universidade do Porto, R. Jorge
Viterbo Ferreira, 228. 4050-313 Porto, Portugal.
*camorim@ff.up.pt

Ranitidine drug has been used to control the excessive acid secretion that can lead to different diseases such peptic ulcer and gastro-esophageal reflux. This drug is widely consumed around the world through different pharmaceutical formulations, including tablets, granules, powders, oral suspensions and injectable solutions.

In this work, a potentiometric ion-selective electrode based on cucurbit[6]uril was developed and applied to the determination of ranitidine. Different membrane compositions were evaluated concerning the use of different ionophore molecules and solvent mediators. The presence of anionic additives was also considered. The best membrane composition comprises 10 mmol kg $^{-1}$ of cucurbit[6]uril as ionophore, 0.3% (w/w) of potassium tetrakis (4-chlorophenyl)borate as ionic additive, 68.7% (w/w) of o-nitrophenyl octyl ether as solvent mediator and 30% (w/w) of poly(vinylchloride) as polymeric matrix.

The main characteristics of the proposed sensors were evaluated by calibration curves, maintaining the ionic strenght adjusted to 0.033 mol L^{-1} with magnesium chloride salt. In these conditions, a slope of 59.4 mV dec^{-1} was obtained in the concentration range between $5.0x10^{-7}$ mol L^{-1} and $4.8x10^{-3}$ mol L^{-1}. The electrode exhibited high selectivity to ranitidine in the presence of different interfering ions, including some of the common excipients present in the pharmaceutical formulations. The sensor is insensitive to pH between 3.0 to 7.5, have a practical detection limit of $3.8x10^{-7}$ mol L^{-1} and a response time below than 10s for solutions with ranitidine concentrations above $5.4x10^{-5}$ mol L^{-1}.

The great figures of merit of the proposed sensor open the door for a future use in flow analysis to obtain an automatized system for determination of ranitidine in pharmaceutical formulations.

Agradecimientos
This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through grant UID/QUI/50006/2019.

Persistência de resíduos de disparo (GSR) de armas longas

Luís Fernandes[1,2], Carla Guedes[1], Patrícia Carvalhosa[1], Edgar Pinto[2], Agostinho A.Almeida[2], Cristina M.C.M.Couto[1,2]

[1] CESPU, IINFACTS – Instituto de Investigação e Formação Avançada em Ciências e Tecnológica, Departamento de Ciências, Instituto Universitário de Ciências da Saúde (IUCS-CESPU), Gandra, Portugal.

[2] LAQV / REQUIMTE – Laboratório de Química Aplicada, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Porto, Portugal

*luism.fernandes@iucs.cespu.pt

A identificação da presença de resíduos de disparo de arma de fogo (GSR, do inglês "gunshot residues") é uma importante perícia forense, podendo ser utilizada para estimar a distância do disparo, identificar perfurações por projéteis e, principalmente, determinar o envolvimento de pessoas no disparo de armas de fogo. Nos últimos anos a técnica de espectrometria de massa com plasma de acoplamento induzido (ICP-MS) tem-se destacado como uma valiosa ferramenta na ciências forenses, dado que permite a análise multielementar com elevada sensibilidade, além de fornecer informação isotópica, permitindo uma análise rápida da composição inorgânica dos GSR [1].

No presente estudo foram usadas duas armas de cano longo (carabina Simonov de calibre 7,62x39 – arma A; e carabina HK 416 de calibre 5,56x45mm NATO – arma B) e recolheram-se os GSR, com recurso a zaragatoa humedecida com água ultrapura, nas mãos e outras zonas corporais não convencionais: sobrancelhas, face, narinas, linha junto ao cabelo, região supraciliar, região das asas nasais (sulco alar) e região auricular. Para a quantificação de Pb, Ba e Sb por ICP-MS, todas as amostras foram submetidas a um processo de lixiviação com 2 mL de solução de HNO_3 10% (v/v) durante um período superior a 24h, à temperatura ambiente. Passado esse período de tempo, adicionou-se 8 mL de água ultrapura e 1 mL de solução de padrão interno, e as soluções assim obtidas foram centrifugadas a 4000 rpm durante 5 min e analisadas por ICP-MS (marca Thermo, modelo iCAP™ Q (Thermo Scientific, Bremen, Alemanha).

Para avaliar a persistência dos GSR nas diferentes zonas corporais consideradas, definiram-se diferentes tempos de colheita de amostras após o disparo: 0 h (i.e., imediatamente após o disparo), 2,
4, 6, 8 e 14h, tendo o atirador prosseguido durante esse período de tempo com as suas atividades da rotina quotidiana.

A região auricular, particularmente a orelha esquerda, forneceu resultados positivos mesmo depois de decorridas 6 horas após o disparo com a arma A [2]. Relativamente aos disparos realizados com a arma B, observou-se a persistência de resíduos até às 14 horas, principalmente na zona da face (direita) e na sobrancelha (direita) [3].

Em estudos futuros, estas zonas corporais poderão considerar-se uma alternativa fiável às regiões mais convencionais (mãos), apresentando desde logo vantagens como a menor possibilidade de transferência e consequente perda dos GSR.

References

[1] R.D Koons, J. Forensic Science, 43 (1998) 748.

[2] C. D. S. Guedes in A Persistência de Resíduos de Disparo de Armas Longas no Atirador, Gandra, Instituto Universitário de Ciências da Saúde, 2018.

[3] P.E. Carvalhosa in Pesquisa de Resíduos de Disparo (GSR) de Arma Longa Semi-Automática na Face, Narinas, Sobrancelha e Mão do Atirador – Análise por ICP-MS, Gandra, Instituto Universitário de Ciências da Saúde, 2019.

Validación de un método rápido y efectivo para la determinación de cloruro de benzalconio en formulaciones farmacéuticas

María J. González-Castro*, Ángela Planas-Franco, M. Carmen Prieto-Blanco, Soledad Muniategui-Lorenzo

Grupo Química Analítica Aplicada, Instituto Universitario de Medio Ambiente, Centro de Investigaciones Científicas Avanzadas Facultade de Ciencias, Universidade da Coruña, Campus da Zapateira, rúa da Fraga nº10, 15071 A Coruña, España, *mjgc@udc.es

El cloruro de benzalconio (BAK) es un tensioactivo catiónico de interés analítico ya que es producido en miles de toneladas por año en todo el mundo, con un amplio uso en formulaciones farmacéuticas, productos desinfectantes, alguicidas etc. El control de su concentración en los productos que lo contienen es de gran importancia con fines sanitarios, comerciales y de cumplimiento de la legislación vigente. Su utilización en la industria farmacéutica es muy amplia y variada, especialmente en las formulaciones oftálmicas, así el 74 % de productos oftalmológicos comercializados en Europa usan el cloruro de benzalconio como excipiente. Igualmente, también se utiliza en formulaciones nasales, óticas y en productos farmacéuticos de tipo cutáneo, oral, rectal, intravenoso y subcutáneo.

Actualmente el desarrollo de métodos rápidos y robustos en cromatografía de líquidos está adquiriendo un gran interés en la industria, por lo que el empleo de nuevas fases estacionarias con distintos mecanismos de retención que permitan acortar el tiempo de análisis es fundamental. Además, deben ser capaces de diferenciar sus principales homólogos (C12, C14, C16 y C18) ya que comercialmente, el BAK se usa como una mezcla de estos homólogos, que a su vez presentan diferencias en sus propiedades biocidas.

En este trabajo se ha empleado por primera vez una fase estacionaria con grupos bifenilo y tecnología *core-shell* para la determinación de cuatro homólogos del cloruro de benzalconio. La fase móvil empleada consiste en una mezcla de acetonitrilo y formiato amónico (pH 4, 100 mM) en proporción 85:15, que permite separar los cuatro homólogos en menos de 4,5 minutos. El tratamiento de la muestra es muy sencillo puesto que sólo es necesario realizar una simple disolución de la misma con la fase móvil en el propio vial de inyección.

El método se validó empleando una formulación oftálmica siguiendo las directrices ICH Q2 (R1) [1], requeridas para productos farmacéuticos. Para todos los compuestos se obtuvieron unos resultados satisfactorios de linealidad (R^2> 0,999), precisión (% RSD $\leq$ 4,5% para repetibilidad y 5,8% para reproducibilidad) y exactitud (recuperaciones en el rango de 92-105%), cumpliendo los criterios de aceptación [2]. Además, los buenos resultados obtenidos en la recuperación analítica para otras formulaciones (oftámicas, cutáneas y óticas) que contienen distintos principios activos y excipientes, indican su versatilidad para el control del cloruro de benzalconio en diferentes formulaciones farmacéuticas. En todas las muestras se encontraron solamente los homólogos C12 y C14 en los órdenes de concentración especificados por la Agencia Europea del Medicamento para cada tipo de formulación [3]. Además, en dos de las formulaciones analizadas se distinguen otros picos con espectros de absorción distintos al BAK, correspondientes a componentes de la formulación que absorben en el UV-visible (posiblemente principios activos o excipientes). Como pueden ser separados del BAK, el método podría ser ampliado a la determinación de otros componentes de la formulación.

Es importante destacar que en la mayoría de los trabajos recogidos en la bibliografía se analizan sólo una o dos formulaciones y que en su mayor parte, sólo se estudian los dos homólogos mayoritarios.

Agradecimientos. Este trabajo fue financiado por la Xunta de Galicia (Programa de Consolidación y Estructuración de Unidades de Investigación Competitivas ED431C 2017/28-2017-2020).

Referencias

[1] ICH Harmonised Tripartite Guideline – Validation of analytical procedures: text and methodology Q2 (R1), 2005. https://www.ich.org/fileadmin/Public_Web_Site/ICH_Products/Guidelines/Quality/Q2_R1/Step4/Q2_R1 Guideline.pdf.

[2] M. Kasukazi, S Ueda., N. Takeuchi, Y. Ohgami, Chromatography, 33 (2012) 65.

[3] EMA/CHMP/352187/2012 – European Medicines Agency, Sciences medicines health - Benzalkonium chloride used as an excipient. https://www.ema.europa.eu/en/documents/report/benzalkonium-chloride-used-excipient-report-published-support-questions-answers-benzalkonium_en.pdf.

Optimization of a MSPD-UAE-GC-QqQ-MS/MS method for the determination of organic tin compounds in sediments

S. Muniategui-Lorenzo*, C. Moscoso-Pérez, V. Fernández-González, J. Moreda-Piñeiro, P. López-Mahía
Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Centro de Investigaciones Científicas Avanzadas (CICA), Facultade de Ciencias, Universidade da Coruña, 15008 A Coruña, Spain.
*soledad.muniategui@udc.es

Organic tin compounds (OTCs), due to their special properties, have been widely used in industry as PVC stabilizers and catalysts, as biocides in agriculture and as antifouling agents in boat paints. Tributyltin (TBT) and triphenyltin (TPhT) are the most abundant compounds in this group in the marine environment. These compounds decompose rapidly in seawater, but tend to adsorb to particles and sediments, where degradation processes are slower and can last between 1-4 years. In this way, they are bioavailable as a result of resuspension, diffusion in the water column or decomposition [1]. Therefore, sediment control is very useful for assessing the status of TBT contamination and assessing its potential environmental risks [2].

A robust method was developed using solid phase matrix dispersion, ultrasonic assisted extraction and gas chromatography - tandem mass spectrometry (MSPD-UAE-GC-QqQ-MS / MS) operating in selected reaction monitoring mode (SRM), which provides great precision when identifying analytes in complex matrices and very low detection limits.
The developed method consists in dispersing the sediment sample with C18, adding in the solid a known concentration of deuterated standards (MBT d9, DBT d18 and TBT d27). A mixture of AcH / MeOH / H_2O in proportion (1:1:1) (v / v) was added and extracted on ultrasound, centrifuging and separating the supernatant. Then, 1.5 M acetic acid / sodium acetate buffer, the internal standard (TeBT) and derivatization reagent ($NaBPr_4$) were added. Finally, they were extracted in 2 mL of isoctane, shaking by hand for 5 minutes and the organic phase is passed to a chromatography vial for the determination by GC-MS / MS.
Under these conditions, the analytical quality parameters of the method were determined. Accuracy was determined by analyzing two reference materials (BCR 462 and PACS 3) and spiking a sediment sample at concentration level of 15 µg L-1, because the reference materials do not have all the compounds analyzed. Average recovery (n = 5) varies between 70 and 113% for all concentrations and compounds. The method shows a linear response for the working range (2-300 µg L^{-1}) with correlation coefficients greater than 0.990. Repeatability and intermediate precision were calculated for two concentrations, 15 and 300 µg L^{-1}, obtaining good results in all cases. The method detection limits (MDL) and quantification (MQL) were calculated taking into account the matrix background.
The developed method was applied to thirteen samples of sediments from Rías Gallegas (NW Spain), with DBT and TBT values found in almost all the points studied. These values were lower than those obtained in the literature for the port of Barcelona [3] or port areas of the Basque Country [4]. In addition, the butyltin degradation index (BDI) was calculated to assess the distribution and impact of these pollutants.

Acknowledgements
Xunta de Galicia-Program for the Consolidation and Structuring of Competitive Research Units co-financed by FEDER under the Galicia Operational Program (reference: ED431C-2017/28) and to the Ministry of Economy and Competitiveness (project CTM2016-77945-C3-3-R (ARPA-ACUA)).

References
[1] Filipkowska G. Kowalewska, B. Pavoni, L. Leczynski, Environ. Monit. Assess, 182 (2011) 455-466.
[2] K. Zhang, J. Shi, B. He, W. Xu, X. Li, G. Jiang, Chinese Science Bulletin, 58 (2013) 231-237.
[3] S. Díez, E. Jover, J. Albaigés, J.M. Bayona, Environment International, 32 (2006) 858-865.
[4] J.G. Rodríguez, O. Solaun, J. Larreta, M.J.B. Segarra, J. Franco, J.I.G Alonso, C. Sariego, V. Valencia, A.Borja, Marine Pollution Bulletin, 60 (2010) 139-151.

Stabilization of herbicide oxadiazon through microencapsulation

E. Manuela Garrido[1,2,*], Jorge M.P.J. Garrido[1,2], Fernanda Borges [2]

[1] Department of Chemical Engineering, School of Engineering (ISEP), Polytechnic of Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Porto, Portugal
[2] CIQUP - Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre 4169-007 Porto, Portugal
*emg@isep.ipp.pt

Pesticides still have an important role in the agricultural economy, since they can fight crop pests and reduce competition from weeds, thus improving yields and protecting the availability, quality, reliability and price of produce to the benefit of farmers and consumers. However, pesticide effectiveness is highly dependent on environmental conditions, which influence pesticide absorption, penetration, translocation, and detoxification.

Oxadiazon, 5-tert-butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazol-2(3H)-one, is a pre- and post-emergence contact herbicide used for the control of annual grasses and many broadleaf weeds in turf and landscape ornamentals. The relatively low toxicity by ingestion and by dermal route of this herbicide is one of the reasons for its widespread use [1]. Although oxadiazon is stable to hydrolysis at neutral pH, at pH 9 is hydrolysed yielding two major hydrolysis metabolites. Moreover, aqueous photolysis can also occurs affecting the environmental fate of this herbicide [2].

There is a need for improved pest control technology both to reduce losses in agricultural production and to reduce the negative environmental impact of pesticides. With this purpose, microencapsulation of pesticides and herbicides has been an active area of development. These type of compounds can be microencapsulated to prolong their activity while reducing toxicity, volatilization losses, phytotoxicity and environmental degradation.

Cyclodextrins (CDs) are cyclic oligosaccharides composed of linked glucopyranose subunits. The main property of CDs is that their hydrophobic inner cavity forms inclusion complexes with a wide range of guest molecules. Because of their molecular inclusion capability, the properties of the materials with which they complex can be significantly modified. Cyclodextrin based formulations can provide controlled release of chemical agents, which improve the efficacy of pest control by keeping the pesticide targeted to the pest.

In order to explore rationally the potentialities of microencapsulation for the development of a new pesticide formulation, in this work an encapsulation process with (2-hydroxypropyl)-β-cyclodextrin has been accomplished in order to increase the chemical and photochemical stability of oxadiazon herbicide. The results obtained will be presented in this communication.

Acknowledgements

This project was supported by Foundation for Science and Technology (FCT) (project UID/QUI/00081/2019)

References

[1] G. Quintás, S. Armenta, J. Moros, S. Garrigues, A. Pastor, M. de la Guardia, J. Braz. Chem. Soc., 19 (2008) 1394.
[2] European Food Safety Authority, EFSA Journal, 8 (2010) 1389.

Voltammetric behaviour of the psychoactive substance benzylpiperazine

Jorge M.P.J. Garrido[1,2,*], Daniel Martins[2], E. Manuela P.J. Garrido[1,2], Fernanda Borges[2]

[1] Department of Chemical Engineering, School of Engineering (ISEP), Polytechnic of Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Porto, Portugal
[2] CIQUP - Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre 4169-007 Porto, Portugal
*jjg@isep.ipp.pt

1-Benzylpiperazine (BZP), a synthetic phenyl analogue of piperazine, has become popular among recreational drug users as the major active ingredient of "party pills" due to its stimulant and euphoric properties. The abuse of BZP was first described in the USA in 1996 although its use remained minimal until the end of the 90s when BZP started to spread particularly among youth as a legal rave/party drug, particularly due to its promotion as "legal," "natural" and "safe" [1]. Its widespread as a recreational drug in Europe only occurred in the second half of 2004, and there has been an increase in the number of notifications to the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA) and Europol relating to it by the end of 2006 [1]. Despite the misconception that BZP-party pills are safe, there are a number of case reports and clinical evidence supporting its toxicity [1]. The pharmacokinetics of BZP is not completely elucidated although literature data suggest that BZP undergoes hydroxylation and dealkylation, as phase I reactions, in the aromatic ring, the benzyl carbon and the piperazine moiety [2].

Electrochemical methods has proven to be very useful methodologies for the study of metabolism, as it has certain advantages compared to conventional methods. In fact, electrochemistry enables the generation and direct identification, in a rapid and clean manner, of both stable species and metabolites with short half-lives. Thus, the study of the electrochemical behaviour is in many cases important because it allows predicting and anticipating the process of biotransformation that a molecule can suffer in the human body as well as the common transformation products that can coexist with the drug.

The purpose of the present work is to explore the voltammetric oxidation behaviour of benzylpiperazine in order to contribute to a more detailed understanding of the electrochemical profile of piperazine designer drugs and to the development of new electrochemical sensors with improved sensitivity and selectivity. The results obtained will be presented in this communication.

Acknowledgements
This project was supported by Foundation for Science and Technology (FCT) (Project UID/QUI/00081/2019).

References

[1] M. S. Monteiro, M. L. Bastos, P. Guedes de Pinho, M. Carvalho, Arch. Toxicol., 87 (2013) 929.
[2] R. F. Staack, G. Fritschi, H. H. Maurer, J. Chromatogr. B Analyt. Technol. Biomed. Life Sci. 773 (2002) 35.

New electroanalytical method for the determination of formaldehyde in wood-based products

Pavel Dvořák[1], Rui M. Ramos[2,*], Vlastimil Vyskočil[1], José A. Rodrigues[2]

[1] Charles University, Faculty of Science, Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Hlavova 2030/8, 12843 Prague 2, Czech Republic
[2] REQUIMTE/LAQV – Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre no. 687, 4169-007, Porto, Portugal

**rui.ramos@fc.up.pt*

Formaldehyde has for long been considered one of the most relevant indoor air pollutants, as a consequence of its carcinogenic and toxic properties and the fact that it is commonly applied in the production of adhesives and resins for wood-based products (WBPs) [1, 2]. Due to the hazardous effects of formaldehyde on health, it is necessary to develop tools that can simply and accurately measure its content in different materials, in particular in indoor building materials. Different European and international standard methods for the determination of formaldehyde in WBPs, like EN 717-3 and ISO 12460-5 [3], use lengthy and non-environmental-friendly procedures, such as the use large amounts of toluene, contradicting the basic green-chemistry principles.

In this work, we present the development of a new electroanalytical approach for the determination of formaldehyde in WBPs. A membraneless extraction module (MLEM) was used for the formaldehyde extraction directly from WBPs. This method, developed for volatile and semi-volatile compounds, allows the simultaneous extraction and derivatization of analytes. For this purpose, a derivatization reaction with acetylacetone (Hantzsch reaction) was used, as it is highly selective towards formaldehyde. The analysis was electrochemically performed by square-wave voltammetry (SWV) using screen-printed carbon electrodes (SPCEs) [4]. SPCEs are disposable, cost-efficient, designed to work with small volumes and can be used to develop specific biosensors. As a first-time application, several extraction and voltammetric parameters were optimized, and the methodology was used to determine the formaldehyde released from different WBPs. Furthermore, the results were compared with the European standard EN 717-3.

The proposed methodology, to the best of our knowledge, represents one of the first applications of formaldehyde electrochemical analysis, using the disposable SPCEs, while presenting significant advantages over other methodologies in terms of procedure simplicity and time of analysis.

Acknowledgements
This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through grant UID/QUI/50006/2019. RMR thanks FCT (Fundação para a Ciência e Tecnologia) for funding through program CEECIND/04259/2017. PD kindly acknowledges the financial support from the Specific University Research of the Charles University (project SVV260440) and from the EU Lifelong Learning Programme (Erasmus+).

References

[1] P. F. Brandão, R. M. Ramos, J. A. Rodrigues, Analytical and Bioanalytical Chemistry, 410 (2018) 6873.
[2] T. Salthammer, International Journal of Hygiene and Environmental Health, 218 (2015) 433.
[3] P. F. Brandão, R. M. Ramos, I. M. Valente, P. J. Almeida, A. Carro, R. Lorenzo, J. A. Rodrigues, Analytical and Bioanalytical Chemistry, 409 (2018) 2885.
[4] R. M. Ramos, L. M. Gonçalves, V. Vyskočil, J. A. Rodrigues, Electrochemistry Communications, 63 (2016) 52.

Essential oils and their individual components: analytical challenges in cosmetics

L. Rubio[1,*], M. Lores[1], C. Garcia-Jares[1]

[1]Laboratory of Research and Development of Analytical Solutions (LIDSA), Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Chemistry. Cretus Strategic Group. Universidade de Santiago de Compostela. E-15782, Santiago de Compostela, Spain

* *laura.rubio.lareu@usc.es*

Plant extracts and essential oils are added to cosmetic products due to their well-recognized properties. Several studies have shown their efficacy [1,2] avoiding for the necessity of additional chemical preservatives. This is known as self-preservation. However, 28 natural extracts have been listed as contact allergens established in humans [3]. In addition, the individual chemical components also belong to the 82 declared allergenic substances [3] and, in general, their names and concentrations do not appear on product labels.

The objective of the proposed analytical approach is to develop appropriate methodologies (sample preparation and analytical determination using chromatographic techniques) with selective phytomarkers for each natural extract or essential oil in order to determine their presence in cosmetics.

This work shows the first experimental tests carried out. At first, a prior assessment of the allergen content is necessary in order to determine the real level of allergens in cosmetics. We search for possible marker substances in groups of essential oils/natural extracts according to their origin similarity (e.g. obtained from flowers), using gas chromatography methods with MS detectors. The ideal would be to achieve a systematic approach that facilitates common analytical developments, and then to further develop a multicomponent methodology that would allow the global determination of the main phytomarkers.

Acknowledgements

This research was supported by project *GPC2017/04* (Consolidated Research Groups Program, Xunta de Galicia, Spain), and L.R. acknowledges Xunta de Galicia for her predoctoral contract.

References

[1] Kerdudo, P. Burger, F. Merck, A. Dingas, Y. Rolland, T. Michel, X. Fernandez, C. R. Chim., 19 (2016) 1077–1089.
[2] E. Antignac, G. J. Nohynek, T. Re, J. Clouzeau, H. Toutain, Food Chem. Toxicol., 49 (2011) 324–341.
[3] Scientific Committee on Consumer Safety (SCCS). OPINION on Fragrance allergens in cosmetic products. The SCCS adopted this opinion at its 15th plenary meeting of 26–27 June 2012.

Evaluation of phenolic compounds and antioxidant activity of medicinal plants with potential for kidney disease treatment

Manyou Yu[1,*], Irene Gouvinhas[1], João Rocha[2], Amélia Silva[1], Ana Isabel Barros[1]

[1]Centre for the Research and Technology of Agro-Environmental and Biological Sciences (CITAB), University of Trás-os-Montes and Alto Douro (UTAD), 5000-801, Vila Real, Portugal
[2]University of Trás-os-Montes and Alto Douro (UTAD), 5000-801, Vila Real, Portugal
**jiangymy518@163.com*

The medicinal plants, are particularly regarded as rich sources of plant-based nutritional supplements, medicinal drugs and active substances, largely due to their phenolic composition [1].These secondary metabolites are of great interest because of numerous biological activities and benefits; among them the antioxidant activity or free radical scavenging capacity is one of the most important due to the capacity to prevent diseases induced by oxidative stress in human body [2,3]. Studies on the application of medicinal plants on kidney problem, an easily ignored body disorder, remains scarcely.

Therefore, to explore a new promising source of functional formula, our initial work screened and selected eight well-known medicinal plant leaves (*Salvia officinalis*, *Rosmarinus officinalis*, *Olea europaea*, *Ruta graveolens*, *Mentha piperita*, *Petroselinum crispum*, *Tribulus terrestris*, *Punica granatum*), owing to their (i) high phenolic content and antioxidant capacity, (ii) potential reno-protective effect, (iii) low/no toxicity, and (iv) available of collection [4,5,6,7,8,9,10]. Then, colorimetric and spectrophotometric assays were applied to evaluate phenolic composition and antioxidant activity in the hydro-methanolic extracts of these plant leaves. Their antioxidant activity in vitro were further assessed by ABTS, DPPH and FRAP spectrophotometric assays.

Overall, the content of total phenols and ortho-diphenols in Punica granatum (pomegranate) leaf extracts was significantly higher than that in the other plant extracts, with a wide variation of about 29 and 15 folds, respectively. Furthermore, the highest antioxidant activity was also observed in pomegranate leaf extracts with around 4-200 folds of other plant species. Therefore, the present findings may reveal that the leaf of Punica granatum would be valuable sources of bioactive phenolics and have the potential to be developed into health-promoting natural products against kidney disease.

Acknowledgments

This work was supported by National Funds by the FCT - Portuguese Foundation for Science and Technology under the project UID/AGR/04033/2019.The first author also acknowledges the financial support provided by the FCT - Portuguese Foundation for Science and Technology (PD/BD/135333/2017), under the Doctoral Programme “Agricultural Production Chains - from fork to farm” (PD/00122/2012). FEDER-Interreg Espaar-Portugal programme for financial support through the project 0377_Iberphenol_6_E.

References

[1] Phenolic Compounds in Food: Characterization and Analysis. Nollet L M L, Gutierrez-Uribe J A, Boca Raton, CRC Press, 2018.
[2] Antioxidants in food, vitamins and supplements: prevention and treatment of disease. Dasgupta A, Klein K, Houston, Academic Press, 2014.
[3] Cai Y, Luo Q, Sun M, et al, Life sciences, 74 (2004) 2157-2184.
[4] Ashour M B, Ahmed O M, Abd El Mawgoud A, et al, International Journal of Prevention and Treatment, 6 (2017) 33-34.
[5] El-Sherif N M, Issa N M, Journal of Interdisciplinary Histopathology, 3 (2015) 24-32.
[6] Mohammed H A, Okail H A, Ibrahim M A, et al, The Journal of Basic and Applied Zoology, 79 (2018) 3.
[7] Figueroa-Pérez M G, Pérez-Ramírez I F, Enciso-Moreno J A, et al, Journal of functional foods, 43 (2018) 55-61.
[8] Alkhalaf A A J, Alrusayni S A, Khalid A, et al, Journal of Chemical and Pharmaceutical Research, 8 (2016) 948-957.
[9] Ghanbari A, Zare F, Khazaei M, et al, International Journal of Morphology, 34 (2016).
[10] Mestry S N, Dhodi J B, Kumbhar S B, et al, Journal of traditional and complementary medicine, 7 (2017) 273-280.

Determination of antibiotics in different wastewater samples by LC-MS/MS

Lúa Vázquez[1*], Thierry Dagnac[2], J. Pablo Lamas[1,3], María Llompart[1]

[a] Laboratory of Research and Development of Analytical Solutions (LIDSA), Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Chemistry, E-15782, Santiago de Compostela, Spain.

[b]Galician Agency for Food Quality, Agronomic and Agrarian Research Centre (AGACAL-CIAM), Unit of Organic Contaminants, Apartado 10, 15080, A Coruña, Spain.

[c] Technological Institute for the Control of the Marine Environment of Galicia (INTECMAR), Peirao de Vilaxoán s/n, Vilagarcía de Arousa, 36611 Pontevedra, Spain

*lua.vazquez.ferreiro@usc.es

Nowadays, pharmaceuticals are considered as environmentally emerging contaminants. Water contamination is a growing, due to the increasing use of these substances by the population and because of the veterinary practices in livestock farming and diseases treatment in aquaculture [1].

One of the most interesting groups are antibiotics, which produce microbial resistance because of their irresponsible and irrational use [2]. The pollution caused by antibiotics makes necessary to develop analytical methods for their identification and quantification at low levels, particularly in wastewater samples from WWTPs (Waste Water Treatment Plant), which are the most important source of these pollutants.

In consequence, a quantitative analytical method based on simultaneous extraction of eight fluoroquinolones and sulphonamides antibiotics was developed. The method was based on solid phase extraction (SPE) followed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). *Non-target* screening, based on a data independent workflow, was also carried out to identify unknown compounds in the samples using liquid chromatography coupled to high-resolution TOF mass spectrometry (LC-TOF-HRMS).

Agradecimientos

This work was supported by project UNST10-1E-491 and IGDC13-1E-2026 (Infrastructure Program, MINECO, Spain) and RED2018-102522-T (Ministry of Science, Innovation and Universities, Spain). The authors belong to the Galician Competitive Research Groups GPC2017/04, GPCIN607B 2019/13, and to the CRETUS Strategic Partnership (ED431E 2018/01). All these programmes are co-funded by FEDER (UE).

Referencias

[1] M. Čizmić, S. Babić, M. Kaštelan-Macan, Environ. Sci. Pollut. Res., 24 (2017) 20521-20539.
[2] S. Yuan, Z. Liu, H. Yin, Z. Dang, P. Wu, N. Zhu, Z. Lin, Sci. Total. Environ., 653 (2019) 815–821.

Variables implicadas en el desarrollo de métodos de análisis por inyección de grandes volúmenes en Cromatografía de Gases utilizando la interfaz TOTAD.

Ana M. Vázquez[1,*]; Francisco Espinosa[1]; Rosa M. Toledano[1]; José M. Cortes[1]; Jesús Villén[2];

[1]Facultad de Educación, Universidad de Castilla-La Mancha, Plaza de la Universidad, 3. 02071 Albacete. Spain
[2] Escuela Técnica Superior de ingenieros Agrónomos y de Montes, Campus Universitario s/n.02071. Albacete. Spain,
**ana.vazquez@uclm.es*

La inyección de grandes volúmenes (LVI) en cromatografía de gases (GC) permite aumentar sustancialmente la sensibilidad del análisis, ya que la cantidad de analito que llega al detector es mucho mayor que cuando se utilizan técnicas de inyección clásica (Split/splitless; on column,..) en las que las cantidades introducidas en GC son del orden de 1-2 uL. Así mismo puede simplificar en gran medida la etapa de preparación de la muestra al evitar la etapa de concentración del extracto e incluso la etapa de extracción inyectando directamente la muestra [1,2]. El problema a resolver es eliminar la gran cantidad de disolvente, para evitar introducirlo en la columna de GC lo que provocaría el deterioro de la misma, sin perder los analitos. Se han desarrollado diferentes inyectores y técnicas que permiten la LVI en GC [3], cada de las cuales presenta sus ventajas e inconvenientes. La LVI es especialmente difícil cuando se utilizan disolventes polares, ya que el volumen de vapor por unidad de líquido es muy superior al que se origina con disolventes apolares. Si se utilizan detectores altamente sensibles a estos disolventes, como el Detector de Nitrógeno Fosforo (NPD) o el espectrómetro de masas (MS), la completa eliminación del disolvente es imprescindible. La interfaz TOTAD (Through Oven Transfer Adsorption Desorption), descrita por primera vez por Pérez y col. en 1999 [4], se basa en un inyector PTV ampliamente modificado [5], permite la inyección de volúmenes de muestra o de extracto en GC, tanto de disolventes apolares como polares, incluso agua, muy superiores a otras técnicas.

Se han desarrollado diversos métodos de análisis mediante LVI, de compuestos traza en muestras de alimentos y medioambientales, utilizando la interfaz TOTAD [6, 7]. El desarrollo de estos métodos de análisis requiere la optimización de una serie de variables que afectan al funcionamiento de la interfaz. Estas variables son la temperatura de adsorción, es decir, la temperatura de la interfaz durante la inyección, el caudal durante la inyección, la temperatura de desorción, el volumen inyectado, el material de retención en el interior del liner, la longitud de dicho material, el flujo de gas inerte que atraviesa el liner, y el flujo de gas inerte exterior al liner que impide la condensación del disolvente. Estas variables hay que optimizarlas teniendo en cuenta la naturaleza de los analitos y las características de la matriz en la que se encuentra. En la presente comunicación se explica como afectan cada una de estas variables.

Agradecimientos
Los autores agradecen a la Consejería de Educación, Cultura y Deporte de la Junta de Comunidades de Castilla-La Mancha y a los Fondos de Desarrollo Regional Europeo por la financiación concedida para el proyecto SBPLY/17/180501/0003777

Referencias

[1] J. Villén, F.J. Señorans, G. Reglero, M. Herraiz, J. Agric. Food. Chem. 43 (1995), 717.
[2] J. Villén, F.J. Señorans, G. Reglero, M. Herraiz, Z. Lebensm. Unters. Forch. 202 (1996), 270.
[3] E. Hoh and K. Mastovska, *J. Chromatrogr. A,* 1186 (2008), 2.
[4] M. Pérez, J. Alario, A. Vázquez and J. Villén, *J. Microcolumn Sep.* 11 (1999), 582.
[5] J. Alario, M. Pérez, A. Vázquez, J. Villén, J. Chromatogr. Sci. 39 (2001) 65.
[6] R. M. Toledano, J. M. Cortés, J. C. Andini, J. Villén and A. Vázquez, *J. Chromatrogr. A,* 1217 (2010), 4738.
[7] Aragón, R.M. Toledano, A. Vázquez, J. Villén and J.M. Cortés, LCGC North America, 37(3) (2019), 194.

Desenvolvemento dun método analítico para a determinación de elementos críticos tecnolóxicos en sedimentos mariños

J.J. López-Mayán*, **L. Regueiro-Camaño, E. Peña-Vázquez, M.C. Barciela-Alonso, P. Bermejo-Barrera**
Departamento de Química Analítica, Nutrición e Bromatoloxía, Facultade de Química, Av. das Ciencias, s/n, 15782, Santiago de Compostela, España.
**juanjoselopez.mayan@usc.es*

Nas últimas décadas aumentou de forma significativa o uso de elementos críticos tecnolóxicos (TCEs) na industria debido a súa grande variedade de aplicacións nas novas tecnoloxías. Ligado ao aumento do seu uso e o seu difícil reciclaxe, é de esperar que estes elementos acaben sendo liberados ao medio ambiente, producindo unha contaminación difusa e global, sendo un dos receptores finais os sedimentos mariños.

Debido a isto desenvolveuse un método para a determinación de TCEs (Sc, Ga, Ge, Y, Nb, Ru, Rh, Te, La, Pr, Ce, Nd, Eu, Sm, Tb, Gd, Dy, Ho, Er, Tm, Yb, Lu, Ta, Pt e Rh) en sedimentos mariños empregando a Espectrometría de Masas con Plasma de Acoplamento Inductivo (ICP-MS). Os sedimentos foron sometidos a unha dixestión ácida asistida por microondas, e analizados directamente por ICP-MS sen necesidade de etapas previas de preconcentración ou separación das interferencias. As medicións no ICP-MS foron realizadas en modo colisión con He (KED) para evitar as interferencias poliatómicas; ademais o equipo emprega correccións matemáticas para evitar as interferencias isobáricas.

Empregouse o Material de Referencia Certificado BCR®-667, correspondente a un sedimento mariño, para escoller as condicións da dixestión e de medida. Decidiuse empregar para a dixestión auga rexia inversa e HF. Ademais o CRM empregouse para seleccionar os isótopos para a cuantificación, e o fluxo de He. As calibracións foron realizadas empregando como patrón interno o In, para reducir posibles interferencias e efecto matriz.

Determináronse axeitadamente as características analíticas do método: os límites de detección foron dende 5,2 ng g^{-1} para Rh ata 792,1 ng g^{-1} para Ce, a recuperación analítica foi próxima ao 100% para todos os elementos, e os coeficientes de variación foron menores ao 3%.O método desenvolvido foi sensible, exacto e preciso, e aplicouse ao análise de sedimentos galegos.

Agradecementos
Os autores pertencen ao Grupo de Investigación de Referencia Competitiva de Galicia ED431C2018 /19. Esta investigación foi parcialmente apoiada pola Consellería de Educación, a través do Programa para o Desenvolvemento da Agrupación Estratéxica de Materiais (AEMAT) na Universidade de Santiago de Compostela baixo a Subvención Nº. ED431E2018 /08, Xunta de Galicia. Estes programas están cofinanciados por FEDER (UE).

Optimización Operacional del Proceso de Extracción Polifenólica a Partir de Residuos de la Industria Vitivinícola

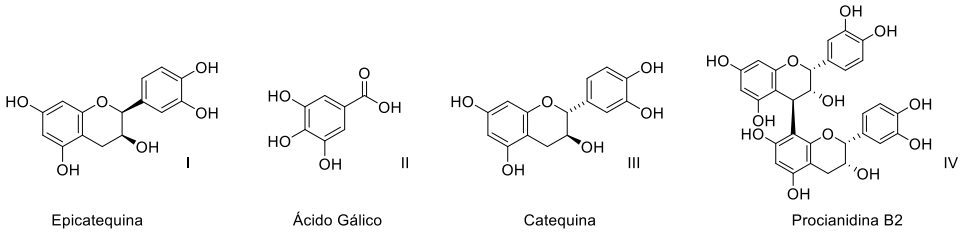
Castillo Z. Aly[1,2], Lores A. Marta[1], García J. Carmen[1], Verdes G. Juan[2]
[1]Laboratorio de Investigación y Desarrollo de Soluciones Analíticas (LIDSA), Santiago de Compostela, España
[2]i-Grape Laboratory S.L., Emprendia, Campus Sur, Universidad de Santiago de Compostela, España
alyjesus.castillo@rai.usc.es

El proceso denominado "extracto polifenólico a partir de residuos de uva blanca" se basa en un proceso patentado para la obtención de extractos con propiedades antioxidantes y antibacterianas a partir de residuos de uva blanca. Este proceso emplea materiales no contaminantes, con condiciones leves de proceso; permitiendo la generación de extractos ricos en polifenoles bioactivos utilizables a nivel industrial, fundamentalmente en los sectores cosmético, veterinario, farmacéutico y/o alimenticio.[1] De esta manera se traza como objetivo obtener un extracto que presente un mayor contenido polifenólico y actividad antioxidante; a la par de realizar una optimización de las condiciones de proceso que disminuyan el tiempo y aumenten el volumen de extracción. Para ello se propone la modificación de los parámetros de operación: recirculación del extracto, relación másica de bagazo/dispersante, tamaño de partícula de filtro y masa del medio filtrante.

El estudio se realiza mediante la generación de una matriz experimental aplicando un diseño multifactorial categórico mediante 24 pruebas extractivas, que determinan la influencia de los factores experimentales en las principales respuestas de la calidad del proceso (IPT y AA) y operación (tiempo y volumen de extracción). El empleo de un HPLC junto con un Detector de Arreglo de Diodos (DAD) permite la rápida y simultánea separación, identificación y cuantificación de los distintos compuestos fenólicos según sus propiedades espectrales y tiempo de retención.[2] De esta manera, a partir de las muestras obtenidas es posible obtener la concentración de los principales polifenoles identificados en el extracto (Fig.1.).

El estudio estadístico, utilizando el método de diferencia mínima significativa de Fisher (LSD) y el análisis de varianza (ANOVA), muestra un efecto significativo en la respuesta del proceso cuando se modifican los parámetros de estudio (recirculación y relación bagazo/dispersante). Se pudo maximizar el IPT y la AA en un 16,95% y 20,90% respectivamente cuando es recirculado el extracto en relación al no recirculado, con un impacto de 14,43% en el volumen extraído. Cuando es modificada la relación bagazo/dispersante se obtiene un aumento del 12,56% en función al IPT.

Fig.1. Principales polifenoles identificados en el extracto



Agradecimientos
i-Grape Laboratory S.L.
Laboratorio de Investigación y Desarrollo de Soluciones Analíticas (LIDSA)

Referencias

[1] Lores, M.; García, C.; Álvarez, M.; Llompart, M. Polyphenol Extract from White-Grape Residue. ES Patent 2,443,547, September 29, 2014.
[2] Álvarez, M.; García, C.; Llompart M.; Lores, M. Food Chemistry, 157(2014) 524.

QUÍMICA FÍSICA

High pressure Taylor dispersion technique as a tool for the measurement of diffusion coefficients in supercritical carbon dioxide

Cecília I.A.V Santos [1], Marisa C.F. Barros[1], Valentina Shevtsova[2] and Ana C.F. Ribeiro[1]
[1]Department of Chemistry, University of Coimbra, 3004 - 535 Coimbra, Portugal,
[2]MRC, CP-165/62, Université Libre de Bruxelles, 50, Av. F.D. Roosevelt, B-1050 Brussels, Belgium
*ceciliasantos@qui.uc.pt

Research in the supercritical fluids (SCFs) science and technology has increased progressively in the past decades, at both academic and industrial level, due to the broadened applications of SCFs to food, cosmetics, pharmaceutics, materials, chemistry, energy and waste treatment [1-2]. Carbon dioxide, among SCFs, has been the widely used due to its chemical stability, considerable inertness, low critical temperature, relatively non-toxicity, non-flammability and availability in high purity at relatively low cost. Therefore, all information about diffusion processes of different substances in supercritical CO_2 is of high importance for various applications.
We present development of high pressure apparatus for measurements of the diffusion coefficient in supercritical fluids, which is built using the principle of the Taylor dispersion method [3]. According to this method, a narrow pulse of solute will broaden into a peak with the combined action of convection along the axis of the diffusion tube and molecular diffusion in the radial direction. Diffusion coefficients in supercritical CO2 can then be calculated by analytical description of the dispersion of the solute pulse. Here a FT-IR Spectrophotometer is used to analyze absorption peaks on a few different wavelengths. Presently, this set-up was tested by measurements binary diffusion coefficients *D* of various compounds at infinite dilution in supercritical carbon dioxide [4,5].
First tests of the set-up were done by measuring diffusion of pure toluene in supercritical carbon dioxide at temperatures in the range 306.15 K and pressure in the range 10.5MPa. The obtained diffusion coefficients are of order of 10^{-8} m^2/s and comparable to available literature data. In a second part, binary diffusion for short chain alcohols in supercritical CO_2, were measured by the Taylor dispersion method in the range of 306.15 K- 321.15 K and at pressure of 10.5 MPa. Influence of molecular weight and temperature on the diffusion coefficients is discussed. Some modeling of the diffusion data is also made.

Acknowledgements
The authors are grateful for the funding granted by FEDER –European Regional Development Fund through the COMPETE Programme and FCT -Fundação para a Ciencia e a Tecnologia, for the KIDIMIX project POCI-01-0145-FEDER-030271.

References

[1] Donato P., Inferrera V., Sciarrone D., Mondello L., J. Sep. Sci., 40 (1) (2017), 361
[2] Middleton R.S., Carey J.W., Currier R.P., Hyman J.D., Kang Q., Karra S., Jiménez-Martínez J., Porter M.L., Viswanathan H.S., Applied Energy 147 (2015) 500.
[3] Taylor G., Proc. R. Soc. Lond. A, 219 (1953) 186.
[4] Ancherbak S., Santos C., Legros J.-C., Mialdun A., Shevtsova V., Eur. Phys. J. E (2016) 39: 111
[5] Gaponenko Y., Gousselnikov V., Santos C.I.A.V., Shevtsova V., Microgravity Sci. Technol., (2019) 12.

Thermodynamic properties of 9-phenylacridine

Vera L. S. Freitas[1,*], Maria D. M. C. Ribeiro da Silva[1]
[1]Centro de Investigação em Química, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, S/N, P-4169-007 Porto, Portugal
**vera.freitas@fc.up.pt*

The thermochemical study of relevant heteropolycylic compounds (oxygen, nitrogen and/or sulphur as heteroatoms) has been carried out in our Research Group over several years, with the main purpose of establishing correlations among structurally related compounds, in order to understand the effect of the structural characteristics on the energetic properties of those compounds [1].

Acridine derivatives are one of the classes of compounds within the scope of our research, being very well known by their therapeutic potential interest which led to their successful clinical use. This reason triggered a significant interest in the search for acridine-based drugs. In general, acridines interact with DNA through intercalation, inhibiting the process of replication, transcription and thereby also inhibiting protein synthesis. The acridine derivatives have also the ability to interact with and to inhibit some key enzymes with a role in cell proliferation, namely the opoisomerases, polymerases and telomerases [2].

Concerning this class of compounds, in previous works we performed the thermodynamic study for 9,10-dihydroacridine [3] and 9-acridanone [4]. The acridine derivative whose thermodynamic study is presented in this communication is the 9-phenylacridine (figure 1). The enthalpy of formation in the crystalline phase of 9-phenylacridine, at T = 298.15 K, was derived from bomb combustion calorimetry experiments, and its enthalpy of sublimation was derived from the Knudsen effusion method. The gas-phase enthalpy of formation, at T = 298.15 K, of 9-phenylacridine was derived from the experimental studies developed. This parameter was also obtained through computational work performed using the composite G3MP2//B3LYP approach and a set of selected working reactions. The experimental and computational enthalpies of formation will be discussed and compared with related heteropolycyclic compounds.

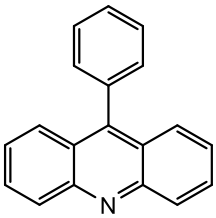


Fig.1. Molecular diagram of 9-phenylacridine.

Acknowledgements: This research was developed within the scope of the projects UID/QUI/00081/2013, POCI-01-0145-FEDER-006980, and NORTE-01-0145-FEDER-000028, awarded to CIQUP, financed by FCT, Lisbon, Portugal, and co-financed in the framework of COMPETE, with community funds (FEDER) and national funds of MEC. Vera Freitas is financed by national funds through the FCT - I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July.

Referencias

[1] V.L.S. Freitas, M.D.M.C. Ribeiro da Silva, J. Therm. Anal. Calorim. 121 (2015) 1059-1071.
[2] R. Ghosh, S. Bhowmik, D. Guha, Mol. Cell. Biochem. 361 (2012) 55.
[3] V.L.S. Freitas, J.R.B. Gomes, M.D.M.C. Ribeiro da Silva, J. Chem. Thermodyn. 115 (2017) 276.
[4] V.L.S. Freitas, P.J.O. Ferreira, M.D.M.C. Ribeiro da Silva, J. Chem. Thermodyn. 118 (2018) 115.

A method for the kinetic study of DNA nitrogenous bases alkylation reactions

M. P. García-Santos[1,*], M. A. Hierro-Estévez[2]
[1]Universidad de Salamanca, Licenciado Méndez Nieto s/n, Salamanca, España
[1]Universidad de Salamanca, Plaza de los Caídos, s/n, Salamanca, España
**pigarsan@usal.es*

The alkylation of the nitrogenous bases of DNA is a possible cause of tumor generation and, eventually, cancer. To approach the mechanisms that could take place at the cellular level, a method has been developed to study the kinetics of the nucleoside alkylation reactions.
An Ultra Fast Liquid Chromatography (UFLC) device coupled on-line to a photo-diode array detector (DAD) and an electrospray ionization (ESI) quadrupole mass spectrometer (MS) was employed. This apparatus (Shimadzu) includes a module with an autosampler that allows temperature to be kept constant during the reaction and, also, a column oven to program the temperature at which the chromatographic separation takes place. The identification of the present compounds in the reaction medium was carried out by the MS analyzer. All modules are connected to the communication module which, in turn, communicates with a high capacity computer to control the whole system and to analyze the chromatograms and spectra obtained.
The alkylation reaction of guanosine by β-butyrolactone at neutral pH has been selected to develop the kinetic method because: a) nitrosation of a primary amino acids forms lactones; specifically the nitrosation of β-aminobutyric acid generate β-butyrolactone; b) β-butyrolactone is possibly carcinogenic to humans (Group 2B, IARC); c) β-butyrolactone can alkylate 4-(p-nitrobenzyl)pyridine (NBP) [2], a trap for alkylating agents [3] with similar reactivity at the N7 position of guanine.
We worked in an excess of lactone concentration related to that of guanosine, with phosphate buffer (pH ≈ 7), within 25.0-37.0 ºC range and using 0.05% formic acid aqueous solution/metanol as the mobile phase. Every certain time 20 µL of the reaction sample was automatically injected into the chromatographic column recording the DAD spectrum between 190 nm and 400 nm; later 254 nm was selected for monitoring of both guanosine and adduct peak areas and their variation with time.
The following results and conclusions were obtained: i) the alkylation reaction of guanosine by β-butyrolactone occurs; ii) at the end of the reaction a big peak of guanosine (7.8 min retention time, m/z 284) and two small and quite similar peaks (6.1 min and 6.7 min, m/z 370) were observed at 254 nm; iii) the two peaks for m/z 370 would indicate the formation of two adducts; iv) the kinetics of the alkylation reaction was followed by the disappearance of the guanosine reagent (7.8 min retention time) and by the formation of Adduct 1 (6.1 min retention time) and of Adduct 2 (6.7 min retention time), observing that the two adducts were formed in a limited extent -probably due to the hydrolysis reaction of the alkylating agent, both were stable and the kinetic profiles were similar -which suggests that they are diastereomers.

Acknowledgement
We thank the University of Salamanca for financial support for this research (2018K113, 2019K125) and for the research contract of M.A.H.E

References

[1] M. P. García-Santos, E. Calle, J. Casado, Journal of the American Chemical Society, 123 (2001) 7506-7510.
[2] J. A. Manso, M. T. Pérez-Prior, M. P. García-Santos, E. Calle, J. Casado, Chemical Research in Toxicology, 18 (2005) 1161-1166.
[3] J. Epstein, R. W. Rosenthal, R. J. Ess, Analytical Chemistry, 27 (1955) 1435-1439.

Viscosidad dinámica de mezclas n-alcano + 1-octanol en función de la temperatura

A. Gayol[1*], S. Castelo[1], J. L. Legido[1]

[1]Departamento de Física Aplicada, Universidad de Vigo, Lagoas-Marcosende s/n, 36310 Vigo. España.
**e-mai:*

Palabras clave: viscosidad, densidad, 1-octanol, n-alcano.
En este trabajo estudiamos el comportamiento de la viscosidad dinámica de mezclas de n-alcanos + 1-octanol en función de la temperatura y a presión atmosférica.

Las medidas de viscosidad se realizaron con un viscosímetro Anton Paar AMV 200, conectado a un baño de circulación de fluido PolyScience que controla la temperatura con una incertidumbre de 10-2 K. Este dispositivo determina la viscosidad del fluido a través de la medición del tiempo de caída de una bola de acero de laminación en el interior de un capilar de vidrio lleno con la muestra [1].

La densidad se midió utilizando un densímetro tubo vibrante Anton Paar DMA 4500. Los detalles sobre el procedimiento experimental, calibración, control de temperatura se pueden encontrar en Lago et al [2]. Usando este método, la densidad se determina con una incertidumbre de 10-4 g cm-3 en todo el rango de temperaturas.

La viscosidad dinámica de las mezclas n-alcano + 1-octanol aumenta al aumentar la concentración de n-octanol y el número de átomos del n-alcano, disminuyendo al aumentar la temperatura. El incremento de la viscosidad es negativo disminuyendo con la temperatura, por otra parte presenta una asimetría encontrándose los máximo a fracciones molares ricas en 1-octanol.

En el trabajo se realiza un estudio del comportamiento de la viscosidad con las ecuaciones de predicción: Grunberg-Nissan [3], McAllister [4], Auslander [5], Teja-Rice [6].

Agradecimientos
Agradecemos la asistencia técnica de Dña. Mª Perfecta Salgado (Dpto. de Física Aplicada, Universidad de Vigo). Esta investigación ha sido financiada por el proyecto “Consolidación e Estructuración” de Unidades de Investigación Competitivas do Sistema Universitario de Galicia 2016, Entidad financiadora: Consellería de Cultura, Educación e Ordenación Universitaria. (Xunta de Galicia) ED431C 2016-034.

Referencias
Deben usarse los siguientes ejemplos para su formato: [Arial 9 pt]

[1] M.J. Pastoriza-Gallego, C. Casanova, , Paramo, R., B. Barbes, J.L.Legido, M.M. Piñeiro, J. Applied Physics 106, (2009), 64301.
[2] A.Lago, M.A. Rivas, J.L. Legido, T.P. Iglesias, . J. Chem. Thermodyn. 41, (2009), 257.
[3] L. Grunberg, A. H. Nissan, Nature 164, (1949), 799.
[4] L. McAllister, AIChE J. 6, (1960), 427.
[5] G. Auslander, Brit. Chem. Eng. 9, (1964), 610.
[6] A.S. Teja, P. Rice, Ind. Eng. Chem. Fund. 20, (1981), 77.

Thermochemical properties of anthranilate derivatives

Carlos A. O. Silva*, **Vera L. S. Freitas, Maria D. M. C. Ribeiro da Silva**

Centro de Investigação em Química, Department of Chemistry and Biochemistry,
Faculty of Sciences, University of Porto, Rua do Campo Alegre, S/N, P-4169-007 Porto, Portugal

**carlos.silva@fc.up.pt*

The olfactory properties of fragrances are desirable for products like perfumes, essential oils, shampoos and cosmetics, among many others. However, the everyday use of fragrance products, as well as their presence in various environments, constitute a concern in understanding their reactivity [1-3].

The aim of this work is to evaluate and discuss the energetic properties of methyl anthranilate and butyl anthranilate (Figure 1), performing experimental and computational studies, in order to provide reliable data for the analysis of their environmental risk assessment.

This communication reports the massic energies of combustion of methyl anthranilate and butyl anthranilate, measured by static bomb combustion calorimetry and the corresponding enthalpies of vaporization measured by Calvet microcalorimetry technique. These results are used to derive the enthalpy of formation of these anthranilate derivatives, in the liquid and gaseous phases, at T = 298.15 K. For the computational studies, the G3(MP2)//B3LYP method was used, since it is an appropriate theoretical procedure for this class of compounds.

The values derived from the experimental measurements and from the complementary computational studies of methyl anthranilate and butyl anthranilate, will be analysed in terms of their structural characteristics.

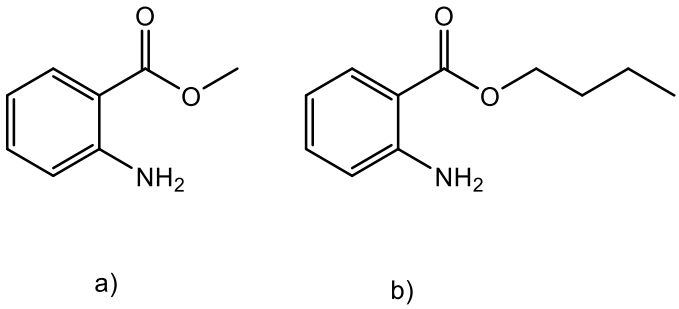


Fig.1. Structural formula for a) methyl anthranilate and b) butyl anthranilate.

Acknowledgments
Thanks are due to Fundação para a Ciência e Tecnologia (FCT) of Portugal, Project UID/QUI/UI0081/2013 and FEDER Projects POCI-01-0145-FEDER-006980. C.A.O.S. thanks FCT for the doctoral grant SFRH/BD/137672/2018. VLSF thanks FCT and FCUP for the Program Contract established under the transition rule of Decree Law 57/2016, amended by Law 57/2017.

References

[1] C.G. Daudhton, T. A. Ternes, Environ. Health Perspect., 107 (1999) 907-938.
[2] D.A. Chase, A. Karnjanapi, Y. Fang, G. P. Cobb, A. N. Morse, T. A. Anderson, Sci. Total Environ., 416 (2012) 253-260.
[3] Personal care products in the aquatic environment. M. S. Díaz-Cruz, D. Barceló, Springer, 2015.

Evaluation of the effects of substituents on reactivity of 2-aminobenzoxazole and 2-metil-6-nitrobenzoxazole

Ana L. R. Silva*, **Maria D. M. C. Ribeiro da Silva**
[1]Centro de Investigação em Química, Faculty of Sciences,
University of Porto, Porto, Portugal
**analuisa.rs@fc.up.pt*

Benzoxazole derivatives constitute basic structural fragments in a wide range of natural products, being attractive targets in drug synthesis [1]. In fact, these compounds have relevant medical applications due to their recognized biological and therapeutic activities.

As part of a broad study on the thermochemical properties of compounds with a benzenic ring fused to a pentagonal ring containing oxygen and nitrogen as heteroatoms [2,3], we intend to evaluate the energetic effects of different substituents, as well as their influence on the reactivity of the corresponding molecules.

In this work we present the experimental results for the energies of combustion and the enthalpies of sublimation of two 1,3-benzoxazoles (Fig. 1), measured by static-bomb calorimetry, at T = 298.15 K, and high temperature Calvet microcalorimetry, respectively. From these results, the standard (p^o = 0.1 MPa) molar enthalpies of formation of 2-aminobenzoxazole (**1a**) and 2-methyl-6-nitrobenzoxazole (**1b**), in condensed and gaseous states, were derived. The standard molar entropies and Gibbs energies of formation in the gas-phase, at T = 298.15 K, were also calculated. The results obtained are discussed in terms of energy-structural relationships, whose main objective is to contribute to evaluate the chemical behaviour of these species.

Additionally, using high level ab initio calculations, the gas-phase standard molar enthalpies of formation of these compounds were obtained. The results obtained from this computational approach are used to support the development of strategies allowing the establishment of reliable prediction schemes of the corresponding properties for other related compounds.

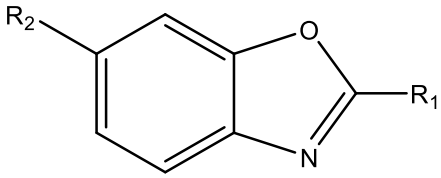


Fig.1. Structures of two benzoxazoles studied:
1a: 2-aminobenzoxazole (R_1 = NH_2 and R_2 = H) and
1b: 2-methyl-6-nitrobenzoxazole (R_1 = CH_3 and R_2 = NO_2)

Acknowledgments
Thanks are due to Fundação para a Ciência e a Tecnologia (FCT) of Portugal, Project UID/QUI/00081/2013, and FEDER, Projects POCI-01-0145-FEDER-006980. Ana L.R. Silva thanks to National Foundation for Research (FCT) for the supporting of a Researcher Position in the Individual Call to Scientific Employment Stimulus 2017 (ref.: CEECIND/01161/2017).

References

[1] S. Rajasekhar, B. Maiti, K. Chanda, Synlett 28 (2017) 521.
[2] A.L.R. Silva, V.M.F. Morais, M.D.M.C. Ribeiro da Silva, J. Chem. Thermodyn. 127 (2018) 45.
[3] A.L.R. Silva, J.M. Gonçalves, M.D.M.C. Ribeiro da Silva, J. Chem. Thermodyn. 120 (2018) 157.

Thermodynamic study of 4,4'-DDD and 4,4'-DDA

A. R. R. P. Almeida, **B. D. A. Pinheiro, M. J. S. Monte**

Centro de Investigação em Química (CIQUP), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto. Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal
**ana.figueira@fc.up.pt*

Organochlorine pesticides (OCPs) are compounds that are included in the group of persistent organic pollutants (POPs). This is a class of compounds of environmental concern due to their persistence, toxicity and accumulation in the terrestrial and aquatic ecosystems. The effects on humans and the environment of pesticide exposure are a constant worry and so the knowledge of properties with important applications in predicting the environmental mobility of these compounds (and of its metabolites) is of great importance. Thus, a thermodynamic study of the phase transitions of two organochlorine compounds was performed. The vapor pressures of the crystalline phase of 2,2-bis(4-chlorophenyl)-1,1-dichloroethane (4,4'-DDD) and bis-(4-chlorophenyl)acetic acid (4,4'-DDA) were measured using the Knudsen effusion technique [1] over the temperature ranges T = (353.1–375.2) K and T = (385.1–407.6) K, respectively. The standard molar enthalpies, entropies and Gibbs energies of sublimation for the compounds studied, at reference temperatures, were derived from the experimental results. Their temperatures and molar enthalpies of fusion were determined using differential scanning calorimetry.

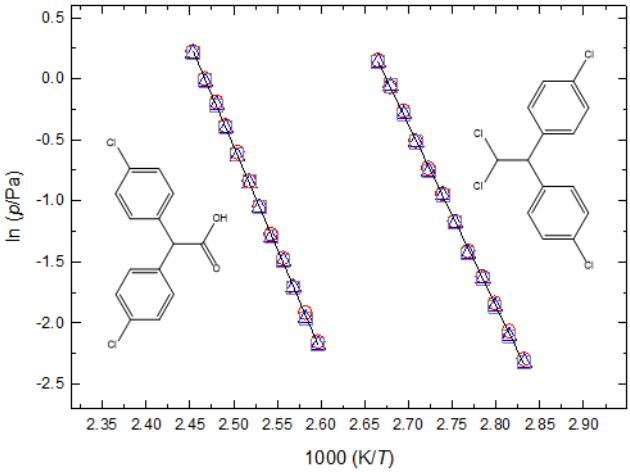


Fig.1. Plots of ln*p* *vs* 1/*T* of 4,4'-DDA and 4,4'-DDD.
○, small effusion orifices; Δ, medium effusion orifices and □, large effusion orifices.

Acknowledgements
This work was developed within the scope of the project UID/QUI/00081/2013 awarded to CIQUP, financed by Fundação para a Ciência e Tecnologia (FCT, Portugal) and of the project POCI-01-0145-FEDER-006980 financed in the framework of Operational Programme for Competitiveness and Internationalisation, COMPETE, with community funds (FEDER, Portugal). Ana Almeida is financed by national funds through the FCT - I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July.

References
[1] M.A.V. Ribeiro da Silva; M.J.S. Monte; L.M.N.B.F. Santos, J. Chem. Thermodyn. 38 (2006) 778.

Synthesis of Pharmaceutical Nanococrystals – Preliminary Approach

João A.V. Santos[1,*], Inês C. Santos[1], João Canotilho[1,2], Ricardo A. E. Castro[1,2], M. Ermelinda S. Eusébio[1]
[1] CQC, Departamento de Química, Universidade de Coimbra, Portugal
[2] Faculdade de Farmácia, Universidade de Coimbra, Portugal
**joao.santos369@gmail.com*

Nanosized pharmaceutical co-crystals, nanoparticles composed by crystals of an API with an acceptable co-former, have recently been growing in interest due to their potential towards improving absorption of poorly soluble drugs.[1],[2],[3] This approach results from the combination of co-crystal formation, that aims to improve physicochemical properties of an API without compromising its biological function, with nanonization processes, that can also improve the aqueous solubility and the dissolution rate of particles.

In this work, (*S*)-naproxen + nicotinamide and (*R*,*S*)-ibuprofen + nicotinamide co-crystals are used as models, and our goal is to investigate the formation of nanosized co-crystals *in situ*, by wet milling in the presence of a surfactant. We are also exploring other techniques such as sonochemistry and high-pressure homogenization, using the same model co-crystals, in order to determine the technique that shows the best yield with reproducible results.

Herein, we present a preliminary study, with focus on wet milling, where the obtained nanosized co-crystals were characterized by differential scanning calorimetry, infrared spectroscopy and powder X-ray diffraction. To confirm the presence of the aimed nanosized particles, we resorted to scanning electron microscopy and dynamic light scattering.

Agradecimientos
Coimbra Chemistry Center, CQC, is supported by national funds through the FCT - Foundation for Science and Technology, I.P., under the project UID / QUI / 00313/2019

Referencias

[1] L. Peltonen, Advanced Drug Delivery Reviews, 131 (2018) 101
[2] Y. Huang, J. M. Li, Z. H. Lai, J. Wu, T. B. Lu, J. M. Chen, European Journal of Pharmaceutical Sciences, 109 (2017), 581
[3] M. Karashima, K. Kimoto, K. Yamamoto, T. Kojima, Y. Ikeda, European Journal of Pharmaceutics and Biopharmaceutics, 107 (2016) 142

Solubility of hesperetin or benzoic acid in eutectic solvents

Heloísa H.S. Almeida[1], Tânia E. Sintra[2], João A.P Coutinho[2], Simão P. Pinho[1], Olga Ferreira[1,*]
[1]LSRE-LCM and CIMO, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5301-857 Bragança, Portugal
[2]CICECO, Departmento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal
*oferreira@ipb.pt

Aqueous solutions of eutectic solvents or ionic liquids are being studied as alternative solvents for the extraction and separation of poorly soluble compounds in water such as flavonoids or phenolic acids [1-3]. However, few fundamental studies are available regarding the corresponding solubilization mechanisms. The main aim of this work was to obtain solubility data of two model compounds (hesperetin and benzoic acid) in three deep eutectic solvents (DES), for which the phase diagrams are well described in the literature: choline chloride + urea (1:2 mole ratio), choline chloride + malonic acid (1:1) and choline chloride + glycolic acid (1:1).
The solubility experiments were performed at 298 K by the isothermal shake-flask method coupled to UV-Vis spectroscopy. The effect of adding water to each DES on the solute solubility was also evaluated (5%, 25%, 50% and 75% of water weight percentage). In parallel, for comparison purposes, aqueous solutions of the individual components urea (U), choline chloride (ChCl), malonic acid (MA) or glycolic acid (GA) were also tested up to their solubility limit in water. In all cases, the solubility increased with the addition of the organic co-solvent. For hesperetin, the best results were obtained with the DES GA:ChCl which increased its solubility by 800 folds, followed by MA:ChCl (360 folds) and U:ChCl (260 folds), all DES containing 5% of water. In the case of benzoic acid, a smaller solubility enhancement was obtained: U:ChCl (26 folds), GA:ChCl (12 folds) and MA:ChCl (7 folds). As an example, Fig.1 clearly demonstrates the relevance of eutectic systems by extending the working concentration range and increasing the solubility of benzoic acid. The designer character of both DES and IL makes them attractive alternatives for increasing the solubility of poorly water soluble compounds. Further studies need to be carried out to understand the complex molecular level interactions occurring in these systems, including also the effect of pH and water content.

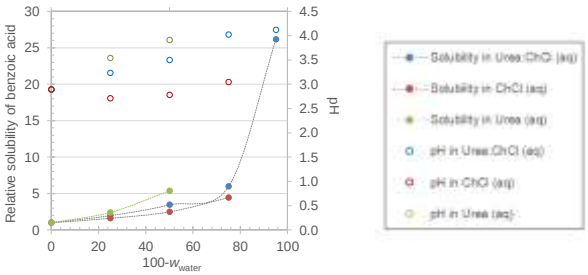


Fig.1. Relative solubility of benzoic acid in aqueous solutions of U, ChCl and U:ChCl (2:1), at 298 K.

Acknowledgements
The authors acknowledge the support of: Foundation for Science and Technology (FCT, Portugal) and FEDER under Programme PT2020 for financial support to CIMO (UID/AGR/00690/2019); UID/CTM/50011/2019 (CICECO), financed by national funds through the FCT/MCTES; Associate Laboratory LSRE-LCM - UID/EQU/50020/2019 - funded by national funds through FCT/MCTES (PIDDAC); Project AllNat - POCI-01-0145-FEDER-030463 (PTDC/EQU-EPQ/30463/2017), funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI), Portugal 2020 and by national funds through FCT/MCTES.

References

[1] H. Vanda, Y. Dai, E.G. Wilson, R. Verpoorte, Y.H. Choi, Comptes Rendus Chim. 21 (2018) 628.
[2] H. Passos, M.G. Freire, J.A.P. Coutinho, Green Chemistry 16 (2014) 4786.
[3] B. Soares, D.J.P. Tavares, J.L. Amaral, A.J.D. Silvestre, C.S.R. Freire, J.A.P. Coutinho, ACS Sustainable Chemistry & Engineering 5 (2017) 4056

Improvement of physical-chemical properties of gemfibrozil

Ricardo A.E. Castro[1,2*], Bruno B.C. Holanda[4], Gilbert Bannach[4], M. Ramos Silva[3], M. Ermelinda S. Eusébio[2]

[1]Faculty of Pharmacy, University of Coimbra, 3000-578, Coimbra, Portugal
[2]CQC, Department of Chemistry, University of Coimbra, 3004-535, Coimbra, Portugal
[3]CfisUC, Department of Physics, University of Coimbra, 3004-516, Coimbra, Portugal
[4]UNESP – São Paulo State University, School of Sciences, Chemistry Department, 17033-260, Bauru, SP, Brazil

**rcastro@ff.uc.pt*

Gemfibrozil is used to treat abnormal blood lipid levels. The polymorphic behaviour was our first line of investigation on this active pharmaceutical ingredient (API) and two polymorphs were identified [1]. According to the Biopharmaceutical Classification System this is a class II drug. This means that it has high permeability but low aqueous solubility, which as consequences on oral bioavailability. In this work, screening of gemfibrozil co-crystals, with high potential to improve the physical chemical properties of the API, with several Generally Recognized as Safe (GRAS) co-formers is carried out. The co-formers used are isonicotinamide (INCT), picolinamide (PA), nicotinamide (NA), benzamide (BZ), nicotinic acid (NCN) and pyrazinamide (PZN).

The screening was performed by ethanol (10 μL) assisted grinding using a Retsch - MM400 mill during 30 minutes at 15 Hz frequency. The resulting powders were analysed by thermal analysis methods (DSC, TG, PLTM), infrared spectroscopy (FTIR-ATR) and X-ray powder diffraction.

The screening process allowed the identification of GEM:INCT (1:1; mol:mol) and GEM:PA (2:1; mol:mol) co-crystals. The other systems form physical mixtures and the eutectic compositions were also identified. Single crystals of the GEM:INCT co-crystal allowed solving the crystalline structure, Figure 1, and thus to identify the intermolecular interactions present in the co-crystal. The GEM:INCT co-crystal exhibits an improvement of intrinsic dissolution rate in comparison with the pure GEM.

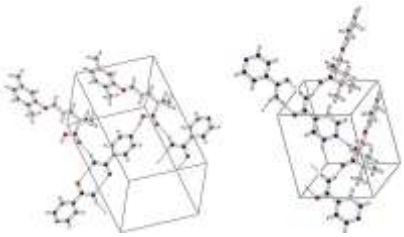


Fig.1. GEM:INCT unit cell.

Acknowledgments

The authors wish to thank CAPES, FAPESP (proc. 2017/08820-8; 88881.189289/2018-01), and CNPq (proc. 302267/2015-8) for financial support. Coimbra Chemistry Center, CQC, is supported by national funds through the FCT - Foundation for Science and Technology, I.P., under the project UID / QUI / 00313/2019. Unidade de Controlo de Qualidade de Produtos Farmacêuticos, UCQFarma, Faculty of Pharmacy of the University of Coimbra for XRPD and Sotax dissolution system facilities.

Referencias

[1] Bruno B.C. Holanda, Gilbert Bannach, M. Ramos Silva, M. Ermelinda S. Eusébio, Ricardo A.E. Castro, Thermochimica Acta 675 (2019) 113.

High pressure Taylor dispersion technique as a tool for the measurement of diffusion coefficients in supercritical carbon dioxide

Cecília I.A.V Santos [1], Marisa C.F. Barros[1], Valentina Shevtsova[2] and Ana C.F. Ribeiro[1]

[1]Department of Chemistry, University of Coimbra, 3004 - 535 Coimbra, Portugal,
[2]MRC, CP-165/62, Université Libre de Bruxelles, 50, Av. F.D. Roosevelt, B-1050 Brussels, Belgium
**ceciliasantos@qui.uc.pt*

Research in the supercritical fluids (SCFs) science and technology has increased progressively in the past decades, at both academic and industrial level, due to the broadened applications of SCFs to food, cosmetics, pharmaceutics, materials, chemistry, energy and waste treatment [1-2]. Carbon dioxide, among SCFs, has been the widely used due to its chemical stability, considerable inertness, low critical temperature, relatively non-toxicity, non-flammability and availability in high purity at relatively low cost. Therefore, all information about diffusion processes of different substances in supercritical CO_2 is of high importance for various applications.

We present development of high pressure apparatus for measurements of the diffusion coefficient in supercritical fluids, which is built using the principle of the Taylor dispersion method [3]. According to this method, a narrow pulse of solute will broaden into a peak with the combined action of convection along the axis of the diffusion tube and molecular diffusion in the radial direction. Diffusion coefficients in supercritical CO2 can then be calculated by analytical description of the dispersion of the solute pulse. Here a FT-IR Spectrophotometer is used to analyze absorption peaks on a few different wavelengths. Presently, this set-up was tested by measurements binary diffusion coefficients *D* of various compounds at infinite dilution in supercritical carbon dioxide [4,5].

First tests of the set-up were done by measuring diffusion of pure toluene in supercritical carbon dioxide at temperatures in the range 306.15 K and pressure in the range 10.5MPa. The obtained diffusion coefficients are of order of 10^{-8} m^2/s and comparable to available literature data. In a second part, binary diffusion for short chain alcohols in supercritical CO_2, were measured by the Taylor dispersion method in the range of 306.15 K- 321.15 K and at pressure of 10.5 MPa. Influence of molecular weight and temperature on the diffusion coefficients is discussed. Some modeling of the diffusion data is also made.

Acknowledgements
The authors are grateful for the funding granted by FEDER –European Regional Development Fund through the COMPETE Programme and FCT -Fundação para a Ciencia e a Tecnologia, for the KIDIMIX project POCI-01-0145-FEDER-030271.

References

[1] Donato P., Inferrera V., Sciarrone D., Mondello L., J. Sep. Sci., 40 (1) (2017), 361
[2] Middleton R.S., Carey J.W., Currier R.P., Hyman J.D., Kang Q., Karra S., Jiménez-Martínez J., Porter M.L., Viswanathan H.S., Applied Energy 147 (2015) 500.
[3] Taylor G., Proc. R. Soc. Lond. A, 219 (1953) 186.
[4] Ancherbak S., Santos C., Legros J.-C., Mialdun A., Shevtsova V., Eur. Phys. J. E (2016) 39: 111
[5] Gaponenko Y., Gousselnikov V., Santos C.I.A.V., Shevtsova V., Microgravity Sci. Technol., (2019) 12.

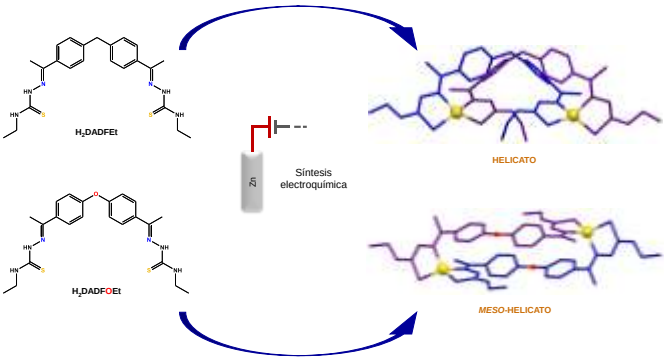
QUÍMICA INORGÁNICA

Estudio de la influencia del ligando en la obtención de arquitecturas helicoidales o *meso*-helicoidales

Sandra Fernández-Fariña[1,*], Ana M. González-Noya[1], Rosa Pedrido[1], Luis M. González-Barcia, María J. Romero[2]

[1]Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, Av. das Ciencias, s/n 15701, Santiago de Compostela, A Coruña, España.
[2]Departamento de Didácticas Aplicadas, Facultade de Formación do Profesorado, Universidade de Santiago de Compostela, Av. de Ramón Ferreiro, s/n 27071, Lugo, España
*sandra.fernandez.farina@usc.es

Entre los diferentes compuestos metalosupramoleculares existentes, los helicatos y los *meso*-helicatos son considerados compuestos de gran importancia debido a su participación en diferentes áreas, entre las que destacan la biomedicina [1] o la nanotecnología [2], respectivamente. La diferencia química principal entre ambas estructuras es que la configuración absoluta de los centros metálicos no es la misma y, por lo tanto, cambia la quiralidad. En los helicatos los ligandos se cruzan al coordinarse dando lugar a estructuras quirales, mientras que en los *meso*-helicatos los ligandos no se cruzan entre sí, formando estructuras aquirales.
Recientemente en nuestro grupo de investigación se ha estudiado el efecto del ión metálico y del ligando en la enantioselectividad de complejos helicoidales neutros de cobalto y zinc derivados de ligandos *bis*tiosemicarbazona [3]. Como continuación de este trabajo, se han diseñado nuevos ligandos *bis*tiosemicarbazona análogos con el fin de analizar el efecto del ligando en la arquitectura final de los compuestos metalosupramoleculares.
En esta comunicación se presenta un ligando *bis*tiosemicarbazona etil-sustituído H_2DADFOEt adecuado para la obtención de compuestos dinucleares neutros de cobalto y zinc. Estos compuestos se han caracterizado mediante las técnicas habituales en estado sólido y en disolución. Asimismo, el compuesto de zinc ha sido estudiado por difracción de rayos X lo que ha permitido analizar como la presencia del átomo de oxígeno en el espaciador permite la obtención de helicatos o *meso*-helicatos de tipo *bis*tiosemicarbazona (Esquema 1).



Esquema 1. Estructuras metalosupramoleculares de Zn(II) derivadas de ligands *bis*tiosemicarbazona.

Agradecimientos
Xunta de Galicia (GRC ED431C 2018/13, Rede MetalBIO 2017/PG111), Ministerio de Economía y Competitividad (CTQ2017-90802- REDT REDT).

Referencias

[1] R. A. Kaner, S. J. Allison, A. D. Faulkner, R. M. Phillips, D. I. Roper, S. L. Shepherd, D. H. Simpson, N. R. Waterfield, P. Scott, Chem. Sci., 7 (2016), 951.
[2] J. Ferrando-Soria, O. Fabelo, M. Castellano, J. Cano, S. Fordham, H.-C. Zhou, Chem. Commun., 51 (2015), 13381.
[3] M. J. Romero, V. Suárez, S. Fernández-Fariña, M. Maneiro, E. Martínez-Núñez, G. Zaragoza, A. M. González-Noya, R. Pedrido, Chem. Eur. J. 23 (2017), 4884.

Evaluation of the effect of tris(3-hydroxy-4-pyridinonate) Fe(III) chelates to treat Iron Deficiency Chlorosis

Carla S. Santos[1], Sofia Ferreira[2], Tânia Moniz[3], Andreia Leite[3], Marta W. Vasconcelos[1], Maria Rangel[2,*]

[1] Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, 4169-005 Porto, Portugal

[2] REQUIMTE-LAQV, Instituto de Ciências Biomédicas de Abel Salazar, Universidade do Porto, 4050-313 Porto, Portugal.

[3] REQUIMTE-LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências ,Universidade do Porto, 40696-007 Porto, Portugal

mrangel@icbas.up.pt

Iron (Fe) is an essential nutrient for most organisms including plants. However, due to the existence of the element in very insoluble forms in earth crust, the uptake of Fe by plants is seriously compromised in alkaline soils, which correspond to 30% of the world's arable land. As a consequence, plants suffer from Fe deficiency chlorosis (IDC), characterized by chlorosis, yield losses, and lower concentrations of Fe in edible plant parts. Farmers rely on supplementing their crops with Fe-chelates to avoid serious growth deficiencies and Fe-EDTA and Fe-EDDHA are the available commercial products. The limited number of distinct Fe chelates that are used as fertilizers calls for the identification of new ligands capable of producing Fe-complexes with properties that allow more efficient pathways for root uptake, root to shoot translocation and maintenance of metal homeostasis.

Herein we report studies regarding the capacity of two *tris*(3-hydroxy-4-pyridinonate) Fe(III) complexes [Fe(mpp)$_3$] and [Fe(dmpp)$_3$] to amend IDC in hydroponically grown soybean (*Glycine max*) plants. The application of all complexes improved plants condition when compared to those grown with no added Fe treatment. Moreover, plants treated with [Fe(mpp)$_3$] exhibited the best overall results. Plants presented: (a) higher relative chlorophyll content; (b) higher biomass development and (c) higher Fe accumulation.

Plants treated with the compound [Fe(mpp)$_3$] were able to translocate more iron from the roots to the shoots not eliciting the expression of the Fe stress related genes. The results suggest that 3,4-HPO Fe-chelates could be economically and environmentally favourable in agricultural contexts

Control FeEDDHA Fe(dmpp)$_3$ Fe(mpp)$_3$

Agradecimientos

This work received financial support from the European Union (FEDER funds through COMPETE) and National Funds (FCT, Fundação para a Ciência e Tecnologia), under the Partnership Agreement PT2020 through project UID/QUI/50006/2013 POCI/01/0145/FEDER/007265 (LAQV/REQUIMTE) and PTDC/AGRPRO/3515/2014-POCI-01-0145-FEDER-016599.

Resolución quiral de complejos de Co(II) y Zn(II) derivados de *bis*tiosemicarbazonas

María J. Romero[1,2*], Ana M. González-Noya[1], Rosa Pedrido[1], Sandra Fernández-Fariña[1], Luis M. González-Barcia[1]

[1] Departamento de Química Inorgánica, Facultad de Química, Campus Vida, Universidade de Santiago de Compostela, Avda. das Ciencias s/n, 15782, Santiago de Compostela, España.

[2] Dirección actual: Departamento de Didácticas Aplicadas, Facultad de Formación del Profesorado, Universidade de Santiago de Compostela, 27071, Lugo, España.

**mariajose.romero@usc.es*

La obtención de isómeros puros es fundamental para el desarrollo de nuevos fármacos y materiales moleculares debido a las diferentes propiedades que pueden presentar dos isómeros de la misma molécula.[1], [2] Los helicatos son compuestos metalosupramoleculares quirales que habitualmente se obtienen como mezcla racémica y cuya quiralidad está inducida por los iones metálicos. En este sentido, los ligandos tiosemicarbazona poseen flexibilidad y características estructurales que permiten la obtención de dichas especies. La resolución de mezclas racémicas de helicatos para obtener compuestos estereoquímicamente puros se ha conseguido en pocos casos, mediante métodos cromatográficos o separación espontánea por cristalización.[3]

Previamente, en nuestro grupo de investigación estudiamos el efecto del ión metálico y del ligando en la enantioselectividad y en la isomería de enlace de helicatos derivados de ligandos *bis*tiosemicarbazona con sustituyentes alifáticos.[3] En esta comunicación, presentamos la síntesis de nuevos helicatos *bis*tiosemicarbazona de zinc y cobalto y el estudio de su resolución quiral.

Los complejos neutros de fórmula general M_2L_2 [M= Zn(II), Co(II); L= L^a o L^b] derivados de ligandos *bis*tiosemicarbazona nitrofenil-substituido (L^a) y metoxifenil-substituido (L^b) respectivamente, se obtuvieron mediante síntesis electroquímica. La estructura de tipo helicato se confirmó en el caso del complejo $Zn_2(L^b)_2$ (Figura 1) mediante difracción de rayos X. Adicionalmente, los estudios de dicroísmo circular realizados corroboraron la formación de compuestos quirales y el aislamiento de uno de los enantiómeros como especie mayoritaria.

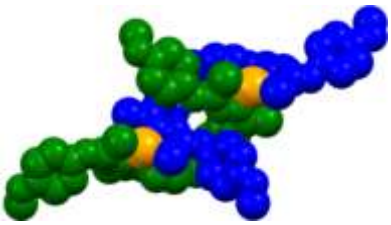


Fig.1. Representación *spacefill* de la estructura del helicato $Zn_2(L^b)_2$.

Agradecimientos

Xunta de Galicia (GRC ED431C 2018/13 y Red de Investigación MetalBIO ED431D 2017/01).

Referencias

[1] M. J. Romero, P. J. Sadler, en Bioorganometallic Chemistry. Applications in Drug Discovery, Biocatalysis and Imaging, G. Jaouen, M. Salmain (Eds.), Weinheim, Wiley-VCH Verlag GmbH & Co. KGaA, 2015, 85.

[2] J. P. Zhang, X. C. Huang, X. M. Chen, Chem. Soc. Rev., 38 (2009) 2385.

[3] M. J. Romero, V. Suárez, S. Fernández-Fariña, M. Maneiro, E. Martínez-Núñez, G. Zaragoza, A. M. González-Noya, R. Pedrido, Chem. Eur. J., 23 (2017) 4884.

Superoxide dismutase activity and neuroprotective effects of salen-manganese complexes

Lara Rouco[1,*], Laura Rodríguez-Silva[1], Rebeca Alvariño[2], Amparo Alfonso[2], Marcelino Maneiro[1]

[1]Universidade de Santiago de Compostela, Facultade de Ciencias, Avda. Alfonso X, Lugo, Spain

[2]Universidade de Santiago de Compostela, Facultade de Veterinaria, Lugo, Spain

**lara.rouco.mendez@usc.es*

Reactive oxygen species (ROS) like superoxide radical anion ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2) or hydroxyl radical ($OH^{\bullet}$), are generated as by-products of mitochondrial electron transport of aerobic respiration [1]. ROS levels are regulated by antioxidant enzymes as superoxide dismutases (SOD). An imbalance in this oxidant-antioxidant status could determine the extent of cell damage, which is particularly risky for brain cells that are susceptible to oxidative damage due to their high rate of energy consumption, and other factors as the relative low levels of brain antioxidant defences or the high concentrations of polyunsaturated fatty acids in this organ. Excessive ROS levels have been associated with neurodegenerative disorders like Alzheimer's Disease that may shorten life span and affect the life quality of aging populations. In this context, efforts have been directed toward the search of antioxidant enzyme mimics [2-3].

In the work described here, we examined the cytoprotective effect of three manganese-salen complexes against oxidative stress in human SH-SY5Y neuroblastoma cells. EC-50 values for SOD activity were determined, showing values from 10-150 nM. We demonstrated for the first time the neuroprotective effects of this type of complex in this human neuronal model. These complexes were found to improve cell survival, with levels between 80 ± 5 % and 95 ± 8%, compared to TBPH control cells (Fig 1).

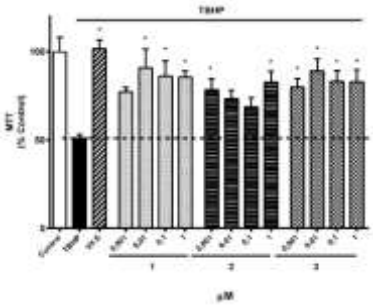


Fig.1. Neuroprotective effect of **1-3** in an oxidative stress model. SH-SY5Y cells were co-treated with 75 µM TBHP and compounds (0.001-1 µM) for 6 h. Then, their effect on cell viability was assessed by MTT test. Data are mean ± SEM of three experiments performed by triplicate. Values are expressed as percentage of control cells and compared to cells treated with TBHP alone by Student's *t* test. *p<0.05

Acknowledgements

Xunta de Galicia (GRC ED431C 2018/13), and Red de Investigación MetalBIO (ED431D 2017/01).

References

[1] M. Oszajca, M. Brindell, L. Orzel, J.M. Dabrowski, K. Spiewak, P. Labuz, M. Pacia, A. Stochel-Gaudyn, W. Macyk, R. van Eldik, G. Stochel, Coord. Chem. Rev., 143 (2016) 327.

[2] S. Signorella, C. Palopoli, G. Ledesma, Coord. Chem. Rev. 365, (2018) 75.

[3] Liberato, M.J. Fernández-Trujillo, Á. Máñez, M. Maneiro, L. Rodríguez-Silva, M.G. Basallote, Inorg. Chem. 57 (2018) 14471.

QUÍMICA ORGÁNICA

The Boron Hot-Spot Methodology: Peptide Functionalization

Rita Padanha[1,*], Roberto Russo[1], Fábio Fernandes[2,3], Luis F. Veiros[4], Pedro M. P. Gois[1]

[1]Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Lisbon, Portugal
[2]Centro de Química-Física Molecular and Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, Universidade de Lisboa, Lisbon, Portugal
[3]IBB-Institute for Bioengineering and Biosciences, Instituto Superior Técnico, Universidade de Lisboa, Lisbon, Portugal
[4]Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisbon, Portugal

**ritapadanha@gmail.com*

Bioconjugation strategies combine biomolecules like peptides and proteins with payloads of specific properties. Recently, several bioconjugates emerged as high-specific therapeutics and reached the market. [1] However, the construction of bioconjugates with reversible properties was overlooked, since most of these strategies focus on obtaining stable constructs under complex physiological conditions over developing stimuli-responsive constructs with potential drug delivery and live-cell imaging applications. [1,2] In this field, boronic acids (BA) can be explored as a molecular construction tool due to their ability to establish reversible covalent bonds with vicinal/nitrogen nucleophiles. [1,3]

Here, we developed a boron hot-spot (BHS) methodology where a 3-hydroxyquinolinone heterocicle (3HQ) is installed at a specific site of peptide chains, promoting the coordination of BA' carbonyl group with a specific amine function, enabling the selective formation of iminoboronates (**Fig. 1**).

The incubation of the BHS-Cys with 2-FBBA in ammonium acetate solution (20 mM, pH 7.0) afforded the desired imine within 2h at 37 °C. ESI-MS studies were performed, showing the compatibility of this BHS with different amino acid side chain and competing functionalities.

In more complex peptides, the BHS favors the N-terminal iminoboronate over the formation of in-chain iminoboronates in c-Ovalbumin and the RGD peptides. Exhibiting an N-terminal and an in-chain Cys residue, RGD was used to install 2 BHS, but only the N-terminal modification promoted the assembly with 2-FBBA.

The resulting iminoboronates are shown to be stable in ammonium acetate solution pH 7 and 4.5 or in the presence of BSA, although reversible in the presence of glutathione.

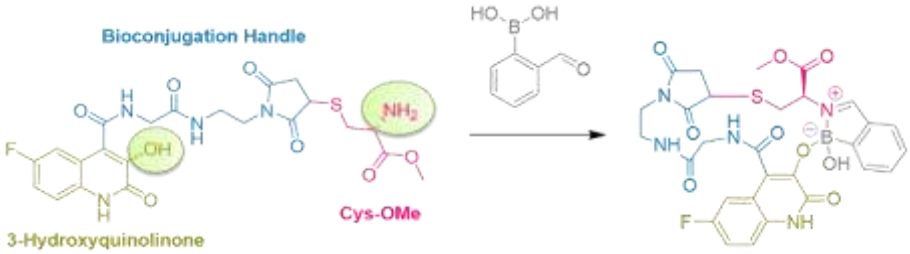


Fig.1. BHS Methodology

Acknowledgements
We thank the Fundação para a Ciência e Tecnologia for financial support (UID/QUI/00100/2013 and PTDC/QEQ-QOR/1434/2014).

References
[1] António, J. P. M.; Russo, R.; Carvalho, C. P.; Cal, P. M. S. D., Chem. Soc. Rev., 2019, 48, 3513.
[2] Koniev, O.; Wagner, A. Chem. Soc. Rev. 2015, 44 (15), 5495–5551.
[3] Boutureira, O.; Bernardes, G. J. L. Chem. Rev. 2015, 115 (5), 2174–2195.

Synthesis and characterization of porphyrin-cyclodextrin bioconjugates

Cláudia P. S. Ribeiro[1,*], João P. C. Tomé[2], Leandro M. O. Lourenço[1]
[1]QOPNA and LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2]CQE and Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal
*e-mail: claudia.santos.ribeiro7@ua.pt

Cancer photodynamic therapy (PDT) have been used for the treatment of localized tumours [1,2]. PDT is based on the combination of three non-toxic elements: a photosensitizer (PS), light and oxygen, which lead to the formation of reactive oxygen species (ROS) that cause lethal oxidative damage into the tumours. The same principle has also been used to treat other diseases, such as age-related macular degeneration and bacterial infections [1-3]. For that, clinical approved tetrapyrrolic macrocycles, with particular emphasis on photoactive porphyrin derivatives, have been used in the different biomedical applications [1]. Novel neutral and cationic water-soluble free-base porphyrins (Pors) peripherally substituted with 4-mercaptopyridine or 4-hydroxypyridine units (**1** and **2**, respectively) and with cyclodextrin (CD) moieties (**3**-**4**) were prepared (Figure 1). The presence of the CD unit and the multi-positive charges at the Pors periphery (**3a**-**4a**) prevent their aggregation, enhance the solubility in aqueous media and increase the specificity for the target cell's receptors.

In this communication, it will be reported and discussed the synthesis, structural and spectroscopic characterization of these novel asymmetric porphyrin-cyclodextrin bioconjugates.

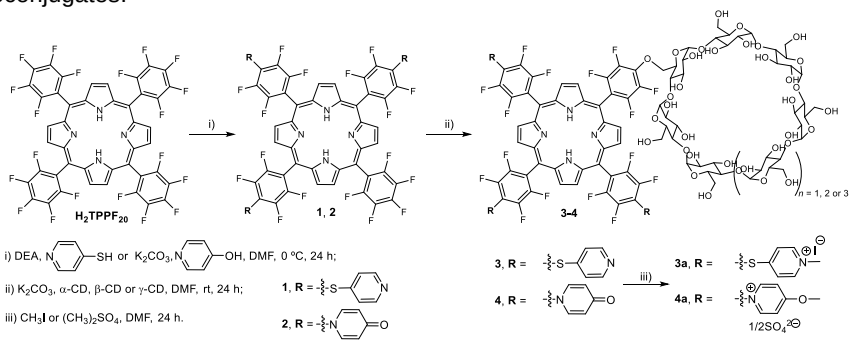


Fig.1. Structure of neutral and cationic porphyrin-cyclodextrin bioconjugates.

Acknowledgements:
Thanks are due to FCT/MCTES for the financial support to QOPNA (FCT UID/QUI/00062/2019) and CQE (FCT UID/QUI/0100/2019) research units, and FCT projects P2020-PTDC/QEQ-SUP/5355/2014 and P2020-PTDC/QUI-QOR/31770/2017, through national founds (PIDDAC) and where applicable co-financed by the FEDER-Operational Thematic Program for Competitiveness and Internationalization-COMPETE 2020, within the PT2020 Partnership Agreement. C. R. thank FCT for the research fellow BM/UI51/8768/2019.

References:

[1] a) P. M. R. Pereira, S. Silva, J. S. Ramalho, C. M. Gomes, H. Girão, J. A. S. Cavaleiro, C. A. F. Ribeiro, J. P. C. Tomé, R. Fernandes, European Journal of Cancer, 68 (2016) 60. b) L. M. O. Lourenço, P. M. R. Pereira, E. Maciel, M. Válega, F. M. J. Domingues, M. R. M. Domingues, M. G. P. M. S. Neves, J. A. S. Cavaleiro, R. Fernandes, J. P. C. Tomé, Chemical Communications 50.61 (2014): 8363-8366.

[2] S. A. Thompson, A. Aggarwal, S. Singh, A. P. Adam, J. P. C. Tome, C. M. Drain, Bioorganic & Medicinal Chemistry, 26 (2018) 5224.

[3] a) L. Marciel, L. Teles, B. Moreira, M. Pacheco, L. M. O. Lourenço, M. G. P. M. S. Neves, J. P. C. Tomé, A. F. Faustino, A. Almeida, Future Med. Chem. 9 (2017) 365. b) A. Tavares, S. R. Dias, C. M. Carvalho, M. A. Faustino, J. P. Tomé, M. G. Neves, Photochemical & Photobiological Sciences, 10 (2011) 1659. c) J. M. D. Calmeiro, C. J. Dias, C. I. V. Ramos, A. Almeida, J. P. C. Tomé, M. A. F. Faustino, L. M. O. Lourenço, Dyes and Pigments, (2019) DOI: https://doi.org/10.1016/j.dyepig.2019.03.021.

Síntese de pigmentos azuis derivados de piranoflavílios e estudo das suas formas de equilíbrio em solução aquosa

Paula Araújo, Ana Rita Pereira, Iva Fernandes, Nuno Mateus, Victor de Freitas, Joana Oliveira

REQUIMTE – Laboratório Associado para a Química Verde, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal,
**paula.araujo@fc.up.pt*

A cor é o primeiro parâmetro percecionado em muitos produtos, nomeadamente alimentos, bebidas, cosméticos, tecidos entre outros [1]. Além disso, os corantes naturais ou sintéticos desenvolvem um papel crucial ao adicionar valor ao produto final. Do ponto de vista tecnológico, os pigmentos azuis, como é o caso de alguns dos derivados de piranoflavílios, são muito interessantes, uma vez que apresentam propriedades cromáticas estáveis, quando comparados com os seus percursores e além disso desenvolvem uma cor azul (λ_{max}>600 nm). Contudo, as propriedades físico-químicas destas moléculas dependem dos grupos substituintes em solução aquosa, que podem sofrer diversas transformações estruturais, provocadas pelas alterações de pH.

Neste sentido, este trabalho teve como objetivo estudar as constantes cinéticas e termodinâmicas de duas famílias de pigmentos azuis piranoflavílios (Fig.1), sintetizados a partir de 2-(4´-dimetilamino)-5,7-dihidroxibenzopirilio e 2-(4´-dimetillaminoestiril)-5,7-dihidroxibenzopirilio com o ácido 3-(4´-dimethylaminofenil)-prop-3-enoico, por UV-VIS.

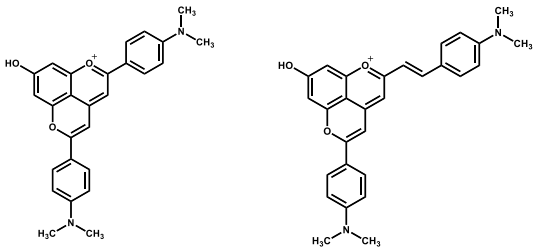


Fig.1. Estrututra dos pigmentos azuis piranoflavilios-4-(dimetilamino)-cinamil.

Agradecimientos
Este trabalho recebeu suporte financeiro da FEDER através dos fundos COMPETE, POPH/FSE, QREN e FCT (Fundação para a Ciência e Tecnologia), por um contrato de bolseiro (SFRH/BPD/84805/2012), um contrato de investigador (IF/00225/2015), e fundos PTDC/QUI-OUT/29013/2017, REDE/1517/RMN/2005. Este trabalho também recebeu suporte financeiro (UID/QUI/50006/2019) com financiamento a partir da FCT/MCTES através de fundos nacionais e programa FEDER-Interreg Espanha-Portugal (projeto referência 0377_IBERPHENOL_6_E).

Referencias
Oliveira. J, Araújo. P, Fernandes. A, Brás. N, Mateus. N, Pina. F, De Freitas. V. Dyes and Pigments 141 (2017) 479-486

Enantiomeric Resolution and Chiroptical Properties of Calix[4]arene-based Chiral Receptors

Patrícia D. Barata,[1,2*] **José V. Prata**[1,2]
[1]Laboratório de Química Orgânica, Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, IPL, R. Conselheiro Emídio Navarro, 1, 1959-007, Lisboa, Portugal; [2]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal.
**pbarata@deq.isel.ipl.pt*

Calix[4]arenes are the most frequently used platforms for the synthesis of inherently chiral calixarenes (ICCs), due to their lower conformational flexibility, well-preorganized bowl-shaped intramolecular cavities, which are particularly valuable for host–guest chemistry. The importance of ICCs is directly associated to their potential applications in chiral recognition processes (*e.g.* as enantioselective sensors, chiral stationary phases for column chromatography, NMR chiral shift reagents), chiral self-assembly, and enantioselective catalysis (as chiral ligands and organocatalysts).[1]
Several examples of non-chiral calixarene applications as highly sensitive and selective sensors towards a variety of organic analytes (*e.g.* explosives, explosive taggants, and aromatic amines) [2,3] and biomolecules (*e.g.* cytochrome c, myoglobin and lysozyme) were reported by us.[4] On other hand, the enantiodiscrimination between (*R*)- and (*S*)-1-phenylethylamine using a bis-calix[4]arene-containing chiral poly(*p*-phenyleneethynylene) possessing main-chain chirality was also investigated.[5]
Recently our group have disclosed through a simple synthetic procedure a new type of luminescent ICCs with planar chirality based on a bicyclic calix[4]arene–oxacyclophane (*e.g.* **CALIX-OCP-CBZs**) and successfully resolved into its enantiomers by chiral HPLC.[1,6]
Herein we report the results concerning the evaluation of **CALIX-OCP-CBZs** chiral nature through ^{1}H NMR studies with (*S*)-Pirkle's alcohol with **CALIX-OCP-CBZs** racemate (***rac*-CALIX-OCP-CBZ**). Additionally, enantiodiscrimination studies of optically pure enantiomers toward chiral analytes, such as racemic hydroxy acids (*e.g.* racemic mandelic acid) will be presented.

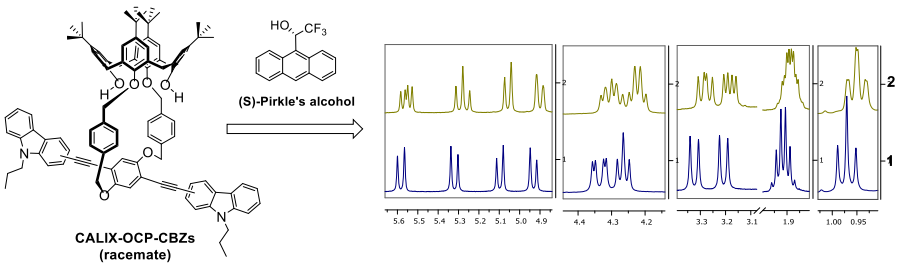


Fig.1. Representative regions of the ^{1}H NMR spectrum of ***rac*-CALIX-OCP-3-CBZ** (5 mM) (**1**) and upon addition of 15 equiv of (*S*)-Pirkle's alcohol (**2**).

Acknowledgements
We thank IPL (Project IPL/2018/INCALIX/ISEL) and FCT/MCTES (UID/QUI/00616/2019) for financial support.

References
[1] J. V. Prata, A. I. Costa, G. Pescitelli, C. M. Teixeira, Tetrahedron: Asymmetry, 25 (2014) 547.
[2] I. Costa, H. D. Pinto, L. F. V. Ferreira, J. V. Prata, Sens. Actuators, B, 161 (2012) 702.
[3] P. D. Barata, J. V. Prata, ChemPlusChem, 79 (2014) 83.
[4] J. V. Prata, P. D. Barata, RSC Adv., 6 (2016) 1659.
[5] J. V. Prata, A. I. Costa, G. Pescitelli, H. D. Pinto, Polym. Chem., 5 (2014) 5793.
[6] J. V. Prata, P. D. Barata, G. Pescitelli, Pure Appl. Chem., 86 (2014) 1819

New Synthetic Approaches for Fluorescent Inherently Chiral Calix[4]arenes

Patrícia D. Barata,[1,2*] Manuel J. Verganista,[1] José V. Prata[1,2]
[1]Laboratório de Química Orgânica, Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, IPL, R. Conselheiro Emídio Navarro, 1, 1959-007, Lisboa, Portugal; [2]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal.
**pbarata@deq.isel.ipl.pt*

Calixarenes are between one of the most investigated macrocyclic scaffolds for molecular recognition. Owing to their well-defined cavity, easiness derivatization of upper and lower rims, and conformational properties, calixarenes are largely known as one of the most valuable classes of synthetic molecular receptors toward neutral and ionic molecular species.[1]

In the past years some different approaches have been developed toward the synthesis of inherently chiral calixarenes (ICCs),[2] including our own synthetic route for the preparation of a new type of luminescent ICCs, whose chirality stems from the presence of a chirality plane in the quinol moiety of the oxacyclophane ring.[3] Additionally, these racemic ICCs were analytically resolved by chiral HPLC affording only small quantities of the enantiopure ICCs, which limited their subsequent use as enantioselective sensors or chiral selectors.

In order to overcome this problem, our main idea includes a new methodology that involves the preparation of diastereomeric derivatives of ICCs, obtained via covalent attachment of appropriate chiral auxiliary (*e.g.* (1*S*)-10-camphorsulphonyl chloride; **CSC**), followed by conventional chromatography separation (*e.g.* flash column, PTLC, or HPLC with non-chiral phases) and removal of chiral auxiliary.

In this communication, we present several synthetic approaches to achieve diastereomeric ICCs (*e.g.* **CALIX-OCP-CBZs**),[4] including attempts toward the direct preparation of diastereomeric derivatives of luminescent ICCs (*e.g.* **CALIX-OCP-CBZ-CSs**) and alternatives routes that includes model chiral mono/disubstituted calixarenes obtained from achiral calixarenes. Synthetic details as well as the NMR of isolated compounds will be discussed.

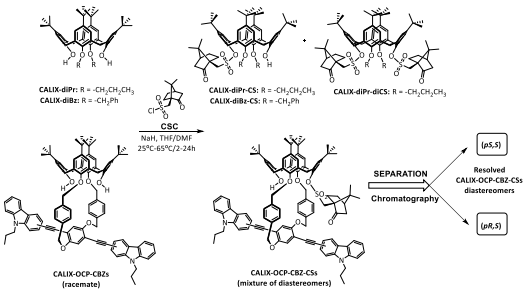


Fig.1. Synthesis and optical resolution attempts of ICCs.

Acknowledgements
We thank IPL (Project IPL/2018/INCALIX/ISEL) and FCT/MCTES (UID/QUI/00616/2019) for financial support.

References

[1] C. D. Gutsche, Calixarenes: An Introduction,2nd ed. – Monographs in Supramolecular Chemistry, J. F. Stoddart (Ed.); The Royal Society of Chemistry: Cambridge, 2008.
[2] S.-Y. Li, Y.-W. Xu, J.-M. Liu, C.-Y. Su, Int. J. Mol. Sci., 12 (2011) 429.
[3] J. V. Prata, A. I. Costa, G. Pescitelli, C. M. Teixeira, Tetrahedron: Asymmetry, 25 (2014) 547.
[4] J. V. Prata, P. D. Barata, G. Pescitelli, Pure Appl. Chem., 86 (2014) 1819.

SÍNTESIS DE EPÍMEROS DE ANÁLOGOS DE SEGUNDA GENERACIÓN DE VITAMINA D

Hugo Santalla[1], Uxía Gómez[1]*, Generosa Gómez[1], Yagamare Fall[1]
[1]Universidade de Vigo, Campus Lagoas Marcosende 36310, Vigo, España
*uxgomez@alumnos.uvigo.es

La 1α, 25-$(OH)_2$-vitamina D_3 posee una importante actividad antiproliferativa con posible uso como agente terapéutico. Sin embargo, las dosis terapéuticas necesarias implican riesgo de hipercalcemia.[1] Se ha promovido la búsqueda de nuevos análogos, surgiendo así la segunda generación de análogos, modificados en la cadena lateral con la finalidad de que sean más selectivos.

Este trabajo se centra en el diseño de una ruta sintética común para la obtención de epímeros en posición C20 de análogos de vitamina D de segunda generación.[2] Desde la ruta inicialmente diseñada para la obtención de análogos de tipo Gémini[3], se puede acceder a la estructura del epímero deseada mediante reducción del grupo hidroxilo en posición C22 del compuesto **3**, tal y como se muestra en el esquema (**Fig. 1**).

Los análogos de vitamina D de segunda generación, algunos de los cuales se comercializan como fármacos, pueden proporcionar mejoras interesantes sobre las propiedades farmacológicas y farmacocinéticas del análogo original.

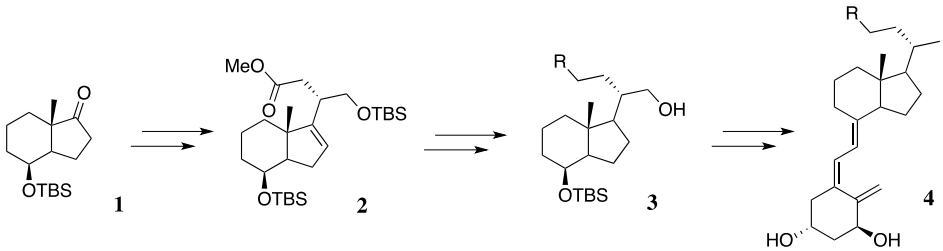


Fig.1. Esquema de síntesis del compuesto **4**.

Referencias

[1] (a) Jones, G.; Strugnell, S. A.; DeLuca, H. F. Physiol. Rev., 78 (1998), 1193. (b) DeLuca, H. F.; Zeierld, C. Nutr. Rev., 56 (1998), 54. (c) Bouillon, R.; Okamura, W. H.; Norman, A. W. Endocr. Rev., 16 (1995), 200.
[2] Santalla, H.; Martínez, A.; Fátima, G.; Gómez, G.; Fall, Y. Org. Chem. Front., 4 (2017), 1999-2001.
[3] Pazos, G. Tesis Doctoral. Universidad de Vigo 2011, 115-163.

QO17

Novel Penicillin-based Sulfones to Unlock Bacterial Resistance to Antibiotics

Esther Colchón Pierna,[1] Concepción González-Bello[1*]

[1] Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Departamento de Química Orgánica, Universidade de Santiago de Compostela, Jenaro de la Fuente s/n, 15782 Santiago de Compostela, Spain.

Contact e-mail: concepcion.gonzalez.bello@usc.es

After many years of success in the battle against infectious diseases, we are now losing ground in this fight with the worldwide increasing appearance of "superbugs", which are resistant to most antibiotics in clinical use. With improvements in the management of chronic diseases and increasingly ageing population, antibiotic resistance is rising to such dangerous levels that the World Health Organization have estimated that it could kill 10 million people per year by 2050.

Among the strategies currently employed for the discovery of novel anti-infective drugs, a great success has been achieved with those approaches that minimize the emergence and impact of resistance to antibiotics by the use of an '*antibiotic adjuvant*' in combination with an antibiotic.[1] Among them, β-lactamase inhibitors are the most successful and clinically used antibiotic adjuvants. In particular, our research group is focused in the inhibition of carbapenem-hydrolyzing class D β-lactamases (CDLDs), which are the most rapidly growing and diverse group of β-lactamases that are found among the most clinically challenging species including *A. baumannii* and *P. aeruginosa*. These enzymes are able to hydrolyze carbapenems, which are the only remaining therapy that is often considered as antibiotics of last resort. It has been proposed that the ability of CDLDs to hydrolyze carbapenems is provided by a tunnel-like entrance to the active site that forms a hydrophobic barrier and controls the access to the active site to only certain substrates.

In our group we are exploring the inhibition of CDLDs by penicillin-based sulfones able to form, after reaction with the catalytic serine of the enzyme, of an aromatic adduct in the active site.[2] This aromatic moiety seems to be able to block the tunnel-like entrance that would protect the enzyme adduct of the subsequent hydrolysis required for catalytic turnover. We present here our recent results in this project.

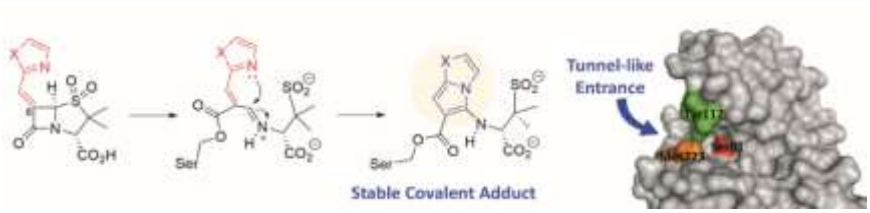


Fig.1. Suggested mechanism for chemical inactivation of CDLDs.

Acknowledgements

Financial support from the Spanish Ministry of Economy and Competiveness (SAF2016-75638-R), the Xunta de Galicia [Centro singular de investigación de Galicia accreditation 2016-2019 (ED431G/09) and ED431B 2018/04] and the European Regional Development Fund is gratefully acknowledged.

References

[1] C. González-Bello, Bioorg. Med. Chem. Lett, 27 (2017) 4221.

[2] K. Coleman, D. R. J. Griffin, J. W. J. Page, P. A. Upshon, Antimicrob. Agents Chemother, 33 (1989), 1580.

Serine-based surfactants: potential drug delivery and antimicrobial agents

Pereira, R.[1], Silva, S.G.[1], Dias, A.R.[1,2,3], Ferraz, R.[1,2], Eaton, P.[1], Pinheiro, M.[4], Reis, S.[4] and Vale, M. L. C[1]

[1] LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Porto (Portugal)
[2] Ciências Químicas e das Biomoléculas, Centro de Investigação em Saúde e Ambiente, Escola Superior de Saúde do Porto, Instituto Politécnico do Porto (Portugal)
[3] Departamento de Biología Funcional y Ciencias de la Salud, Universidad de Vigo, Vigo (Spain)
[4] LAQV/REQUIMTE, Department of Chemistry, Faculty of Pharmacy, University of Porto
sandra.silva@fc.up.pt; mcvale@fc.up.pt

Quaternary ammonium surfactants have shown to present antimicrobial properties; however, their applicability is somewhat limited due to their high cytotoxicity. [1] Therefore, the development of novel cationic amphiphiles having antibacterial activity is of great importance given the existence of bacterial resistance to commercial antibiotics. [2]

Taking advantage of the therapeutic/economic benefits of using the classical antibiotics in current therapies, while attempting to bypass the mechanisms of antibiotic resistance, one possible strategy regards suitable delivery approaches.

Our research group has been devoted to the synthesis and physicochemical evaluation of several serine-based cationic surfactants.[3-5] Herein, we present the results obtained in the evaluation of the *in vitro* antibacterial activity of liposome-forming surfactants, aiming at the establishment of a novel strategy to fight infection: encapsulation of antibiotics in liposomes that show antimicrobial activity *per se*. Biophysical interactions with model lipid membranes were also studied and the results will also be presented.

Acknowledgements
The present work was supported by R&D project UID/QUI/50006/2019 with funding from FCT/MCTES through national funds.

References
[1] Pérez, L., Pinazo, A., Pons, R., Infante, M. R., Adv. Colloids Int. Sci., 205 (2014) 134.
[2] Fair, R. J., Tor, Y., Perpect. Medicin. Chem., 6, (2014) 25.
[3] Silva, S. G., Fernandes, R. F., Marques, E. F., do Vale, M. L. C., Eur. J. Org. Chem. (2012) 345.
[4] Silva, S. G., Alves, C., Cardoso, A. M. S., Jurado, A. S., Pedroso de Lima, M. C., Vale, M. L. C. Marques, E. F., Eur. J. Org. Chem. (2013), 1758.
[5] Silva, S. G., Oliveira, I., Vale, M.L.C., Marques, E. F. Soft Matter,10, (2014) 9352.

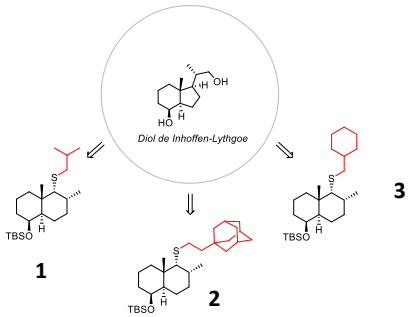
SULFUROS QUIRAIS COMO CATALIZADORES ASIMÉTRICOS

Antonio Obelleiro[1]*, Hugo Santalla[1], Generosa Gómez[1], Yagamare Fall[1]
Universidade de Vigo, Campus Lagoas Marcosende 36310, Vigo, España
**Obelleiro20@gmail.com*

O uso de compostos sulfurados está á orde do día no campo da organocatálise asimétrica, polo que a obtención de sulfuros enantiopuros adquire un gran interese. Estes compostos son principalmente empregados como promotores na epoxidación asimétrica de aldehidos.[1]

A síntese de oxiranos de forma enantioselectiva partindo dun composto cun grupo carbonilo ten dúas rutas principais, unha das cales consiste nunha alquilidación enantioselectiva que permite obter o oxirano desexado en un so paso, onde se poden empregar os sulfuros como catalizadores.[2] Nestas reaccións os sulfuros son inicialmente convertidos a sales de sulfonio que posteriormente se convirten in situ nos correspondentes iluros, que son recuperables de xeito sinxelo tras a reacción.[3]

No contexto do noso interese na síntese estereoselectiva de produtos naturais e análogos con potencial actividade biolóxica, neste traballo amósase a obtención dos sulfuros **1**, **2** e **3** de interese como catalizadores en reaccións de síntese asimétrica. Como substrato inicial empregouse o diol de Inhoffen-Lythgoe de dispoñibilidade comercial.



Esquema 1. Sulfuros obtidos neste traballo sintetizados a partir do diol de Inhoffen-Lythgoe.

Referencias

[1] Lefranc, B.; Valla, A.; Ethiraj, K.; Jaubert, J. N.; Metzner, P.; Brière, J. F. *Synlett* **2008**, No. 11, 1679–1683.

[2] Aggarwal, V. K.; Winn, C. L. Varinder k. Aggarwal* and Caroline l. Winn. *Acc. Chem. Res.* **2004**, *37* (8), 611–620.

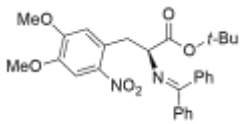
[3] Furukawa, N.; Sugihara, Y.; Fujihara, H. *J. Org. Chem.* **1989**, *54* (17), 4222–4224.

Asymmetric Synthesis of a promising [^{18}F]F-DOPA precursor

Inês C.F. Fonseca[1*], Ângela C.B. Neves[1], Ivanna Hrynchak[1], M. M. Pereira[2], A. J. Abrunhosa[1]

[1]ICNAS/CIBIT - Institute for Nuclear Sciences Applied to Health - University of Coimbra, Pólo das Ciências da Saúde, Azinhaga de Santa Comba, 3000-548 Coimbra, Portugal
[2]Coimbra Chemistry Center, Chemistry Department, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal
**inescffonseca@gmail.com*

6-[^{18}F]-fluoro-L-DOPA ([^{18}F]F-DOPA) has been used for over 30 years as a radiopharmaceutical for the evaluation of the presynaptic dopaminergic system in the human brain using Positron Emission Tomography (PET), allowing the investigation of several central nervous system disorders, such as schizophrenia and Parkinson's disease. Generally, [^{18}F]F-DOPA can be produced via nucleophilic methods, even though these processes implicate a complex chemistry with multiple steps, long reaction times (2h) and moderate yields. Among these nucleophilic processes, one approach is the enantioselective synthesis from no-carrier-added [^{18}F]F$^-$, which involves the radiolabelling of 6-nitroveratraldehyde, followed by the reaction with a chiral phase transfer catalyst and a Schiff base, forming an intermediary compound that is then hydrolysed. [1,2] In order to optimize the [^{18}F]F-DOPA synthesis, the main goal of this work was to synthesize new organic precursors, that can be radiolabelled with ^{18}F$^-$ and hydrolysed, originating [^{18}F]F-DOPA with good yields.
For this purpose, we transposed the enantioselective synthesis strategy into a reaction of asymmetric phase-transfer catalysis to achieve the alkylation of a glycinate Schiff's base using a chiral phase transfer catalyst, namely chiral quaternary cinchonidinium salt.[3] This type of reactions are advantageous as they require simple experimental procedures, mild conditions, inexpensive and environmentally friendly reagents and solvents and the possibility of conducting large-scale preparations.[4]
Product **1** (Fig. 1) was synthesized through the reaction of 4,5-dimethoxy-2-nitrobenzyl bromide with N-(diphenylmethylene)glycine tert-butyl ester, O-allyl-N-(9-anthracenylmethyl)cinchonidinium bromide and CsOH.H_2O (aq.) in toluene, with the addition of a catalytic amount of potassium iodide. The reagents stoichiometry, CsOH.H_2O (aq.) solution concentration, reaction times and temperatures were optimized. Product was obtained with a yield of 23% and was further characterized through ^{1}H, ^{13}C and two-bidimensional NMR spectroscopy, infra-red spectroscopy, HPLC and HPLC-MS.
Even though the yields were low, we expect that further optimization could improve them. Also, further radiolabelling studies with ^{18}F and optimization of the radiolabelling process is crucial in order to obtain [^{18}F]F-DOPA with higher yields.



1

Fig.1. Chemical structure of the synthesized product **1**.

Acknowledgments
The authors wish to thank the financial support from Program COMPETE 2020 through project DOPAPET-DCP: POCI-01-0247-FEDER-023474.

References

[1] M. Pretze, C. Wängler, B. Wängler, BioMed Research International, 2014 (2014) 1.
[2] L. C. Libert, X. Franci, A. R. Plevenaux, T. Ooi, K. Marouka, A. J.Luxen, C. F. Lemaire, The Journal of Nuclear Medicine 54 (2013) 1154.
[3] T. Ooi, K. Marouka, Angew. Chem. Int. Ed., 46 (2007) 4222.
[4] Handbook of Phase Transfer Catalysis. Y. Sasson, Y., R. Neumann, Ronny (Eds.), London, Blackie Academic & Professional, 1997.

Extração, isolamento e transformação química da lenhina proveniente da lenha da videira

Ana Rita Pereira*, **Paula Araújo, Iva Fernandes, Nuno Mateus, Victor de Freitas, Joana Oliveira**

REQUIMTE – Laboratório Associado para a Química Verde, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal
**anarita@fc.up.pt*

A lenhina é um polímero fenólico natural, de elevado peso molecular, presente nas paredes das células vegetais. É o segundo polímero mais abundante na natureza, representando em média 10%-25% da biomassa das plantas terrestres[1]. Trata-se de uma macromolécula tridimensional complexa, formada a partir da polimerização de diferentes álcoois: álcool p-cumarílico, álcool sinapílico e o álcool coniferílico (fig.1). A presença dos distintos grupos funcionais e a sua estrutura aromática conferem-lhe uma vasta aplicação industrial, nomeadamente em adesivos, dispersantes, surfactantes, espumas e resinas[2]. A estrutura e as propriedades dos diferentes tipos de lenhina diferem da sua origem, das condições de polpação e dos métodos de isolamento aplicados[3].
Desta forma, o objetivo do trabalho foi extrair e isolar a lenhina proveniente da lenha da videira e proceder à sua transformação química por glucosilação com acetobromo-α-D-glucose, de forma a aumentar a sua solubilidade em soluções aquosas.

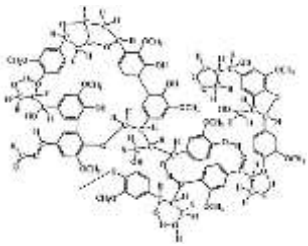


Fig.1. Estrutura química da lenhina

Agradecimentos

Este trabalho recebeu apoio financeiro dos fundos FEDER através do COMPETE, POPH/FSE, QREN, e FCT (Fundação para a Ciência e Tecnologia) por uma bolsa pós-doutoral (SFRH/BPD/84805/2012), um contrato de investigador (IF/00225/2015), and grants PTDC/QUI-OUT/29013/2017, REDE/1517/RMN/2005. Este trabalho também recebeu apoio financeiro (UID/QUI/50006/2019 - POCI/ 01/0145/FEDER/007265) da FCT/MEC através de fundos nacionais e foi co-financiado pela FEDER, no âmbito do acordo da parceria PT2020 e o programa FEDER-Interreg Espanha-Portugal (projecto ref 0377_IBERPHENOL_6_E).

Referências

[1] P. Araujo, N. Basilio, J. Azevedo, A. Fernandes, N. Mateus, F. Pina, V. de Freitas and J. Oliveira, *Dyes and Pigments* 2018, *153*, 150-159.
[2] P. C. R. Pinto, C. Oliveira, C. A. E. Costa and A. E. Rodrigues, *Industrial & Engineering Chemistry Research* 2016, *55*, 516-526.
[3] P. Araujo, A. Costa, I. Fernandes, N. Mateus, V. De Freitas, B. Sarmento and J. Oliveira, *Dyes and Pigments* 2019, *166*, 367-374.

Disarming *Pseudomonas aeruginosa* by Modulators of the Master Regulator of Quorum Sensing LasR

Ángela Rodríguez,[1] Concepción González-Bello[1]*

[1]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), Departamento de Química Orgánica, Universidade de Santiago de Compostela, Jenaro de la Fuente s/n, 15782 Santiago de Compostela, Spain

*e-mail: *angela.rodriguez.costa@gmail.com*

In recent years a great deal of effort has been devoted to the development of alternative therapies that target the bacterial pathogenicity.[1] This approach reduces the capacity of the bacterium to cause infection and, in consequence, it is cleared by the host immune system. Anti-virulence drugs will therefore disarm bacteria and will create an *in vivo* scenario similar to that achieved by vaccination with a live attenuated strain. The bacterial infection mechanism is based on a sophisticated cell-cell communication system known as Quorum Sensing (QS) that relies on the activation of receptor proteins by small diffusible molecules, and which results in the regulation of important cellular processes including virulence, antibiotic resistance and biofilm formation. This phenomenon is particular relevant in *Pseudomonas aeruginosa,* which is one of the three most critical, common and highly antibiotic-resistant nosocomial pathogens in the world. The master regulator of QS in *P. aeruginosa* is the LasR transcriptional receptor that has recently garnered significant interest as an attractive new therapeutic target for the development of antagonists of QS (namely Quorum Quenching, QQ) as treatments of a variety of human infections caused by this pathogen.[2] It is believed that the binding of the cognate ligand, *N*-(3-oxododecanoyl)-homoserine lactone (C12-AHL), to the ligand binding domain triggers a conformational change in the polypeptide, presumably enabling the binding of the protein to specific promoters leading to transcriptional activation of QS genes. Based on the latter, in this project the development of analogues of the natural autoinducer C12-AHL that will be able to deactivate the QS gene expression in *P. aeruginosa* by the formation of complexes LasR/ligand of inappropriate conformation for binding with specific promoters is proposed. Our recent results in this project will be presented.

Fig.1. Schematic representation of the QS and QQ processes. LB = ligand binding domain. DB = DNA binding domain.

Acknowledgements
Financial support from the Spanish Ministry of Economy and Competiveness (SAF2016-75638-R), the Xunta de Galicia [Centro singular de investigación de Galicia accreditation 2016-2019 (ED431G/09) and ED431B 2018/04] and the European Regional Development Fund is gratefully acknowledged. AR acknowledges the Spanish Ministry of Science, Innovation and Universities for her predoctoral and FPI fellowship.

References

[6] A. E. Clatworthy, E. Pierson, D. T. Hung, Nature Chem. Biol, 3 (2007) 541.
[7] R. C. Allen, R. Popat, S. P. Diggle, S. P. Brown, Nature Rev. Microbiol, 12 (2014) 300.

New pathways for paroxetine synthesis and nitration of the sesamol group for antibody binding.

J. Santos[a], **A. J. Rodrigues**[b]; **P. Patrício**[b]; **H. S. Domingues**[c]; **M. F. Proença***[a]
[a] Center of Chemistry, Campus de Gualtar, Universidade do Minho,
4710 -057 Braga, Portugal; pg33718@alunos.uminho.pt.
[b] Life and Health Sciences Research Institute (ICVS), School of Medicine,
University of Minho, Campus of Gualtar, Braga, Portugal;
[c] ICVS/3B's - PT Government Associate Laboratory,
Braga/Guimarães, Portugal;
*fproenca@quimica.uminho.pt

Major depression is a common but serious mood disorder. This disorder is characterized by a persistent feeling of sadness or a lack of interest in outside stimuli. Between 2–8% of adults with major depression die by suicide. Antidepressant drugs are the first line treatment for depression. However approximately one third of depressed patients do not respond to treatment and high relapse rates have been observed for this disorder.

Paroxetine **1** is the most potent and one of the most specific selective serotonin reuptake inhibitors (SSRIs) used to treat depression. This molecule is metabolized by the enzyme CYP2D6, involving oxidation, methylation, and conjugation. All these factors lead to wide interindividual variation in the pharmacokinetics of paroxetine and, consequently, to variations in response to treatment as side effects. Thus, it is crucial to develop new tools to evaluate paroxetine metabolization to predict patient's response.

A research group of the Medical School at UMinho is interested in developing an antibody that binds to paroxetine in blood samples. To create this antibody, it is necessary to prepare substituted paroxetine derivatives, such as the amino-substituted paroxetine **2**. The work in progress deals with the synthesis the nitro-substituted paroxetine **3**, where the nitro group can be used as a precursor of the amino group, upon reduction. The synthetic approach designed for the preparation of this compound will be presented and the experimental results currently obtained will also be discussed.

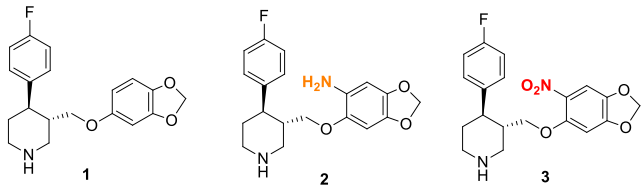


Figure 1. Structure for Paroxetine **1** and the amino- and nitro-substituted paroxetine derivatives **2** and **3**, respectively.

Acknowledgments:
We acknowledge the financial support from UMinho and ICVS (Life and Health Sciences Research Institute). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network (RNRMN) was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

References:
[1] Davis, B. A.; Nagarajan, A.; Forrest, L. R.; Singh, S. K. Mechanism of Paroxetine (Paxil) Inhibition of the Serotonin Transporter. Sci. Rep. **2016**, *6*, 1–13.
[2] Despiau, C. F.; Dominey, A. P.; Harrowven, D. C.; Linclau, B. Total Synthesis of (±)-Paroxetine by Diastereoconvergent Cobalt-Catalysed Arylation. European J. Org. Chem. **2014**, No. 20, 4335–4341.
[3] Zhang, Y.; Liao, Y.; Liu, X.; Yao, Q.; Zhou, Y.; Lin, L.; Feng, X. Catalytic Michael/Ring-Closure Reaction of α,β-Unsaturated Pyrazoleamides with Amidomalonates: Asymmetric Synthesis of (−)-Paroxetine. Chem. - A Eur. J. **2016**, *22* (42), 15119–15124.

Design and synthesis of a novel family of serine-derived surfactants: the serine Ester-Quats

Silva, S.G., Pereira, C. and Vale, M. L. C.
LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Porto Portugal
sandra.silva@fc.up.pt; mcvale@fc.up.pt

Conventional surfactants have proved to be highly promising in delivering genetic material to cells, as additives in formulations for drug delivery and as antimicrobial agents.[1] However, they often exhibit relatively high levels of cytotoxicity which is detrimental to their use in biomedical and pharmaceutical applications. In the last two decades, considerable efforts have been made to synthesize novel surfactants, possessing enhanced toxicological profiles, by inclusion of natural synthons (like amino acids) into their molecular structure. [2]

In this context, our research team has been engaged in the synthesis and evaluation of the physicochemical and biological properties of serine-based monomeric and dimeric surfactants. [3-5] Herein we present the synthetic methodologies followed for the obtention of a novel family of gemini surfactants designated as serine Ester-Quats.

Acknowledgements
The present work was supported by R&D project UID/QUI/50006/2019 with funding from FCT/MCTES through national funds.

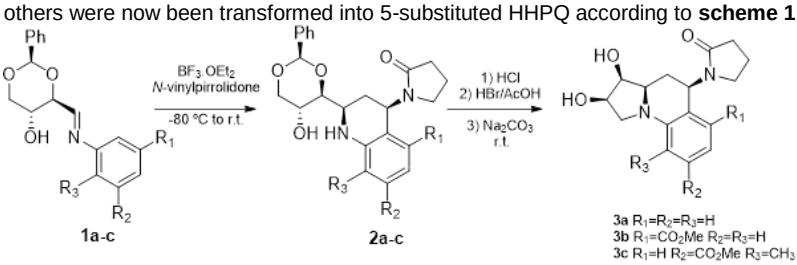
References

[1] a) Donkuru, M., Badea, I., Wettig, S., Verral, R., Elsabahy, M. Foldvari, M., Nanomedicine, 5 (2010) 1103. b) Savić, S., Tamburić, S., Savić, M. M. *Exp.* Opin. Drug Deliv., 7 (2010) 353.
[2] Holmberg, K., Curr. Opin. Colloid Interface Sci.,6, (2001), 148.
[3] Silva, S. G., Rodríguez-Borges, J. E., Marques, E. F., do Vale, M. L. C., Tetrahedron, 65 (2009) 4156.
[4] Silva, S. G., Fernandes, R. F., Marques, E. F., do Vale, M. L. C., Eur. J. Org. Chem. (2012) 345.
[5] Silva, S. G., Alves, C., Cardoso, A. M. S., Jurado, A. S., Pedroso de Lima, M. C., Vale, M. L. C. Marques, E. F., Eur. J. Org. Chem. (2013) 1758

Stereoselective synthesis of 5-substituted hexahydropyrroquinolines-2,3-diol from functionalized tetrahydroquinolines.

Artem Drogalin[1,*], Maria José Alves[1], Tarsila G. Castro[2]
[1]Universidade do Minho, Departamento de Química, Braga, Portugal
[2]Universidade do Minho, Centro de Engenharia Biológica, Braga, Portugal
**e-mail del autor de contacto: pg33723@alunos.uminho.pt*

1,2,3,4-Tetrahydroquinolines (THQ) had shown diverse biological activities such as antiarrhythmic, cardiovascular, anticancer and immunosuppressor agents [1]. In this work tetrahydroquinolines **2** were synthesized by Povarov's reaction [3] from Schiff base **1**, being subsequently cyclized to hexahydropyrroquinolines-2,3-diol (HHPQ) **3a-c** using trivial reagents**.** Some new THQ bearing a trihydroxypropyl arm have already been synthetized. Those and others were now been transformed into 5-substituted HHPQ according to **scheme 1**. [2]



Scheme 1. Synthesis of tetrahydroquinolines of type **2**, and its further cyclization into hexahydropyrroquinolines

The synthetic process consists in: 1) *in situ* condensation of *m*-substituted anilines containing electron-withdrawing groups or aniline itself to D-erythrose; 2) cycloaddition of the obtained Schiff base **1**, with electron-rich *N*-vinylpyrrolidone in the presence of BF_3.etherate (0.3 eq.) giving **2a-c** compounds; 3) acetal cleavage, bromination of terminal hydroxyl, and amino-cyclization to give final products **3a-c**. A single cycloadduct was obtained when R_1=CO_2Me in yield 44%; two structural isomers were obtained in cases where larger alkyl groups are present in the ester function [4]. To guide the ester group into the position where R_2 is in **2c**, an *ortho-meta* substituted aniline was used.

Docking studies shed light on the interaction patterns of compounds of type **3** to Golgi α-mannosidase II and lysosomal α-mannosidases. These results represent a starting point in the rational design of type **3** based molecules towards selective Golgi α-mannosidase inhibition, assisted by molecular modelling techniques.

Acknowledgments: NMR Portuguese network (PTNMR, Bruker Avance III 400-Univ. Minho), and FCT and FEDER (European Fund for Regional Development)-COMPETE-QREN-EU for financial support to CQ/UM. Search-ON2: Revitalization of HPC infrastructure of UMinho, (NORTE-07-0162-FEDER-000086), co-funded by the North Portugal Regional Operational Programme (ON.2-O Novo Norte), under the National Strategic Reference Framework (NSRF), through the European Regional Development Fund (ERDF).

References:

[1] Vallaisamy S., Suryavanshi P. A., Mendez J. C., *Chem. Rev.* **2011**, 111, pg. 7160;
[2] Drogalin A., Alvés M. J., Fortes A. G., (November 2018) *Synthesis of functionalized tetrahydroquinolines, and its further transformation into hexahydropyrroloquinoline-2,3-diol by aminocyclization.* Poster session presented at the XXIV Encontro Luso-Galego de Química;
[3] Povarov L. S., Mikhailov B. M. *Izv. Akad. Nauk SSR, Ser. Khim.* **1963**, 953–956;
[4] Drogalin A., Alvés M. J., (May 2019) *Regio-selectivity studies of D-erythrosyl 4-substituted-phenylimines in Povarov's reaction with N-vinylpyrrolidone in the synthesis of Swainsonine precursors.* Poster session presented at the 4th Symposium on Medicinal Chemistry of the University of Minho

QUIMICA Y SALUD

Nanopartículas lipídicas como transportadores de compostos derivados das antocianinas para aplicação tópica

Alexandra Borges[1*], Paula Araújo[1], Ana Rita Pereira[1], Nuno Mateus[1], Victor de Freitas[1], Iva Fernandes[1], Joana Oliveira[1]

[1]REQUIMTE-LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre SN, 4169-007, Porto, Portugal

**alexandraborgespnf@gmail.com*

As antocianinas são moléculas produzidas pelo metabolismo secundário das plantas, estão presentes em diversos alimentos e bebidas de origem vegetal e têm um papel importante na coloração, crescimento celular e regulação da maturação. Diferentes atividades benéficas para a saúde humana têm sido atribuídas a estes pigmentos, incluindo propriedades antioxidantes e antimutagénicas. As cores vibrantes (do vermelho ao azul) apresentadas por estas moléculas fazem delas um alvo de interesse para as indústrias alimentares e cosméticas. No entanto, em soluções aquosas as antocianinas são muito instáveis podendo estar presentes em diferentes formas de equílibrio cuja cor depende do pH do meio, o que dificulta a sua aplicação a diferentes matrizes. Ao longo dos anos têm sido identificados diferentes pigmentos derivados das antocianinas, moléculas mais estáveis em sistemas aquosos e que têm vindo a despertar o interesse da indústria podendo representar uma boa alternativa aos corantes sintéticos.
O objetivo deste trabalho é preparar diferentes nanopartículas lipídicas (SLN e NLC) e verificar a sua eficácia como transportadores de compostos derivados de antocianinas com vista a aplicação tópica dos mesmos. As nanopartículas serão preparadas por sonicação com diferentes lípidos em que se irá analisar a influência da percentagem de surfactante, o tempo de sonicação e a intensidade de sonicação nos tamanhos, polidispersividade e potencial zeta das nanopartículas.

Agradecimentos
This work received financial support from FEDER funds through COMPETE, POPH/FSE, QREN, and FCT (Fundação para a Ciência e Tecnologia) by a research contract (SFRH/BPD/84805/2012), an investigator contract (IF/00225/2015), and grants PTDC/QUI-OUT/29013/2017, REDE/1517/RMN/2005. This work also received financial support (UID/QUI/50006/2019) with funding from FCT/MCTES through national funds and FEDER-Interreg España-Portugal Programme (project ref 0377_IBERPHENOL_6_E).

Referencias

[1] Oliveira, J., et al. (2017). "Wine-Inspired Chemistry: Anthocyanin Transformations for a Portfolio of Natural Colors." Synlett 28X. Author, Y. Author, Z. Author, Proc. of congress name, City, Country, 2014, 10.
[2] Garces, A., et al. (2018). "Formulations based on solid lipid nanoparticles (SLN) and nanostructured lipid carriers (NLC) for cutaneous use: A review." Eur J Pharm Sci 112: 159-167X. Author, Y. Author, Z. Author, in Book name, X. Editor, Y. Editor, Z. Editor (Eds.), City, Publisher, 2011, 10.
[3] [3] Fang, Z. and B. Bhandari (2010). "Encapsulation of polyphenols – a review." Trends in Food Science & Technology 21(10): 510-523.

Recubrimiento antibacterial de una superficie de Ti6Al7Nb para implantes biomédicos

R. García[1*], J. Fernández[2], O. Castaño[3], N.García[4], J.Lorenzo[5]
[1]Universitat de Barcelona, Facultat de Química, Barcelona, Spain *[raisha.garcia@ub.edu]*
[2]Universitat de Barcelona, Facultat de Química, Barcelona, Spain *[javier.fernandez@ub.edu]*
[3]Institute for Bioengineering of Catalonia (IBEC), Barcelona, Spain *[oscar.castano@ub.edu]*
[4]IMIM (Hospital del Mar Medical Research Institute), Barcelona, Spain *[ngarcia@imim.es]*
[5]Universitat Autónoma de Barcelona (UAB), Cerdanyola del Valles, Spain *[julia.lorenzo@uab.es]*

En España se insertan anualmente 30.000 implantes ortopédicos de cadera[1,2]. Después de la cirugía, la probabilidad de infección de estos implantes es de entre 2-5%[3]. Cada año la sanidad pública invierte más de 40 millones de euros en el tratamiento de infecciones nosocomiales implantologicas[45].

Este proyecto pretende desarrollar recubrimientos antibacteriales para implantes de Ti6Al7Nb[6,7] mediante el uso de péptidos antimicrobianos (AMPs) como compuesto antibacterial. Los péptidos antimicrobianos son biomoléculas sintetizadas por un gran número de organismos y tienen un espectro de acción muy amplio. KR-12 es un péptido sintético que contiene los residuos 18-29 de LL-37, proteína de la familia de la cathelicidina, que juega un papel esencial en el sistema inmunológico de los mamíferos.

Mediante el uso de CPTES (3-cloropropil)trietoxisilano se puede generar un enlace covalente entre el sustrato y el compuesto antimicrobial[8–10]. Mediante esta estrategia se pretende reducir los efectos adversos generados por el poco control de la liberación de los compuestos citotóxicos[11].

La eficiencia de funcionalización se ha estudiado mediante medidas de rugosidad, ángulo de contacto, la composición elemental del recubrimiento por XPS. Las propiedades antibacteriales de las muestras funcionalizadas se han determinado contra Staphylococcus aureus (SAU). Se ha realizado un estudio de citotoxicidad usando células osteoblásticas humanas obtenidas después de una artroplastia de rodilla.

Se ha realizado exitosamente la funcionalización de las muestras. Se ha observado una reducción de la proliferación de Staphylococcus aureus en un 60% con la incorporación del péptido antimicrobiano KR-12. Los resultados obtenidos no muestran problemas de citotoxicidad in-vitro en contra de células osteoblásticas humanas.

Referencias

1. Niinomi M. Recent metallic materials for biomedical applications. *Metall Mater Trans A*. 2002;33(3):477-486.
2. Chen Q, Thouas GA. Metallic implant biomaterials. *Mater Sci Eng R Reports*. 2015;87:1-57. doi:10.1016/J.MSER.2014.10.001
3. Peivandi MT, Yusof-Sani SMR, Amel-Farzad H. Exploring the reasons for orthopedic implant failure in traumatic fractures of the lower limb. *Arch Iran Med*. 2013;16(8):478-482.
4. Darouiche RO. *Device-Associated Infections: A Macroproblem That Starts with Microadherence*. Vol 33.; 2001. https://academic.oup.com/cid/article-abstract/33/9/1567/1746437.
5. Kapadia BH, Berg RA, Daley JA, Fritz J, Bhave A, Mont MA. Periprosthetic joint infection. *Lancet*. 2016;387(10016):386-394.
6. Matlakhova LA, Matlakhov AN, Monteiro SN, Fedotov SG, Goncharenko BA. Properties and structural characteristics of Ti-Nb-Al alloys. *Mater Sci Eng A*. 2005;393(1-2):320-326.
7. Fellah M, Labaïz M, Assala O, et al. Tribological behavior of Ti-6Al-4V and Ti-6Al-7Nb Alloys for Total Hip Prosthesis. *Adv Tribol*. 2014;2014.
8. Hermanson GT, Hermanson GT. Silane Coupling Agents. *Bioconjugate Tech*. 2013:535-548.
9. Gabriel M, Nazmi K, Veerman EC, Amerongen AVN, Zentner A. Preparation of LL-37-grafted titanium surfaces with bactericidal activity. *Bioconjug Chem*. 2006;17(2):548-550. doi:10.1021/bc050091v
10. Zhou L, Lin Z, Ding J, Huang W, Chen J, Wu D. Inflammatory and biocompatibility evaluation of antimicrobial peptide GL13K immobilized onto titanium by silanization. *Colloids Surfaces B Biointerfaces*. 2017;160:581-588. doi:10.1016/j.colsurfb.2017.10.007
11. Kazemzadeh-Narbat M, Lai BFL, Ding C, Kizhakkedathu JN, Hancock REW, Wang R. Multilayered coating on titanium for controlled release of antimicrobial peptides for the prevention of implant-associated infections. *Biomaterials*. 2013;34(24):5969-5977. doi:10.1016/j.biomaterials.2013.04.036

Use of Phenanthroline Derivatives in Chemotherapy Treatments for Cancer and as Alternative Therapeutics in the Era of Antibiotic Resistance: Interaction with DNA and Modulation of the Efficiency

Adrià Gil[1,2*], Ángel Sánchez-González[1], Iker Ortiz de Luzuriaga[2,3], Sawssen Elleuchi[4], Khaled Jarraya[4], Xabier Lopez[3,5], Maria José Calhorda[1]

[1]BioISI – Biosystems and Integrative Sciences Institute, DQB, Faculdade de Ciências, Universidade de Lisboa, Campo Grande 1749-016, Lisboa, Portugal

[2]CIC Nanogune, Tolosa Hiribidea 76, 20018, Donostia – San Sebastian, Basque Country, Spain

[3]Universidad del País Vasco / Euskal – Herriko Unibertsitatea, Facultad de Ciencias Químicas, Donostia – San Sebastián, Basque Country, Spain

[4]University of Sfax, Laboratory of Inorganic Chemistry, Sfax, Tunisia

[5]DIPC – Donostia International Physics Center, Computational Chemistry and Physical Chemistry, Donostia – San Sebastián, Basque Country, Spain

*agmestres@fc.ul.pt; a.gil@nanogune.eu

Flat ligands, alone or within metal complexes, are active against tumor cells and may be used in chemotherapy. The activity of these drugs is related to their mode of interaction with DNA being the intercalation mode identified as the cytotoxic mode against tumor cells.[1] 1,10-phenanthroline (phen) was demonstated to be effective towards several tumor cell lines,[2] and their derivatives also showed cytotoxicity. Moreover, it was observed that this cytotoxicity was deeply connected to the number and position of the functional groups incorporated in phen.[1] Different studies on the intercalation of small molecules in DNA have appeared in the bibliography during the last years[3],[4] and some debate still remains about the intercalation/deintercalation process[3],[4] and the mechanism that could explain the modulation of the cytotoxicity. In our work, we try to rationalize the role of weak interactions with the stability of the interaction and we extrapolate our results to the cytotoxic effects. The systems were mainly optimized by using semiempirical methods including dispersión effects. We also carried out DFT calculations including dispersion effects for the Energy Decomposition Analysis (EDA) and to perform the Quantum Theory of Atoms in Molecules (QTAIM) and the Non-Covalent Interaction (NCI) analyses to obtain topological pictures of the weak interactions that rule the intercalation process. Solvent effects were also taken into account by continuum approaches. Our results confirm the importance of weak interactions and we extrapolate the link with the cytotoxicity by means of a subtle balance between the stabilizing weak interactions and the destabilizing steric contribution (Fig. 1). The role of desolvation energy is also crucial when looking at the stability of the studied systems.

Fig.1. Attractive (green) and repulsive (red) interactions for the 5,6-Me_2phen and 3,4,7,8-Me_4phen ligands intercalated between GC/CG base pairs via the Minor Groove.

Acknowledgements

We thank the Fundação para a Ciência e Tecnología for financial support by means of the project PTDC/QUI-QFI/29236/2017. A. G. is thankful to Diputación de Gipuzkoa for current funding in the frame of Gipuzkoa Fellows program

References

[1] C. R. Brodie, J. R. Collings, J. R. Aldrich-Wright, Dalton Trans., 2004 (2004) 1145.
[2] D. Bandarra, M. Lopes, T. Lopes, J. Almeida, M. A. Saraiva, M. V. Días, C. D. Nunes, V. Félix, P. Brandão, P. D. Vaz, M. Meireles, M. J. Calhorda, J. Inorg. Biochem., 104 (2010) 1171.
[3] Mukherjee, W. D. Sasikala, Adv. Protein Chem. Struct. Biol. 92 (2013) 1.
[4] V. Vargiu, A. Magistrato, ChemMedChem 9 (2014) 1966.

The effects of *N*-alkyl chain length on the physicochemical and *in vitro* phototherapeutic properties of squaraine cyanine dyes

Eurico Lima[1,*], Octávio Ferreira[2], Adriana O. Santos[2], Renato E. Boto[2], José R. Fernandes[1], Paulo Almeida[2], Samuel M. Silvestre[2], Lucinda V. Reis[1]

[1] Chemistry Centre of Vila Real (CQ-VR), University of Trás-os-Montes and Alto Douro, Vila Real, Portugal
[2] Health Sciences Research Centre (CICS-UBI), University of Beira Interior, Covilhã, Portugal

**eurico_lima@icloud.com*

Photodynamic therapy (PDT) is a promising noninvasive approach for the treatment of oncological and nononcological diseases by combining photosensitizer, triplet molecular oxygen and suitable light, which has attempted to address the shortcomings and disadvantages of conventional cancer therapies. Photosensitizers used in this medical procedure should have several properties, such as innocuity in the absence of light and high photocytotoxicity and high singlet oxygen formation ability [1]. As candidates for PDT photosensitizers, squaraine cyanine dyes are a core of dyes of particular interest given their intense and sharp absorption bands at long-wavelengths and moderate singlet oxygen production ability [2].

The aim of this work was the synthesis and spectroscopic characterization of symmetrical squaraine cyanine dyes derived from indolenine, as well as the evaluation of the influence of the *N*-alkyl chain length (*N*-ethyl and *N*-hexyl chains) in their potential use as PDT photosensitizers and their photophysical properties. The compounds were obtained in moderate yields according to procedures adapted from the literature [3] and were fully characterized by ^{1}H and ^{13}C-NMR, IR, Vis, HRMS and m.p. techniques. To evaluate its singlet oxygen formation ability, 1,3-diphenylisobenzofuran (DPBF) assay was used, in which its decay was assessed over 40 minutes. The degeneration of the compounds when exposed to light was also analyzed to evaluate its photostability. In order to evaluate their *in vitro* phototherapeutic effect, 3-[4,5-dimethylthiazole-2-yl]-2,5-diphenyltetrazolium bromide (MTT) assay and flow cytometry with propidium iodide as a probe were the methodologies used. As *in vitro* models, tumor (Caco-2, MCF-7 and PC-3) and non-tumor cell lines (NHDF) were used. The intracellular location of the dyes was also determined by confocal microscopy using the Hoescht 33342 and Rhodamine 123 probes.

Both dyes displayed strong absorption within the tissue transparency spectral region (600-850 nm), moderate to good photostability, and great singlet oxygen production ability. It is noteworthy that both dyes showed high photodynamic activity and, interestingly, tumor selectivity effects. While the dye with *N*-ethyl chains showed selective cytotoxic effects for the PC-3 cell line, the N-hexyl chain dye showed against the Caco-2 cell line. Cell localization studies indicate that indolenine-based dyes should be within a cytoplasmatic organelle, however, only partial colocalization of the mitochondrial-specific probe and dye-emitting fluorescence was observed.

Acknowledgments

We acknowledge the European Investment Funds by FEDER/COMPETE/POCI under projects and POCI-01-0145-FEDER-007491 (CICS-UBI) and Funds by FCT – Portuguese Foundation for Science and technology, under the project UID/QUI/UI0616/2019 (CQ-VR). This work was also supported by funds from the Health Sciences Research Center (CICS-UBI) through National Funds by FCT – Foundation for Science and Technology (UID/Multi/00709/2019).

Referencias

[1] P. Agostinis, K. Berg, K. A. Cengel, T. H. Foster, A. W. Girotti, S. O. Gollnick, S. M. Hahn, M. R. Hamblin, A. Juzeniene, D. Kessel, M. Korbelik, J. Moan, P. Mroz, D. Nowis, J. Piette, B. C. Wilson, J. Golab, CA: A Cancer Journal for Clinicians, 61 (2011) 250-281
[2] E. Lima, O. Ferreira, V. S. D. Gomes, A. O. Santos, R. E. Boto, J. R. Fernandes, P. Almeida, S. M. Silvestre, L. V. Reis, Dyes and Pigments, 167 (2019) 98-108.
[3] L. V. Reis, J. P. Serrano, P. Almeida, P. F. Santos, Dyes and Pigments, 81 (2009) 197-202

Estudio comparativo de la citotoxicidad en células de cáncer de pulmón A549 del efecto del grupo funcional enlazado al anillo piridoxal del ligando en complejos de vanadio.

Lucía Mato-López[1], Antía Sar[1], Miguel Riopedre[1], Josefina Méndez[1], Natalia Fernández-Bertólez[2], Fernando Avecilla[1], Vanessa Valdiglesias[2]

[1]Grupo XENOMAR, Centro de Investigaciones Científicas Avanzadas (CICA), As Carballeiras s/n, Campus de Elviña, 15071, A Coruña, España. l.mato@udc.es
[2]Grupo DICOMOSA, Departamento de Psicología, Facultad de Ciencias de la Educación, Campus de Elviña, 15071, A Coruña, España.

En este trabajo se hace un estudio comparativo del efecto citiotoxico de cuatro compuestos de vanadio y sus estructuras. Los compuestos fueron obtenidos mediante la ruta sintética descrita por Maurya et al.[1]. Estos complejos presentan diferentes ligandos hidrazona derivados de piridoxal que contienen un anillo fenílico funcionalizado con diferentes grupos en las posiciones "*meta*" o "*para*". Los esquemas de los compuestos del estudio se observan en la figura 1 en la que se observa las diferentes especies aisladas y caracterizadas.

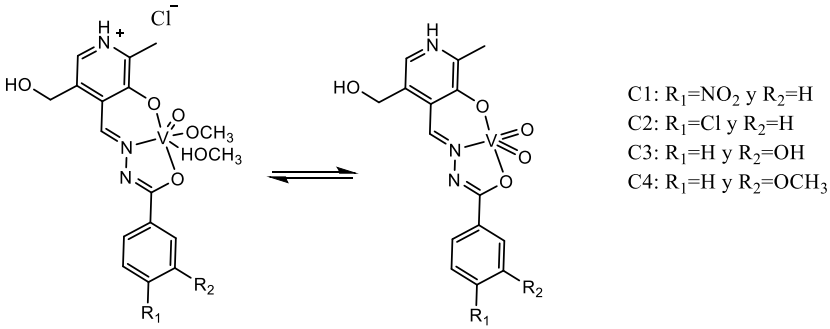


Fig. 1. Esquema de los compuestos de vanadio con ligandos derivados de piridoxal $[V^VO(HL)(MeOH)(OMe)]Cl$(izda) y $[V^VO_2(HL)]$(dcha)

La determinación de la citotoxicidad se estudia mediante un ensayo colorimetrico de MTT (3-(4,5-dimetiltiazol-2-ilo)-2,5-difeniltetrazol)[2]. La realización de los ensayos biológicos se llevó a cabo con células cancerígenas de pulmón (línea celular A549). Se realizaron tratamientos con un tiempo de exposición de 48h testando dosis de 0,1-500µM. Los resultados mostraron un descenso de viabilidad celular significativo a las concentraciones más elevadas. Para los complejos que presentan el grupo funcional enlazado en posición "*para*" del grupo fenilo, se observa un mayor descenso de la viabilidad respecto a los que presentan el enlace en posición "*meta*". También se observa mayor citotoxicidad en el caso del compuesto C2, lo que puede deberse a una mejor interacción de este compuesto con las dianas biológicas[3].

Referencias

[1] M. R. Maurya, S. Agarwal, C. Bader, D. Rehder, Eur. J. Inorg. Chem. 1, (2005), 147
[2] T. Mosmann, T. J. Immunol. Methods 65(1-2), (1983), 55.
[3] S. P. Dash; A. K.Panda, S. Pasayat, R. Dinda, A. Biswas, A. R. Tiekink, Y. P. Patil, M. Nethaji, W. Kaminsky, S. Mukhopadhyayf, S. K. Bhutiaf, Dalton Trans., (2014), 43, 10139.

Estudio de la interacción de un compuesto de molibdeno con una hidrazona con el ADN y de sus efectos citotóxicos en la línea celular humana de cáncer de pulmón A549.

Lucía Mato-López[1], Miguel Riopedre[1*], Antía Sar[1], Natalia Fernández-Bertólez[2], Josefina Méndez[1], Vanessa Valdiglesias[2], Fernando Avecilla[1]

[1]Grupo XENOMAR, Centro de Investigaciones Científicas Avanzadas (CICA), As Carballeiras s/n, Campus de Elviña, 15071, A Coruña, España. l.mato@udc.es
[2]Grupo DICOMOSA, Departamento de Psicología, Facultad de Ciencias de la Educación, Campus de Elviña, 15071, A Coruña, España.

La actividad antitumoral de complejos de molibdeno fue registrada por primera vez en 1979 por Köpf-Maier en sus estudios en ratas con dicloruro de molibdoceno[1]. La baja toxicidad del Mo, su presencia en numerosas enzimas y la posibilidad de que pueda participar en numerosos procesos biológicos debido a su variada química, abre un campo de estudio en la quimioterapía todavía bastante inexplorado [2]. En este trabajo, se ha sintetizado y caracterizado por las técnicas de análisis elemental, espectroscopia IR, RMN y espectrometría de masas el compuesto $[Mo^{VI}O_2(L)(MeOH)]$ con el ligando hidrazona L. Se han obtenido cristales aptos para su estudio por difracción de Rayos X (ver Figura 1)

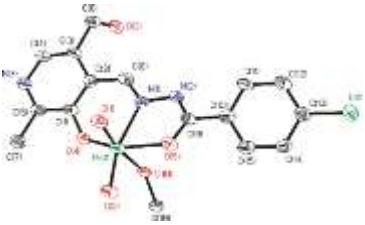


Fig. 1. Representación en elipsoides de probabilidad al 50% del complejo $[Mo^{VI}O_2(L)(MeOH)]$.

Se ha estudiado la interacción del ligando y del complejo de molibdeno con el ADN, mediante la técnica de espectroscopia UV-Vis y se ha determinado su constante de interacción K_b. También se ha valorado el modo de interacción mediante estudios *in silic*o de molecular docking. La interacción predominante entre el compuesto de molibdeno y el ADN es por intercalación entre las bases nitrogenadas. Se han realizado ensayos MTT de citotoxicidad en la línea celular de cáncer de pulmón A549[3], procedentes del banco de células de la *European Collection of Authenticated Cell Cultures (ECACC)*. Los resultados obtenidos a 48h muestran un descenso de viabilidad estadísticamente significativo a partir de concentración 5µM. La viabilidad celular alcanza valores menores al 60 y 20% para las concentraciones de 25 y 100 µM, respectivamente.

Referencias

[1] P. Köpf-Maier, M. Leitner, R. Voiqtländer, H. Köpf . Z Naturforsch C, (1979), 12.
[2] D. Bandarra, M. Lopes, M.; T. Lopes, J. Almeida, M. S. Saraiva, M. Vasconcellos-Dias, C. D. Nunes, V. Félix, P. Brandão, P. D. Vaz, M. Meireles, M. J. Calhorda, J. Inorg. Biochem., 104, (2010), 1171.
[3] T. Mosmann, T. J. Immunol. Methods 65(1-2), (1983), 55.

Brain activity of white wine polyphenols on Alzheimer's disease-like pathology: a first step toward a reliable therapeutic concept for brain degeneration

Mendes D.[1,*], Oliveira M.M.[2], Moreira P.I.[3], Pereira D.M.[1], Valentão P.[1], Andrade P.B.[1], Videira R.A.[1]

[1] REQUIMTE/LAQV, Laboratory of Pharmacognosy, Department of Chemistry, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, nº 228, Porto 4050-313, Portugal.
[2] Chemistry Center – Vila Real (CQ-VR), Chemistry Department, School of Life and Environmental Sciences, University of Trás-os-Montes e Alto Douro, UTAD, P.O. Box 1013; 5001-801 Vila Real, Portugal.
[3] CNC – Center for Neuroscience and Cell Biology, University of Coimbra and Laboratory of Physiology, Faculty of Medicine, University of Coimbra, 3000-548 Coimbra, Portugal

**mendesdaniela04@hotmail.com*

It is well known that mitochondrial dysfunction, anomalous cell redox status, changes in membrane lipid profile and aggregation of unfolded proteins play key roles on progressive brain degeneration underlying Alzheimer's disease (AD). Thus, therapeutic strategies to simultaneously target all these interlinked pathologic events may be able to alter the course of disease progression. In the present work, a selected pool of polyphenols, obtained from white wine by adsorption to polyvinylpyrrolidone polymer (PVPP), were used to prepare a polyphenols-enriched diet, supplementing the drinking water with 100 mg/L (as Gallic acid equivalents) of wine polyphenolic extract. The impact of daily consumption of water supplemented with polyphenols (25 mg/kg/d) for two months on brain of 10-month-old 3xTg-AD and NonTg mice was rationalized, considering i) brain levels of polyphenols, ii) the capacity to modulate the redox status of brain cells, assessing enzymatic and non-enzymatic antioxidant parameters in whole brain homogenates, mitochondria-enriched and mitochondria-free cytosolic fractions, iii) brain levels of amyloid-β peptides, iv) mitochondrial bioenergetics, and v) fatty acid profile of whole membrane phospholipids. HPLC-DAD analysis revealed that the PVPP with wine extract (880.38±58.68 µg phenols/mg of freeze-dried extract) is a complex mixture with 20 phenolic compounds, dominated by proanthocyanidin (as oligomers of catechin), *trans*-caftaric and gallic acids, which together represent more than 80% of the total phenolic content. The polyphenols-enriched diet promotes the brain accumulation of six phenolic compounds, a catechin-derivative being the most abundant (1.951±0.070 ng/mg of 3xTg-AD brain protein). Additionally, the functional diet decreases the 3xTg-AD brain levels of both amyloid-β peptides, Aβ1-40 and Aβ1-42. It modulates the redox state of brain cells of 3xTg-AD mice, restoring the GSH/GSSG ratio, improving the catalase activity and reducing the accumulation of oxidized membrane lipids. However, the brain mitochondrial dysfunction of 3xTg-AD animals was not attenuated by the polyphenols-enriched diet. Lipidomic studies show an increase of DHA (C22:6n-3) and a decrease of AA (C20:4n-6) levels. The increased DHA/AA ratio may have a beneficial impact on the chronic inflammatory process associated with AD-pathology. Therefore, the polyphenolic-enriched diet promotes significant benefit in multiple pathways of the pathophysiological cascade associated to the neuropathology developed by 3xTg-AD mice, highlighting the potential of white wine polyphenols to support reliable therapeutic to alter the course of Alzheimer's disease progression.

Acknowledgments
The work was supported by UID/QUI/50006/2019 with funding from FCT/MCTES through national funds, and by Programa de Cooperación Interreg V-A España – Portugal (POCTEP) 2014–2020 (project 0377_IBERPHENOL_6_E). Research Unit in Vila Real (PEst-OE/QUI/UI0616/2014) by FCT - Portugal and COMPETE. D. Mendes (SFRH/BD/138206/2018) thanks FCT/MCTES.

C5-Curcuminoids: a promising starting point for discovery of new dual inhibitors of p53-MDM2/X

Joana Moreira[1, 2 #], **Joana Almeida**[1#], **Madalena Pinto**[1, 2], **Lucília Saraiva**[3], **Honorina Cidade**[1, 2]

[1]Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal
[2] Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto, Portugal [3]LAQV/REQUIMTE, Laboratório de Microbiologia, Departamento de Ciências Biológicas, Faculdade de Farmácia, Universidade do Porto, Portugal
#Authors contributed equally to this work
**hcidade@ff.up.pt*

In about half of human cancers retaining wild-type (wt) p53, the p53 pathway is inactivated due to the overexpression of endogenous negative regulators, namely murine double minute 2 (MDM2) and X (MDMX). Therefore, the disruption of p53-MDM2/X interactions represents an efficient and selective therapeutic strategy against wt p53-expressing tumors [1].

Curcumin, a secondary metabolite isolated from *Curcuma domestica* [2], is a polyphenol well known for its pharmacological potential. In contrast to curcumin, which has low stability caused by the presence of unstable β-diketone moiety [2], C5-curcuminoids are chemically and metabolically stable analogues which have been also reported to have several interesting pharmacological properties [3-4]. The antitumor activity of these compounds has been extensively studied and the interference with the p53 pathway has been described [3-4]. However, the interference with p53-MDM2/X interactions was never explored.

Aiming the discovery of new dual antagonists of p53-MDM2/X interaction, a small library of C5-curcuminoids was synthesized by the reaction of ketones with appropriately substituted benzaldehydes in alkaline medium. The effect on p53-MDM2/X interactions was evaluated using a yeast-based screening assay previously developed by our group [5]. Using this phenotypic assay, one of the tested compounds revealed to be potential inhibitor of the p53-MDM2/X interactions.

Acknowledgments
This research was partially supported by the Strategic Funding UID/Multi/04423/2019, UID/QUI/50006/2019 through national funds provided by the FCT-Foundation for Science and Technology and European Regional Development Fund (ERDF), within the framework of the program PT2020 and the projects PTDC/MAR-BIO/4694/2014 (reference POCI-01-0145-FEDER-016790; Project 3599–PPCDT), and PTDC/SAUPUB/28736/2017 (reference POCI-01-0145-FEDER-028736). Joana Moreira acknowledges her grant (SFRH/BD/135852/2018).

References

[1] Lemos A, Leao M, Soares J, Palmeira A, Pinto M, Saraiva L, Sousa E., Med. Res. Rev., 36 (2016) 789-844.
[2] Aggarwal B, Kumar A, Bharti AC, Anticancer res., 23 (1/A) (2003) 363-98.
[3] A. Modzelewska A, Pettit C, Achanta G, Davidson NE, Huang P, Khan SR., Bioorganic Med. Chem., 14 (10) (2006) 3491–3495.
[4] Selvendiran k, Tong L, Vishwanath S, Bratasz A, Trigg NJ, Kutala VK, Hideg K, Kuppusamy P, J. Biol.Chem., 282 (39) (2007) 28609–28618.
[5] Leão M, Soares J, Gomes S, Raimundo L, Ramos H, Bessa C, Queiroz G, Domingues S, Pinto M, Inga A, Saraiva L, Life Sci, 142 (2015) 60-65.

Ingredients of permanent and temporary tattoos: current analytical perspective

L. Rubio[1,*], E. Guerra[1], C. Garcia-Jares[1], M. Lores[1]
[1]Laboratory of Research and Development of Analytical Solutions (LIDSA), Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Chemistry. Cretus Strategic Group. Universidade de Santiago de Compostela. E-15782, Santiago de Compostela, Spain

* *laura.rubio.lareu@usc.es*

Tattoos, both permanent and temporary, can be included in the group of new format cosmetics or those considered as *borderline* products [1]. Their regulation and the absence of systematic surveillance on their safety are recently important issues [2], in particular with regard to their main ingredients, the pigments. These ingredients are synthetic and organic hydro- or liposoluble compounds, with a wide range of solubilities. Most of them are photochemical unstable, but little is known about potential degradation products.

This work compares the analytical approaches developed so far to control the safety of tattoo products: inks, permanent make-up, sticker tattoos and henna products. The ingredients included were the pigments along with their impurities and degradation products [3]. They can contain hazardous chemicals such as PAH mainly from black inks, primary aromatic amines from azo-colorants or metals from inorganic and organometallic pigments. Other undesirable additives, such as plasticizers or *para*-phenylenediamine, are also considered.

A pre-treatment step is recommended prior to the analysis, to avoid possible matrix interferences. In most cases a simple approach is used, an easy extraction normally assisted by ultrasound followed by centrifugation. Analytical procedures are quite varied: from spectroscopic to chromatography techniques, depending on the type of analysis required: qualitative or quantitative; and it is common to find combinations of complementary methods.

Acknowledgements

This research was supported by project *GPC2017/04* (Consolidated Research Groups Program, Xunta de Galicia, Spain), and L.R. acknowledges Xunta de Galicia for her predoctoral contract.

References

[1] Manual of the Working Group on Cosmetic Products (Sub-Group on Borderline Products) on the Scope of Application of the Cosmetics Regulation (EC) No 1223/2009 (Art. 2(1)(A)) Version 3.1 (November 2017).
[2] J. Serup, N. Kluger, W. Bäumler, Current Problems in Dermatology, 48 (2015) 118-127.
[3] L. Rubio, E. Guerra, C. Garcia-Jares, M.Lores, Analytica Chimica Acta, In Press (2019).

Estudio de la interacción con ADN de hidrazonas derivadas de piridoxal y de su citotoxicidad sobre la línea celular A549

Antía Sar[1], Lucía Mato-López[1], Miguel Riopedre[1], Vanessa Valdiglesias[2], Natalia Fernández-Bertólez[2], Josefina Méndez[1], Fernando Avecilla[1]

[1]Grupo XENOMAR, Centro de Investigaciones Científicas Avanzadas (CICA), As Carballeiras s/n, Campus de Elviña, 15071, A Coruña, España. antia.sar@udc.es
[2]Grupo DICOMOSA, Departamento de Psicología, Facultad de Ciencias de la Educación, Campus de Elviña, 15071, A Coruña, España.

En este trabajo se han obtenido distintas hidrozonas mediante la condensación de diferentes hidracidas con hidrocloruro de piridoxal [1]. La figura 1 muestra cuatro de las hidrazonas sintetizadas, que fueron caracterizadas mediante distintas técnicas: análisis elemental, espectroscopia IR, RMN y espectrometría de masas. Se han obtenidos cristales aptos para su estudio mediante difracción de Rayos X de monocristal de todos los compuestos. Los resultados obtenidos muestran que en el empaquetamiento critalino predominan los apilamientos de los compuestos favorecidos por interacciones π-π stacking a través de los anillos y grupos con enlaces dobles y otras interacciones, par solitario de un átomo electronegarivo-nube π de un anillo.

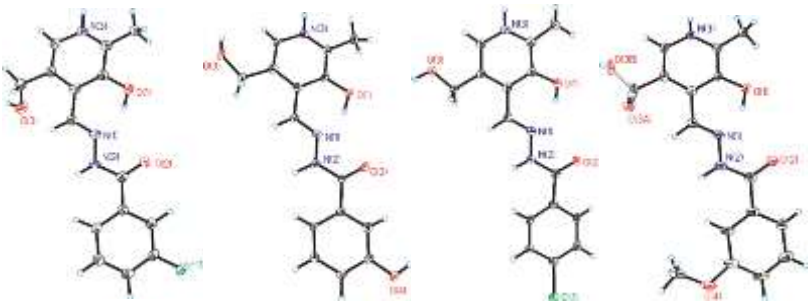


Fig. 1. Representación en elipsoides de probabilidad del 50% de los cationes moleculares HL^+ correspondientes a los compuestos HL^1Cl, HL^2Cl, HL^3Cl y HL^4Cl, de izda a dcha.

Se ha estudiado la interacción de estos compuestos con el ADN mediante estudios de molecular docking. Estos ensayos *in silico* indican que la interacción más favorable para los compuestos con L^1, L^2 y L^4 se produce por interacalación entre los pares de bases nitrogenadas del ADN. El compuesto con L^3, que presenta un átomo de cloro como grupo funcional en el anillo fenílico, muestra una interacción energéticamente más favorable en el surco menor del ADN.
Se ha evaluado la citotoxicidad de los compuestos mediante ensayos MTT sobre la linea celular A549[2], correspondiente a cáncer humano de pulmón. Se testaron siete dosis de 0,1-500 μM. Tras 48h de tratamiento, se puede observar un descenso de viabilidad del 40-55% a partir de la concentración 100 μM en los compuestos con L^1, L^2 y L^4. El compuesto con L^3 presenta un mayor efecto citotóxico, con descensos del 45 y 70% a concentraciones de 25 y 100 μM, respectivamente.
Se puede apreciar una correlación entre el tipo de interacción con el ADN y el perfil citotóxico, siendo el compuesto con L^3, el que presenta más actividad citotóxica. Los compuestos que intercalan presentan valores de viabilidad similares.

Referencias

[1] M. R. Maurya, S. Agarwal, C. Bader, D. Rehder, Eur. J. Inorg. Chem. (2005), 147.
[2] T. Mosmann, T. J. Immunol. Methods 65(1-2), (1983), 55.

Estudio de potenciales aplicaciones antitumorales de complejos de vanadio(V) con ligandos derivados de 2,6-diformil-4-metilfenol.

Antía Sar[1], Antía Mourelos[1], Lucía Mato-López[1], Oscar D Lennis[1], Josefina Méndez[1], Natalia Fernández-Bertólez[2], Fernando Avecilla[1], Vanessa Valdiglesias[2]

[1]Grupo XENOMAR, Centro de Investigaciones Científicas Avanzadas (CICA), As Carballeiras s/n, Campus de Elviña, 15071, A Coruña, España. antia.sar@udc.es
[2]Grupo DICOMOSA, Departamento de Psicología, Facultad de Ciencias de la Educación, Campus de Elviña, 15071, A Coruña, España.

El uso de compuestos de vanadio en sistemas biológicos se ha estudiado en las últimas décadas ya que han demostrado poseer actividad anticancerígena en ensayos de MTT *in vitro*[1]. Este trabajo se centra en la síntesis de una serie de complejos de vanadio(V) con diferentes ligandos hidrazona derivados de 2,6-diformil-4-metilfenol, para estudiar su efecto citotóxico en cultivos con células cancerosas. El procedimiento sintético experimental consiste en hacer reaccionar hidrazidas que presentan diferentes sustituyentes con un dialdehído, el 2-6- diformil-4-metilfenol, formando así los diferentes ligandos hidrazona que posteriormente se harán reaccionar con acetilacetonato de vanadilo(IV), ruta sintética descrita por Maurya *et al*.[2]. Siguiendo dicha ruta se produce la complejación del vanadio y se obtienen los tres compuestos a estudio, dos de ellos mononucleares y el tercero dinuclear. En la figura 1 podemos observar los esquemas de las estructuras de los tres compuestos.

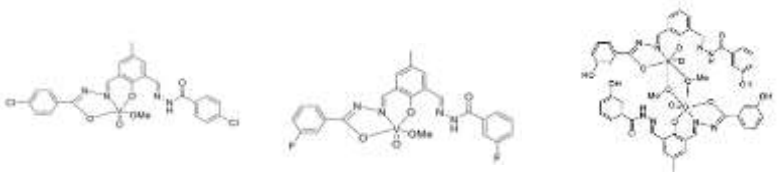


Fig. 1. Esquema de los complejos de vanadio(V) con los ligandos hidrazona.

Para medir el potencial antitumoral de los compuestos se usó la línea celular A549 correspondiente a células humanas de carcinoma pulmonar. Los tratamientos se realizaron a 24 y 48h y se testaron en dosis entre 0,1-500μM. Los tres compuestos presentan un descenso estadísticamente significativo a partir de la concentración 100 μM en el estudio realizado a 48h. Para esta concentración el descenso más acusado, entorno al 60%, lo presentan los compuestos mononucleares, mientras que el dinuclear experimenta un descenso del 20%. A partir de la concentración 250μM, los resultados de los tres compuestos son comparables, con una viabilidad próxima al 10% (descenso del 90%).

Referencias

[1] T. Mosmann, T. J. Immunol. Methods 65(1-2), (1983), 55.
[2] M. R. Maurya, C. Haldar, A. Kumar, M. L. Kuznetsov, F. Avecilla , J. Costa Pessoa , Dalton Trans. 42 (2013), 11941.

Synthesis and characterization of cationic *meso*-substituted porphyrins for theranostic

Mariana C. S. Vallejo[1,*], Sofia G. Serra [2], Vanda Vaz Serra[2], Nuno M. M. Moura[1], M. Graça P. M. S. Neves[1]

[1] QOPNA & LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal
*mariana.vallejo@ua.pt

Porphyrins are tetrapyrrolic macrocycles well-known by their role in vital processes like respiration, photosynthesis, electron transportation and storage of relevant molecules [1]. The physico- and photochemical features displayed by the natural macrocycles but also by synthetic analogues render them particularly attractive to be used in a wide range of fields like supramolecular chemistry, catalysis, electronic materials, sensors and medicine [2].
A particular attractive application for this type of molecules is related with their use in cancer Theranostic, an emerging strategy where the simultaneous diagnostic and treatment has a desirable cost-effective for the healthcare system [3]. In fact, some porphyrins due to the preferential accumulation in cancer cells, efficiency upon light exposure to generate cytotoxic singlet oxygen and unique photochemical/ photophysical properties, are being used as photosensitisers (PS) in Photodynamic Therapy (PDT). However it is recognized that the low fluorescent quantum yields, small Stokes shifts and aggregation in physiological media must be improved for their simultaneous application as fluorescence markers for *in vivo* imaging and effective PS against tumoral cells [4].
In this work, it will be presented and discussed the synthesis and the characterization of a series of positively charged *meso*-substituted tetraarylporphyrins to be incorporated on potential carriers/delivery systems. The characterization of polyelectrolyte microcapsules prepared by layer by layer methodologies after the porphyrin incorporation will be also shown (**Fig 1**).

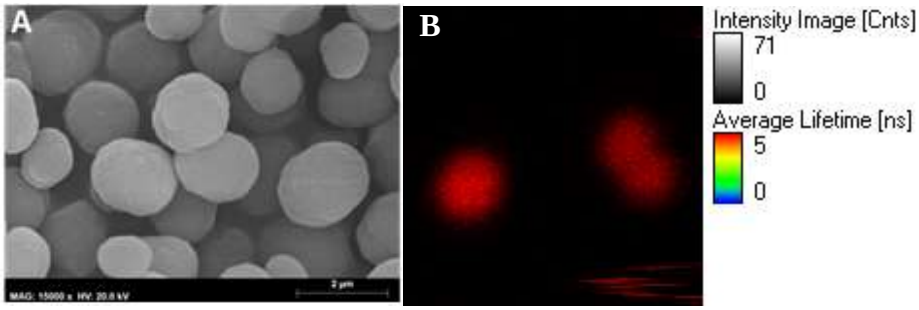


Fig. 1- (A) SEM image of non-functionalized polyelectrolyte microcapsules. (B) FLIM image of a cationic porphyrin doped on a polyelectrolyte microcapsules 6x6 µm.

Acknowledgements
The authors are grateful to University of Aveiro and FCT/MCT for the financial support for QOPNA research Unit (FCT UID/QUI/00062/2019), and the FCT project THERMIC (PTDC/QUI-COL/29379/2017), through national founds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement, and to the Portuguese NMR Network. The research grants of M.C.S. Vallejo (REF: BI-UI51-8642-2019) and Sofia G. Serra are supported by the project THERMIC (PTDC/QUI-COL/29379/2017), and the research contracts of N.M.M. Moura (REF.-048-88-ARH/2018) and Vanda Vaz Serra are funded by national funds (OE), through FCT.

References

[1] A. F. R. Cerqueira, N. M. M. Moura, V. V. Serra, M. A. F. Faustino, A. C. Tomé, J. A. S. Cavaleiro, M. G. P. M. S. Neves, Molecules, 22 (2017) 1269.
[2] K. M. Kadish, K. M. Smith, R. Guilard R., *In* Handbook of Porphyrin Science, World Scientific Publishing Company Co, Singapore, 2010, Vol 10-12.
[3] E.-K. Lim. T. Kim, S. Paik, S. Haam, Y.-M. Huh, K. Lee, Chem. Rev., 115 (2015) 327.
[4] S. Singh, A. Aggarwal, N. V. S. D. K. Bhupathiraju, G. Arianna, K. Tiwari, C. M. Drain, Chemical. Rev., 115, (2015) 10261.

Atividade antioxidante de derivados do hidroxitirosol em lipossomas

Marlene Costa[1], Rafaela Lopes[1], Mariana Ferreira[1], Albertina P. Gameiro[1], Fátima Paiva-Martins[1]

[1]REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, Porto, Portugal

O conhecimento da interação dos antioxidantes (AO) com as membranas lipídicas é crucial para entender a distribuição dessas moléculas no organismo e estabelecer relações entre as propriedades físico-químicas e seus efeitos biológicos. O hidroxitirosol (HT) é uma molécula com grande atividade antirradicalar e tem uma natureza hidrofílica e, portanto, possui uma difusão muito baixa nas biomembranas. Deste modo, com o objetivo de aumentar a hidrofobicidade do HT, sintetizaram-se bis-ésteres de HT com diferentes tamanhos de cadeia alquílica (C12, C16 e C22).

Estudou-se a atividade antioxidante dos bis-ésteres de hidroxitirosol (fenolípidos), contendo assim os mesmos grupos reativos, mas com diferente hidrofobicidade, frente à oxidação iniciada pelo cloridrato de 2,2′-azobis (2-amidinopropano) (AAPH) num sistema lipídico. A estabilidade dos lipossomas aumentou entre 0,2 – 1 vezes quando os compostos foram adicionados à suspensão lipídica. No entanto, a atividade antioxidante desses fenolípidos diminuiu progressivamente com o aumento do comprimento da cadeia. Quando os compostos foram incorporados no lipossoma durante a sua preparação, a estabilidade dos lipossomas aumentou ainda mais (de 1,9 para 2,1 vezes) e o composto com a melhor atividade antioxidante foi o derivado HTC22HT. As diferenças entre os resultados podem refletir a melhor localização dos compostos na estrutura lipídica quando adicionados durante a sua preparação. Estes resultados apoiam fortemente a ideia de que a eficiência de um AO correlaciona-se com a sua localização na membrana.

Agradecimentos: O trabalho foi apoiado por UID/QUI/50006/2019 com financiamento da FCT/MCTES através de fundos nacionais e pela PTDC/OCE-ETA/32492/2017 – POCI-01-0145-FEDER-032492 - PHENOLIVA.

New chalcone derivatives with antimitotic activity: synthesis, antitumor activity and chemosensitivity studies

Patrícia Pinto[a,#], Carmen Mariana Machado[a,#], Joana Moreira[a,b,#], José Diogo P. Almeida[c], Patrícia M. A. Silva[c], Ana C. Henriques[c], Jorge Salvador[d], Madalena Pinto[a,b], H. Bousbaa[c,*], Honorina Cidade[a,b,*]

[a]Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal

[b]Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto, Portugal

[c]CESPU, Instituto de Investigação e Formação Avançada em Ciências e Tecnologias da Saúde (IINFACTS), Portugal.

[d]Laboratório de Química Farmacêutica e Centro de Neurociências e Biologia celular, Faculdade de Farmácia, Universidade de Coimbra, Pólo III - Polo das Ciências da Saúde, Portugal

[#]Authors contributed equally to this work

**hcidade@ff.up.pt*

Chalcones are natural flavonoid precursors that have been reported for their wide range of biological activities, namely antitumor [1-2]. In addition, the presence of an α,β-unsaturated ketone moiety makes these compounds a valuable chemical substrate for the synthesis of bioactive derivatives, namely pyrazoles [3]. Hence, in continuation of our efforts to obtain new chalcone derivatives with improved antitumor and antimitotic activity [4,5] a series of new chalcone derivatives, including pyrazole and α,β-epoxide derivatives, was synthesized and evaluated for their cell growth inhibitory activity in three human tumor cell lines. From this work, nine chalcones with antimitotic effect were identified. Moreover, one of the compounds was able to enhance chemosensitivity of tumor cells to paclitaxel in NCI-H460 cells.

Acknowledgments

This research was partially supported by the Strategic Funding UID/Multi/04423/2019 and under the project PTDC/SAU-PUB/28736/2017 (reference POCI-01-0145-FEDER-028736), co-financed by COMPETE 2020, Portugal 2020 and the European Union through the ERDF and by FCT through national funds. This work was also supported through funds provided by CESPU, CrI under the project ComeTarget_CESPU_2017. Ana Henriques, and Joana Moreira acknowledge for their FCT grants (SFRH/BD/111365/2015 and SFRH/BD/135852/2018, respectively).

References

[1] Singh P., Anand A., Kumar V., Recent developments in biological activities of chalcones: A mini review, Eur. J. Med. Chem., 85 (2014) 758-777.

[2] Ducki S., Antimitotic chalcones and related compounds as inhibitors of tubulin assembly, Anti-cancer Agent Me., 9(3) (2009) 336.

[3] MT Albuquerque H., MM Santos C., AS Cavaleiro J., MS Silva A., Chalcones as Versatile Synthons for the Synthesis of 5-and 6-membered Nitrogen Heterocycles, Curr. Org. Chem., 18(21) (2014) 2750-2775.

[4] Masawang K., Pedro M., Cidade H., Reis R.M., Neves M. P., Corrêa A. G., Sudprasert W., Bousbaa H., Pinto M.M., Evaluation of 2′, 4′-dihydroxy-3, 4, 5-trimethoxychalcone as antimitotic agent that induces mitotic catastrophe in MCF-7 breast cancer cells, Toxicol. Lett., 229(2) (2014) 393-401.

[5] Fonseca J., Marques S., SilvaP., Brandão P., Cidade H., Pinto M., Bousbaa H., Prenylated chalcone 2 acts as an antimitotic agent and enhances the chemosensitivity of tumor cells to paclitaxel, Molecules, 21(8) (2016) 982.

QUÍMICA TEÓRICA

Automatization of a Nucleus-Independent Chemical Shift (NICS) Analysis as an Indicator of Aromaticity in Rings

Ó. Iglesias González[1,*], Á. Vidal-Vidal[1,2], C. Silva López[1,2]
[1]Departamento de Química Orgánica, Facultade de Química, Universidade de Vigo. Lagoas Marcosende s/n E36310 Vigo, Spain.
[2]CITACA, Agri-Food Research and Transfer Cluster, Campus da Auga, University of Vigo, 32004-Ourense, Spain
**osiglesias@alumnos.uvigo.es*

Few concepts are as frequently used as aromaticity in the current chemical literature. This may be quantified by more than 300000 papers dealing with the aromatic properties of chemical systems published in the scientific literature in the last 40 years.[1]
Aromaticity is a property of molecules with a ring or chain of resonance bonds that gives increased stability compared to other geometric or connective arrangements with the same set of atoms. While it's tipically found in cyclic (ring-shaped), planar (flat) structures, there exist other varieties such as homoaromatic and three-dimensional aromatic systems. Aromaticity is typically tied to other important properties such as chemical stability, reactivity, and interactions with other molecules. Therefore, when studying such structures, determining if they are aromatic, antiaromatic or non-aromatic is of great chemical interest.
There are several ways of characterizing aromaticity available on the literature and among them, Nucleus Independent Chemical Shift (NICS)[2] is one of the most popular.
In this work, after the fundamentals of this method are explained, a custom code that is able to automatize the calculation of NICS in a chosen surface is presented. With this automatization procedure, the aromaticity of different systems can be revealed in a few minutes. To show the capabilities of this code, the NICS index is computed in a variety of systems that include some simple and common ones such as benzene and cyclobutadiene, and other novel molecules such as "sulflowers"[3] that have never been analyzed before.

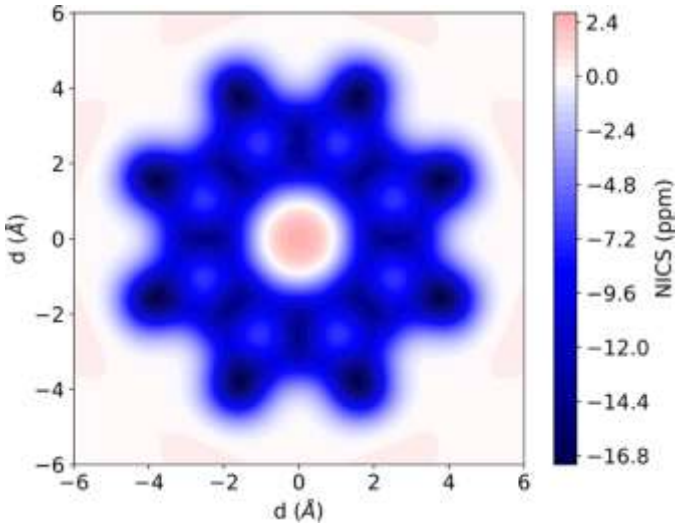


Fig.1. Graphic depicting the results of an automatized NICS calculation on a "sulflower" molecule.

Referencias

[1] Zhongfang Chen, Chaitanya S. Wannere, Clémence Corminboeuf, Ralph Puchta, Paul von Ragué Schleyer *Chem. Rev.,* 105 (2005) 3842-3888
[2] Paul von Ragué Schleyer, Cristoph Mærker, Alk Dransfeld, Haijun Jiau, Nicolaas J. R. van Eikema Hommes, J. Am. Chem. Soc., 118 (1996) 6317-6318
[3] Yu. Chernichenko Konstantin., Viktor V. Sumerin, Roman V. Shpanchenko, Elizabeth S. Balenkova, Valentine G. Nenajdenko, Angew. Chem. Int. Ed., 45 (2006) 7367-7370.

QT06

Optimization of an *in silico* Virtual Screening Protocol for the Identification of Biofim Formation Inhibitors in *LasR*

Rita P. Magalhães[1,*], Tatiana F. Vieira[1], André Melo[2] and Sérgio F. Sousa[1]

[1]UCIBIO/REQUIMTE, BioSIM – Departamento de Medicina, Faculdade de Medicina da Universidade Do Porto, Alameda Prof. Hernâni Monteiro, 4200-319 Porto, Portugal
[2]LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal

**rpmagalhaes@med.up.pt*

Biofilms can be prevalent in natural, industrial and hospital settings and are associated to ca. 80% of all human infections [1]. The increased antimicrobial resistance and mutation rate of bacteria in biofilms contributes to the development of antibiotic resistance, greatly limiting the therapeutic options to a variety of infections. Preventing biofilm formation could dramatically reduce the effects of infectious diseases [2]. Several bacterial mechanisms such as motility, Quorum-Sensing (QS) and matrix synthesis are involved in biofilm formation and development [3]. QS is the cell-to-cell communication in bacteria that regulates gene expression. This mechanism allows bacterial communities to adapt their behavior in a population density dependent manner [4].

P.*aeruginosa (P.a)* is an aerobic rod-shaped gram negative opportunistic pathogen responsible for up to 20 % of hospital infections. This pathogen causes urinary tract and nosocomial infections and largely affects cystic fibrosis patients. Besides, the bacteria invade medical devices such as prosthetic joints and catheters, constituting a danger for public health [5]. The pathogenesis of *P.a* is highly correlated with its ability to form biofilms through QS. One of the main QS mechanisms in this bacteria involves a synthase, *LasI*, that produces a molecule (autoinducer) that binds to a receptor, *LasR,* triggering alterations in gene expression that lead to biofilm formation. The development of potent inhibitors against this receptor is a promising therapeutic strategy to combat *P.a* related infections [6].

Protein-ligand docking [7] is a methodology that uses computers to predict the pose and affinity of specific molecules to receptors or enzymes. When employed in a context of virtual screening [8], docking can be used to evaluate the possibility of millions of compounds in binding to a particular protein target, limiting the amount of molecules that have to be tested experimentally, while ensuring a greater exploration of the chemical space.
This work reports on the development and optimization of a Virtual Screening methodology and scoring function for increased active/decoy discrimination for *LasR*. Several docking software (AutoDock, VINA, LeDOCK, DOCK and GOLD) were tested and explored. The optimized protocol was used to scan and analyse extensive databases of compounds with unknown activity, including natural products (TimTec), marine compounds (MNPD), drug-like compounds (DrugBank), amongst others. Compounds with a high probability of inhibiting *LasR* can now be tested experimentally in search of new leads for drug development with anti-biofilm potential.

Agradecimientos
This work has been supported by the Fundação para a Ciência e a Tecnologia (FCT) (UID/Multi/04378/2019)

Referencias

[1] R. J. Worthington, J. J. Richards, C. Melander, Org. Biomol. Chem. 10 (2012) 37.
[2] C. Dias, A. Borges, D. Oliveira, A. Martinez-Murcia, M. J. Saavedra, M. Simões, Peer J, 6 (2018).
[3] H. Koo, R. N. Allan, R. P. Howlin, P. Stoodley, L. Hall-Stoodley, Nat. Publ. Gr (2017)
[4] Ng Wai-Leung, B. L. Bassler, Annu. Rev. Genet. 43 (2009) 1.
[5] A. H. Sheikh, B. Raghuram, L. Eschen-lippold, D. Scheel, Am J Respir Cell Mol Biol, 58 (2018) 4.
[6] R. S. Smith, B. H. Iglewski, Curr Opin Microbiol, 6 (2003), 1.
[7] S. F. Sousa, A. J. M. Ribeiro, J. T. S. Coimbra, R. P. P. Neves, S. A. Martins, N. S. H. N. Moorthy, P. A. Fernandes, M. J. Ramos, Curr. Med. Chem, 20 (2013) 18.
[8] S. F. Sousa, N. M. F. S. A. Cerqueira, P. A. Fernandes, M. J. Ramos, Comb. Chem. High. T. SCR, 13 (2010) 5.

ÍNDICE DE AUTORES

A. C. Lima, 265
A. C. Silva, 250
A. Gayol, 143, 330
A. Gomes, 48
A. López-Prieto, 212, 213
A. Oliveira, 77
A. R. R. P. Almeida, 333
A. Sousa, 185
A.G Pereira, 204
A.M. Ribeiro, 275, 283
Abel Muñiz-Mouro, 87
Acosta N. Gema, 225, 226, 236
Adelaide Sousa, 184
Adrià Gil, 197, 362
Adrián M.T. Silva, 16, 44
Ahinara Francisco López, 234
Alexandra Borges, 360
Alexandra I. Costa, 291, 300
Alexandre Viana, 151
Alfredo Esteves, 55, 215
Alnilan Lobato, 126
Ana Arias Rodríguez, 141
Ana C. S. Lobo, 183
Ana L. R. Silva, 332
Ana M. Vázquez, 323
Ana R. Neves, 76, 252
Ana R. Teixeira, 239
Ana Reis, 186
Ana Rita Pereira, 354
Andreia Barbosa, 83
Andreia D. Veloso, 119
Andreia F. R. Silva, 60
Andreia Granja, 297
Ángel Vidal-Vidal, 97, 273
Ângela C.B. Neves, 193
Ángela Rodríguez., 355
António O. S. S. Rangel, 305
Antonio Obelleiro, 352
Anxo Carreira-Casais, 223
Araújo, J. L., 96
Aravena Sanhueza F., 306
Arnosa Prieto Ángela, 111
Artem Drogalin, 358
B. Ferreiro, 309, 310
Bebiana L.C. Santos, 269
Bernal Miriam[1], 64
Bianca R. Albuquerque, 58, 220
Bruna Carbas, 128
Bruno Henriques, 73
C. Braga, 168
C. Caleja, 50, 51
C. Jiménez-López, 52, 53
C. Llorente Pérez, 281
C. Lourenço-Lopes, 312
C.G. Amorim, 313
Carina Proença, 181
Carla S. Francisco, 165
Carla S. Silva Teixeira, 198
Carlos A. O. Silva, 331
Carlos F. M. Silva, 190
Carlos J. P. Monteiro, 188
Carlos Martins-Gomes, 54, 237
Carmem N.P. Gonçalves, 103
Castillo Z. Aly, 325
Cecília I.A.V Santos, 140, 327, 337
Cláudia P. S. Ribeiro, 345
Constantino C. Coelho, 129
Covadonga Salgado, 45
Cristina J. Dias, 158
Custódio Lobo Roriz, 39
Daniel Armada, 125
Daniel F. de Castro, 277
Daniel J. Prieto Vieites, 240
Daniel O. Carvalho[2], 42
Daniela Ribeiro, 187
David Viruega Sevilla, 287
Diana Almeida, 203
Diana C.G.A. Pinto, 80
Diego Vázquez Ares, 245
Dina Neves, 177
E. Manuela Garrido, 317
Eduarda Pereira, 42
Eliana Pereira, 38
Esnaider Rodriguez Suárez, 246
Esther Colchón Pierna, 350
Eurico Lima, 175, 363
F. Mirante, 94
F. Rincón, 288
Fabio A. Schaberle, 148
Fábio Conceição, 159
Fachal M, 67
Fernández-Marcos, M.L., 233
Filipa A. Fernandes, 57, 219
Filipa Mandim, 176, 214
Flávia F. Magalhães, 257
Flórez-Fernández N, 113
Francisca Lopes, 191
Francisca T. S. M. Ferreira, 311
G. Laender, 74
Gomes B. Vânia, 211
H. Diniz, 266
Helder M. Rafael, 301

Helder T. Gomes, 69, 235
Helena M.V.M. Soares, 81
Heloísa H.S. Almeida, 335
Henrique S. Fernandes, 196
Hugo Goes, 85
Hugo Santalla, 163
Inês C.F. Fonseca, 353
Inês M. Valente, 135
Irene Gouvinhas, 70
Isilda Amorim, 91
Ivana H. Šrámková, 131
Ivo E. Sampaio-Dias, 162
Ivo Oliveira, 218
J. Esther Chavez[1], 65
J. L. Francisco-Fuentes, 164
J. M. Fernández Solís, 272
J. Sánchez-Piñero, 248, 249
J. Santos, 356
J.J. López-Mayán, 133, 324
J.Vindeirinho, 244
Jaime Caza Caza, 232
Javier Andrés Dávila, 105
Jhoan H. Piermattey, 161
Joana F.C. Silva, 146
Joana M. D. Calmeiro, 170
Joana Moreira, 367, 373
Joana S. Teixeira, 118
João A. Baptista, 142
João A.V. Santos, 334
João Braga, 100
João C. F. Nunes, 88
João Rodrigo Santos, 222
João Siopa[1], 61
Jonathan S. Cardoso, 109
Jorge M.P.J. Garrido, 318
José A. Peres, 78
José Antonio Murillo, 98
Jose L. Diaz de Tuesta, 92, 116
José Luis Legido Soto, 43
Jose M. Andrade, 227
José Mª Fernández Solís, 251
José Miguel P. Ferreira de Oliveira, 178
José Pinela, 192
José Pinheiro Torres, 79
José V. Prata, 114, 270
Juan Carlos Becerra Rodríguez, 229
Juan José Tarrío, 122
Julia González-Álvarez, 279
Julieta Puig, 241
Karen G. João, 173
Karolina Ptaszyńska, 267
Katarzyna Morawa Eblagon, 145
Kohlová Michaela, 169, 174
L. A. Lema, 75
L. Alves[1], 66
L. Espírito Santo, 209
L. López-Hortas, 280, 289
L. Monteiro, 189
L. Rodríguez-Silva, 152
L. Rubio, 320, 368
Lara Rouco, 342
Leandro M. O. Lourenço, 160
Lúa Vázquez, 136, 322
Lucía Mato-López, 364, 365
Luís Fernandes, 314
M. Guimarães, 72, 106
M. M. Castro López[1], 112
M. M. Castro-López, 121
M. P. García-Santos, 329
M.D. Torres, 253, 285, 286
Magda C. Semedo, 255, 256
Magda Fonseca, 293
Manyou Yu, 321
Mar López, 108, 284
Marcelino Maneiro, 153
Marcelo D. Catarino, 171
Márcia Carvalho, 86
María Covadonga Salgado Blanco, 16
María Eduarda Pereira, 16
Maria Inês P. Mendes, 180
María Isabel Pividori, 134
Maria J. Perry, 179
María J. Romero, 341
Maria Rangel, 340
Mariana C. S. Vallejo, 371
Mariana Emilia Ghica, 130, 295
Marina Pinheiro, 296
Marlene Costa, 56, 372
Max José Belo de Souza, 127
Mehriban Aliyeva, 139
Melani J.A. Reis, 242
Mendes D., 366
Mercedes Novo, 194
Mikel Añibarro-Ortega, 167
Mónica M. Lopes, 282
N. Cañás-Carro, 307, 308
N. Flórez-Fernández, 278
N. Gavieiro, 264
Natalia Rey-Raap, 115
Nicole Ferreira, 137
Nuno Jorge, 63
Ó. Iglesias González, 375
O.T. Andrade[1], 228

Oludemi Taofiq, 259, 260
P. A. Calvo, 303
P. Brântuas, 104
P. Cantinho, 230, 231
P. Rocha, 243
Patrícia D. Barata, 347, 348
Paula Araújo, 346
Paula García-Oliveira, 47
Paulina Guevara García, 71
Pelayo García Acevedo, 294
R. B. Martins, 41
R. García, 361
R. Lima, 268
R. Moreira, 216
R.L. Gil, 132
Raquel B. R. Mesquita, 238
Reigía B. Mónica, 101
Rezende, S.C, 292
Rezende, S.C., 207
Ricardo A.E. Castro, 336
Ricardo M.S. Sendão, 117
Rita P. Magalhães, 376
Rita Padanha, 344
Rodríguez Vidal - Francisco Javier, 247
Rodríguez-Olalde Nancy Eloísa, 199
Rodríguez-Solana R., 221
Rossana V. C. Cardoso, 205
Rossana V. C. Cardoso[1], 43
Rúbia C.G. Corrêa, 44
Rui M. F. Bento, 262
Rui M. Ramos, 319
S. Muniategui-Lorenzo, 316
S. Vinhas, 154
Sandra Fernández-Fariña, 339
Sandra Matos, 299, 302
Sara Illodo Brea, 144
Sara R. D. Gamelas, 182
Seco-Gudiña R, 261
Sérgio M. Vilas-Boas, 147, 149
Silva Samanta, 49, 59
Silva, S.G., 351, 357
Sílvia Afonso, 202
Sineiro, J., 217
Soledad Muniategui-Lorenzo, 315
Sónia Martins, 258
Tânia C.S.P. Pires, 45, 208
Tania Ferreira Anta, 276
Tania Gerpe Amor, 156
Tatiana B. Schreiner, 107
Telmo Francisco, 46
Thainara Viana, 68
Tiago E. Coutinho, 84, 206
Tiago G. Paiva, 123
Tiane C. Finimundy, 40, 210
Tiane C. Finimundy[1], 40
Tomas Lindahl, 16, 41
Uxía Gómez, 349
Vânia Gomes, 157
Vasco F. Batista, 93
Vera L. S. Freitas, 328
Víctor K. Abdelkader-Fernández, 90
Xosé Luis Legido Soto, 16

galicia

Xacobeo 2021
Galicia