BOOK OF
ABSTRACTS

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2nd GREENERING INTERNATIONAL conference

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IN SCIENCE & TECHNOLOGY

Greenering

BioEcoUVa
The Institute of Bioeconomy
of University of Valladolid

21st- 23rd March, Valladolid, SPAIN

2ND GREENERING
INTERNATIONAL CONFERENCE

Valladolid (Spain), 21st to 23rd March 2023

ORGANIZERS

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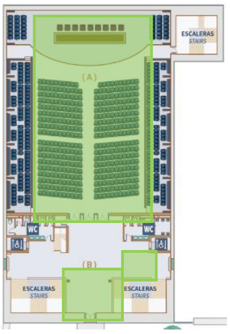
VENUE

PALACIO DE CONGRESOS CONDE ANSÚREZ

Locations

Registration

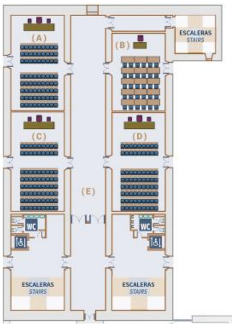
- Paraninfo Hall – 2nd Floor
- Timetable:
  Tuesday 21st, 10.30 – 18.30 h;
  Wednesday 22nd, 8.30 – 18.00 h;
  Thursday 23rd, 8.30 – 11.30 h.



2nd Floor

Conference Rooms

- Room A: Paraninfo – 2nd Floor
- Room B: Sala Rey Felipe II – 1st Floor



1st Floor

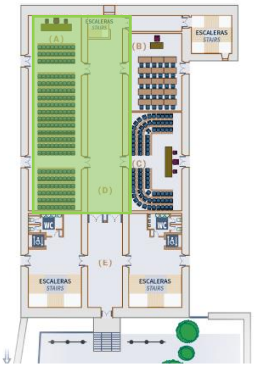
Posters Session

- Sala Cardenal Mendoza and main aisle – 0/ Entrance Floor

Posters will be displayed during the whole duration of the conference. Any poster remaining after 15.00 h of 23rd March will be discarded.

Sponsors

- Paraninfo Hall – 2nd Floor



0 – Entrance Floor

Lunches and coffee breaks

- Sala Cardenal Mendoza - 0/ Entrance Floor

Social Program

Gala Dinner

- Club 1844. El Circulo de Recreo.
  c/ Duque de la Victoria, 6 (Next to Plaza Mayor)
  Wednesday 22nd at 21.00h

Historical Valladolid Tour (Tuesday).

- Plaza de la Universidad. Meeting point from 18.45. Start at 19.00.

Final Program

TUESDAY 21ST MARCH		
10.30	REGISTRATION	
11.00	GREENERING: CORE GROUP MEETING (Room B)	
12.20	OPENING & PLENARY LECTURE (Room A) A.R. DUARTE: EUTECTIC SYSTEMS TARGETING CURRENT CHALLENGES IN LIFE SCIENCE APPLICATIONS	
13.30	WELCOME LUNCH	
15.00	Room A 1. GREEN EXTRACTION, FRACTIONATION AND FORMULATION OF BIOACTIVE COMPOUNDS & 6. APPLICATIONS	Room B 3. CARBON CAPTURE AND UTILIZATION
15.00	Keynote Christelle Crampon Supercritical CO_2 fractionation – a green and continuous process for complex separations (T1.21)	Keynote Raúl Piñero Converting CO_2 emissions from bio-based industries into sustainable chemicals to mitigate climate change (T3.17)
15.30	Selva Pereda Phase equilibrium engineering for winterization of natural extracts with CO_2 (T1.14)	Felix Llovell Understanding the potential of des for GHG capture and separation: from thermodynamics to process design (T3.15)
15.45	Stoja Milovanovic The separation of biologically active extracts from chamomile seeds (T6.15)	Maira I. Chinchilla Hydrothermal reduction of CO_2 by using catalysts and biomass residues (T3.5)
16.00	Anja Saveljić Use of biobased solvents in carotenoid extractions from red yeast *Rhodotorula mucilaginosa* (T1.4)	Ana Inês Paninho Cyclic carbonates production from CO2 and epoxides using sustainable solvents. Quaternary ammonium based-ionic liquids versus -deep eutectic mixtures (T3.13)
16.15	Discussion	Discussion
16.30	COFFEE BREAK AND POSTERS SESSION	
17.00	Ana Aguiar Ricardo Supercritical CO_2 applied on the production of quercetin-loaded liposomal dry powder formulations for the treatment of inflammatory lung diseases (T6.9)	J. Mc Gregor Catalytic hydrothermal conversion of carbon dioxide and organic waste under sub-critical conditions (T3.10)
17.15	Merichel Plaza New strategy based on hydrophobic natural deep eutectic solvents and cyclodextrins for carotenoid extraction-encapsulation from persimmon peels (T1.3)	Sabrina Belén Rodríguez Reartes Evaluation of the potential of phosphonium-based ionic liquids for CO_2 absortion through soft-saft (T3.14)
17.30	Erika Vagi Extraction and utilization of bioactives from agro- and food industrial wastes by green technologies (T6.14)	Mónica Viciano Sustainable formulations from CO_2 and orange peel waste (T3.7)
17.45	Flash Orals T1.11 Mirjana Sulejmanović T1.13. María del Mar Contreras T6.21. Marie Cerhová	Flash Orals T3.02. Ángel Galán Martín T3.03. Miguel Almarza T3.11. Sofia Messias

19.00	HISTORICAL TOURISTIC GUIDED TOUR

WEDNESDAY 22nd MARCH		
9.00	Room A PLENARY LECTURE W. de Vos: SUSTAINABLE MEMBRANE TECHNOLOGY THROUGH POLYELECTROLYTE SELF ASSEMBLY	
10.00	Georgina Durowoju OPEN RESEARCH EUROPE	
	Room A 2. BIOREFINERY. BIOPRODUCTS AND BIOENERGY	Room B 5. POLYMERS AND ADVANCE MATERIALS
10.30	Keynote Eulogio Castro Key elements for agricultural residues-based biorefinery development	Keynote Carlos A. García-González Advanced synthetic bone grafts by supercritical fluid technology (T5.10)
11.00	Oscar Benito-Román Valorization of onion skin wastes using subcritical water. flavonoids and pectin recovery (T2.28)	Luis Eduardo Alonso Pastor Self-healing tire rubber composites: environmental implications of technical advances (T5.08)
11.15	COFFEE BREAK AND POSTERS SESSION	
11.45	Esther Del Amo Mateos Recovery of pectin from sugar beet pulp using emerging extraction technologies (T2.04)	Mónica de la Viuda Is there any suitable alternative solvent for membranes? (T5.20)
12.00	Francisco Martín-Martínez Computational generation of molecular models for atomistic simulations of biocrude oils (T2.25)	Daniel Cuadra-Rodríguez Reducing thickness or inducing porous structure? A methodology to increase the permeance in gas separation membranes (T5.21)
12.15	Vesna Leontijevic Bio-polyesters from tomato peels, enabled by SCW (T2.26)	Judit Martín de León Towards the production of green and advanced thermal insulators (T5.07)
12.30	Enkeledo Menalla Hydrolysis of triacetin in subcritical and supercritical water (T2.16)	Mercedes Santiago-Calvo Closed-loop recycling of fiber-reinforced polymer composites waste from aeronautic industry (T5.1)
12.45	Cristina González Changing the sugar-based platform by the carboxylates platform when targeting at microbial oils productions. Lessons learnt (T2.9)	Flash orals T5.06. Beatriz. Merillas T5.17. María Asensio T5.29. Manuel Herrero
13.00	Discussion	Discussion
13.15	COCKTAIL LUNCH	

WEDNESDAY 22nd MARCH		
	2. BIOREFINERY. BIOPRODUCTS AND BIOENERGY	5. POLYMERS AND ADVANCE MATERIALS
14.30	Rebecca Serna García Evaluating the potential of transforming CO_2 into value added products: biomethane and polyhydrohybutyrate (T3.01)	Ana M. Lopez Periago Synthesis and applications of porphyrin based-MOFs using supercritical CO_2 (T5.19)
14.45	Cristina Martínez Fraile Biohydrogen production from the organic fraction of municipal solid waste (OFMSW) via lactate-driven dark fermentation (T2.31)	Mariolino Carta Tröger's base network PIMs with tunable pore size for heterogeneous catalysis (T5.04)
15.00	David Moldes Green extraction of microalgal proteins with aqueous two-phase systems based on deep eutectic solvents (T2.03)	Suset Barroso-Solares Advanced functional polymeric nanocomposites for the remediation of nitrates-polluted water (T5.02)
15.15	Riccardo Lo Coco Recovery of bio-based volatile fatty acids by pertraction techniques using green solvents (T2.02)	Clara Amezúa-Arranz Effect of egg white protein and water content in the stabilization mechanisms of biobased rubber latex foams (T5.11)
15.30	Discussion	Discussion
15.45	COFFEE BREAK AND POSTER SESSION	
16.30	William Gustavo Sganzerla Sustainable bioprocess for the recovery of biobased products and bioenergy from brewer's spent grains (T2.21)	Davor Kržišnik Preparation and characterisation of mycelium and lignocellulosic waste composites (T5.12)
16.45	Stelios Fanourakis A techno-economic analysis and life cycle assessment of an olive-based multiproduct biorefinery coupled with carbon, capture and storage (T2.11)	Amparo López-Rubio Improving water resistance of rice straw cellulose-based aerogels (T5.27)
17.00	Flash Orals T2.1. Nicola Frison T2.20. Alejandro Filipigh T2.24. Tahereh Soleymani Angili	Zaida Pérez Bassart Biodegradable packaging materials based on *Agaricus bisporus* (T5.26)
17.20	Discussion	Discussion
17.30 18.30	Room A ROUND TABLE Green Policies and Innovation	

21.00	GALA DINNER

THURSDAY 23rd MARCH		
9.00 10.00	Room A PLENARY LECTURE: Dr. M. GOTO: GREEN PROCESSES WITH SUPERCRITICAL FLUIDS	
	Room A 6. APPLICATIONS	Room B 4. GREEN REACTION AND CATALYSIS
10.00	Keynote Lourdes Calvo Garrido Sterilization of PPE with supercritical carbon dioxide (T6.20)	Keynote Armando Quitain CO_2-H_2O Based Green Engineering for Biomass Valorization (T4.10)
10.30	Anastasia Detsi A green approach for the development of chitosan hydrogels using olive leaf extract as dissolution and gelating agent (T 6.11)	Bojan Bondzic Microfluidic approaches for the sustainable and green synthesis (T4.02)
10.45	Thoa Duong Green inhalers containing beclomethasone dipropionate-loaded aerogels (T6.08)	Maria Helena de Sá Green H_2 from water splitting: the critical role of the choice of electrodes (T4.7)
11.00	Discussion	Discussion
11.15	COFFEE BREAK AND POSTERS SESSION	
	7. SCALE UP AND INDUSTRIAL APPLICATIONS	4. GREEN REACTION AND CATALYSIS
11.45	Nicola Frison Scale-up of a new flexible process for phosphorus and PHA recovery from sewage sludge and organic wastes treatment (T7.2)	Mario Martínez Martínez Catalyst-free acetylation of starch using a green deep eutectic solvent as reaction promoter (T4.8)
12.00	Georg Rudelstorfer Stirred extraction columns for industrial reaction processes (T7.6)	Manuela Panić Biocatalysis in deep eutectic solvents. designing safe and sustainable processes (T4.9)
12.15	Flash Orals T6.2. Ana Rita Jesus T6.22. Ivana Radojčić Redovniković T2.11. Viktoriia Komarysta	Ana Quilez Green method to functionalize melamine foams with silver nanoparticles in a single step (T4.3)
12.30	Discussion	Discussion
	CLOSSING CEREMONY	
13.00	COCKTAIL LUNCH	

PLENARY LECTURES

- *Duarte, A.R.C. Deep eutectic systems targeting current challenges in life science applications*. LAQV/Requimte, Universidade Nova de Lisboa (Portugal)

Dr. Ana Rita C. Duarte is Associate Professor with habillitation at the Chemistry Department from Nova School of Science and Technology of the NOVA University of Lisbon. Her main research interests are the use of green technologies for the development of biomaterials. In particular, the use of water, and supercritical fluids together with the exploration of natural deep eutectic solvents for pharmaceutical and cosmetic applications. She is highly committed with the translation of research into sustainable industry. In 2016 she co-founded the start-up HydrUStent as result of her work as Research Assistant at the 3B's research group at Universidade do Minho, where she worked for 10 years. In 2016 she was awarded an ERC consolidator grant entitled: DES.solve – When Solids Become Liquids: Natural Deep Eutectic solvents for Chemical Process Engineering, to proceed the developments on green technologies. After this5 year project, in 2022 she was awarded an ERC Proof of Concept grant to pursue one of the technologies developed withing DES Solve. In between, 2018, she co-founded Des Solutio, a spin-off company from FCT-NOVA to develop safer and greener alternatives to the chemicals that are usually used in the production of beauty, pharmaceutical, personal care and other products, based in the new knowledge acquired in her research career. She is the Action Chair of COST Action Greenering which involves more than 250 participants from 34 different countries.

- *De Vos, Wiebe M.* Sustainable membrane technology through polyelectrolyte self-assembly. University of Twente (The Netherlands).

Prof. Dr. Ir. Wiebe M. de Vos initiated and chairs the research group "Membrane Surface Science" (MSuS) at the University of Twente. Within his group Prof. de Vos successfully combines his background in the fundamentals of colloid and surface science with the much more applied field of membranes. His work in encompasses the coating of membranes for various functional enhancements, including anti-fouling, enhanced separations, easy-to-clean membranes and virus in-activation, but also entails the production of membranes using sustainable approaches such as aqueous phase separation. The unique membranes developed in this way, often also lead to new membrane processes, allowing effective and sustainable approaches to produce clean water from challenging sources.

- *Goto M.* Green processes with supercritical fluids. Nagoya University (Japan).

Dr. Eng. Motonobu Goto is Emeritus Professor at Nagoya University. During his long and fruitful career (more than 450 published papers in international academic journals) in Chemical Engineering and Materials Processing Engineering, he has received numerous awards, the latest The SCEJ Award of The Society of Chemical Engineering of Japan in 2020. His research interests include supercritical fluid technology such as extraction, reaction, and material processing and plasma technology. Hi is vice-president of International Society for Advancement of Supercritical Fluids. Since beginning of 2022, he is director of Super Critical Technology Centre, Co, Ltd. A company oriented to the industrial implementation of cleaner processes in a recycle oriented processes.

OPEN RESEARCH EUROPE

- Multidisciplinary publishing platform “Open Research Europe”: services & benefits for authors. *Georgina Durowoju*, Content Acquisition Editor.

Open Research Europe (ORE) is the European Commission’s open access publishing platform which offers Horizon-funding program beneficiaries and their collaborators, with a high-quality publishing venue at no cost. The platform follows high scientific standards and open data sharing practices.

Open Research Europe was launched in March 2021, covering 6 major research areas: agricultural and veterinary sciences, engineering & technology, humanities & the arts, medical & health sciences, natural sciences, and social sciences. The multidisciplinary platform currently has over 300 publications, and has been accepted for indexation in Scopus, ERIH PLUS, Reaxys, Inspec, as well as awarded the Directory of Open Access Journals (DOAJ) seal.

In this session, we invite attendees to learn about the unique publishing model utilized on Open Research Europe, how to benefit from our post-publication open peer review and how to participate in open science.

ROUND TABLE

GREEN POLICIES AND INNOVATION

Speakers

- **Ignacio Gracia**

Professor of Chemical Engineering at Universidad de Castilla La Mancha (Spain) and member of the Committee for Socio-Economic Analysis of the European Chemicals Agency (ECHA). His current research interests are focused in the synthesis of biocompatible biodegradable polymers for medical applications and in economical evaluation of processes. He is President of the Iberian Association for the Advancement of High Pressure Technologies (FLUCOMP), and co-founder of Alycin, a private spin-off that produce and commercialized garlic extracts.

- **Martín Santos Martínez**

Senior Scientist in Repsol Technology Lab. He is working in Decarbonization and Circular Economy projects related with Hydroprocessing, as main expertise area. He has been involved in different activities and projects related to Hydrotreaters and Hydrocracking units in all refineries at Repsol since 2006.

- **Francisco J. Martín Martínez**

Senior Lecturer in Computational Chemistry at Swansea University (UK), and Research Affiliate at the Massachusetts Institute of Technology (MIT). He has been president of the Association of Spanish Scientists in the USA (ECUSA), he sits at the advisory board of Sweetwater energy, an integrated biorefinery, he is program leader in the course "Circular Economy and Sustainable Strategies" by the University of Cambridge. In 2022, he was selected as Google Cloud Research Innovator.

- **Monica Viciano**

Senior researcher of Decarbonization department in AIMPLAS (Spain), a researcher center that provide innovative solutions and technical and legal advice to plastic sector through its whole value chain. Specifically, she is expert in decarbonization (carbon capture and utilization CCU) through catalysis solutions for the industry.

TOPIC 1

GREEN EXTRACTION, FRACTIONATION AND FORMULATION OF BIOACTIVES

Keynote Lecture

- **T1.17.** Supercritical CO_2 fractionation – a green and continuous process for complex separations. *Crampon C., Fabien A., Dufour C., Pieck A. and Badens E.* Aix Marseille University (France) and Bontoux SAS (Francia).

Oral Communications

- **T1.2.** New strategy based on hydrophobic natural deep eutectic solvents and cyclodextrins for carotenoid extraction-encapsulation from persimmon peels. *Plaza M. and Marina M.L.* Universidad de Alcalá (Spain).

- **T1.3.** Use of biobased solvents in carotenoid extractions from red yeast *Rhodotorula mucilaginosa*. *Saveljić A., Šovljanski O., Chadni M., Dosso A., Tomić A., Cvanić T., Travičić V., Ionnou I., Čanadanović-Brunet J.* University of Novi Sad (Serbia) and AgroParisTech (France).

- **T1.14.** Phase equilibrium engeneering for winterization of natural extracts with CO_2. *Fortunatti Montoya, M., Hegel P., Pereda S.* PLAPIQUI (Argentina) and University of KwaZulu Natal (South Africa)

Flash Oral Communications

- **T1.11.** Integration of green-based extraction approaches in the isolation of valuable molecules from ginger by-product. *Sulejmanović M., Rodríguez Rojo S., Cocero M.J., Kyriakoudi A., Mourtzinos I., Vidović S., Nastić N., Krivošija S.* University of Novi Sad (Serbia), University of Valladolid (Spain) and Aristotle University of Thessaloniki (Greece).

- **T1.13.** Low energy demanding extraction of triterpenic acids. *Gómez-Cruz I., Contreras M.d.M., Romero I., Castro E.* Universidad de Jaén (Spain).

Poster Communications

- **T1.1.** A green strategy to improve the recovery of flavanones from orange byproducts based on the combination of ultrasound-assisted extraction and natural deep eutectic solvents. *Plaza M. and Marina M.L.* Universidad de Alcalá (Spain).

- **T1.4.** Supercritical CO_2 extract of *Lavandula stoechas* dispersed in natural deep eutectic solvents. Aroma stabilisation potential. *Vladić J., Jerković, Kovačević S., Rebocho S., Paiva A., Jokić S. and Duarte A.R.* Universidade NOVA de Lisboa (Portugal), University of Novi Sad (Serbia), University of Split (Croatia) and University Osijek (Croatia).

- **T1.5.** Supercritical CO2 extraction of non-polar bioactive compounds from turmeric (*Curcuma longa L.*). *Christaki S., Sulejmanović M., Simić S., Kyriakoudi A., Mourtzinos I., and Vidović S.* Aristotle University of Thessaloniki (Greece) and University of Novi Sad (Serbia).

- **T1.6.** *Caulerpa prolifera* green alga as source of high valuable compounds. *Inoubli S., Flórez-Fernández, N., Shili, A., Ksouri R., Domínguez, H. and Torres M.D.* Universidade de Vigo (Spain) and Carthage University (Tunisia)

- **T1.7.** Characterization of vine shoots extract obtained by a green methodology. *Contreras M.d.M., Gómez-Cruz I., Romero I. and Castro E.* Universidad de Jaén (Spain).

- **T1.8.** Evaluation of choline chloride/glycerol as a deep eutectic solvent on recovery of phenolic compounds from avocado seeds. *Del Castillo-Llamosas A., Rodríguez-Rebelo F., Rodríguez-Martínez B., Mallo-Fraga A., Gullón B. and del Río P.G.* University of Vigo (Spain) and University of Limerick (Ireland).

- **T1.9.** Characterization and extraction of bioactives from halophyte plants. *Carvalho, B., Mecha, E., Carvalho Partidário A.M., Bronze, M. R. and Fernández, N*. iBET, Universidade de Lisboa, Universidade Nova de Lisboa and Unidade de Tecnologia e Inovação (Portugal).

- **T1.10.** Semi-continuous flow-through pressurized liquid extraction of phenolic compounds from grape peel. *Sganzerla WG., Francisco AP., da Silva APG., Barroso TLCT., Castro LEN., Forster-Carneiro T.* University of Campinas (Brazil) and Michigan State University (USA).

- **T1.12.** Comparative chemical profiling of underexploited *Citrus sinensis* l. Herbal dust extracts obtained by subcritical water and pressurized ethanol extractions. *Krivošija S., Ballesteros-Gómez A., Dueñas-Mas M.J., Tomić M., Nastić N., Sulejmanović M., Vidović S.* University of Novi Sad (Serbia) and Universidad de Córdoba (Spain).

- **T1.15.** Impact of biopolymers use on physico-chemical stability of blue maize extract microencapsulates. *Ćujić Nikolić N., Žilić S., Mutavski Z., Simić M., Nikolić V., Marković S., Šavikin K.* Institute for Medicinal Plant Research "Dr Josif Pančić", Maize Research Institute and Institute of Technical Sciences of SASA (Serbia).

- **T1.16.** Microencapsulated bioactive extracts from *Diplotaxis erucoides* isolated through green strategies. *Clemente-Villalba J., Jurić S., Burló F., Hernández F., Carbonell-Barrachina A.A., Vinceković M.* Centro de Investigación e Innovación Agroalimentaria y Agroambiental, Universidad Miguel Hernández (CIAGRO-UMH) (Spain) and University of Zagreb (Croatia).

- **T1.18.** Microencapsulation by spray drying of bioactive green tea extracts – carrageenan, alginate and starch as carriers. *Baltrusch, K.L., Torres, M.D., Domínguez, H., Flórez-Fernández, N.* CINBIO, Universidade de Vigo (Spain).

- **T1.19.** Encapsulation of raspberry by-product extract using PGSS process. *Mutavski Z., Fernández N., Živković J., Vidović S., Nastić N., Šavikin K.* University of Novi Sad (Serbia), Institute for Medicinal Plant Research "Dr Josif Pančić" (Serbia) and Instituto de Biologia Experimental e Tecnológica (Portugal).

- **T1.20.** Pressurized fluid extraction of bioactive compounds from peanut by-products to promote waste recovery and circular economy. *Ares A.M., Schumann-Pérez C., Valverde S. Bernal J.* IU Cinquima, Universidad de Valladolid (Spain).

- **T1.21.** Valorisation of sweet cherry leftovers to produce antioxidant rich extracts. *González J., Bouaid, A., Calvo L.* Universidad Complutense de Madrid (Spain).

- **T1.23.** Exploitation of rice hulls as sources of natural phenolic antioxidants for food applications. *Kyriakoudi A., Misirli, K., Nenadis N., Mourtzinos I.* Aristotle University of Thessaloniki (Greece).

- **T1.24.** Ultrasound assisted extraction as a possible solution for ginger (*Zingiber officinale*) herbal dust utilization. *Vidović S., Sulejmanović M., Kyriakoudi A., Mourtzinos I., Gavarić A., Nastić N.* University of Novi Sad (Serbia) and Aristotle University of Thessaloniki (Greece).

- **T1.25.** Antioxidants recovery from avocado seeds using microwaves-assisted autohydrolysis treatment. *Del Castillo-Llamosas A., Ferreira-Santos P., del Río P.G., Gullón B.* University of Vigo (Spain), CEB - Centre of Biological Engineering, University of Minho (Portugal) and University of Limerick (Ireland)

TOPIC 2

BIOREFINERY: BIOPRODUCTS AND BIOENERGY

Keynote Lecture

- **T2.34.** Key elements for agricultural residues-based biorefinery development. *Eulogio C.* University of Jaen (Spain).

Oral Communications

- **T2.3.** Recovery of bio-based volatile fatty acids by pertraction techniques using green solvents. *Lo Coco R., Zuliani A., Battista F., Bolzonella D., Frison N.* University of Verona (Italy).

- **T2.4.** Green extraction of microalgal proteins with aqueous two-phase systems based on deep eutectic solvents. *Moldes D., Requejo P.F., Vega M., Bolado S.* Institute of Sustainable Processes (ISP), University of Valladolid (Spain).

- **T2.5.** Recovery of pectin from sugar beet pulp using emerging extraction technologies. Del *Amo Mateos E., Fernández Delgado M., Lucas, S., García Cubero M.T., Coca, M.* Institute of Sustainable Processes (ISP) - University of Valladolid (Spain).

- **T2.9.** Changing the sugar-based platform by the carboxylates platform when targeting at microbial oils productions. Lessons learnt. *González-Fernández C., Morales-Palomo, S., Tomás-Pejó E.* IMDEA Energia and Institute of Sustainable Processes (ISP) - University of Valladolid (Spain)

- **T2.12.** A techno-economic analysis and life cycle assessment of an olive-based multiproduct biorefinery coupled with carbon, capture and storage. *Fanourakis S.E., Garcia J.M.R., Castro E., Jiménez L., Boer D.T., Galán-Martín A.* Universitat Rovira i Virgili and Universidad de Jaén (Spain).

- **T2.17.** Hydrolysis of triacetin in subcritical and supercritical water. *Menalla E., García-Serna J., Cocero M.J.* Bioeconomy Research Institute - Universidad de Valladolid (BioEcoUVa) (Spain)

- **T2.22**. Sustainable bioprocess for the recovery of biobased products and bioenergy from brewer's spent grains. *Sganzerla W.G., Tena M., Sillero M., Solera R., Perez, M., Mussatto S.I., Forster-Carneiro T.* University of Cádiz (Spain), University of Campinas (Brazil) and Technical University of Denmark (Denmark).

- **T2.23.** Bio-polyesters from tomato peels, enabled by SCW. *Leontijevic V., Cantero D., Cocero M.J.* Bioeconomy Research Institute, Universidad de Valladolid (BioEcoUVa) (Spain).

- **T2.25.** Computational generation of molecular models for atomistic simulations of biocrude oils. *York D., Vidal-Daza I., Segura C., Norambuena-Contreras J., Martin-Martínez F.J.* Swansea University (UK), University of Conception and University of Bío-Bío (Chile).

- **T2.29**. Valorization of onion skin wastes using subcritical water. flavonoids and pectin recovery. *Benito-Román O., Sanz M.T., Beltrán S.* University of Burgos (Spain)

- **T2.31.** Biohydrogen production from the organic fraction of municipal solid waste (OFMSW) via lactate-driven dark fermentation. *Martínez C., García-Depraect O., Simorte M.T., Carreño P., Sanz I., Muñoz R.* Institute of Sustainable Processes (ISP) - University of Valladolid (Spain) and FCC Medio Ambiente (Spain).

Flash Oral Communications

- **T2.1.** A biorefinery approach for the production of PHAs. *Pesante G., Bastianelli C., Jelik, A., Zuliani A. and Frison N.* University of Verona (Italy)

- **T2.11.** Quantitative assessment of culture condition contributions into cell concentrations and astaxanthin content in alga *Haematococcus pluvialis*. *Komarysta V.P*. V.N. Karazin Kharkiv National University (Ukrania)

- **T2.20.** Protein and carbohydrate recovery from secondary sludge biomass generated in urban wastewater treatment plants. *Filipigh A., Rojo E.M. and Bolado, S.* Institute of Sustainable Processes (ISP)-University of Valladolid (Spain).

- **T2.24.** Life Cycle Analysis of Pyrolysis by Using ZSM-5 and Zeolite Y catalysts. *Soleymani Angili T., Grzesik K., Jerzak W.* AGH University of Science and Technology (Poland).

Poster communications

- **T2.2.** A sustainable strategy for the withdrawl of cellulose from eucalyptus tree wood waste using deep eutetic solvents and microwave-assisted extraction. *Sarraguça M., Moniz T., Vinhas S., Reis S., Rangel M.* LAQV, REQUIMTE, Universidade do Porto (Portugal).

- **T2.6.** Production and recovery of medium chain fatty acids from *Opuntia ficus-indica*. *Rizzioli F., Magonara C., Bolzonella D., Battista F.* University of Verona (Italy).

- **T2.7.** Adsorptive pretreatment of waste cooking oil using quicklime for two-step biodiesel production. *Lukic I., Kesic Z., Zdujic M., Skala D.* University of Belgrade and Institute of Technical Sciences of the Serbian Academy of Sciences and Arts (Serbia).

- **T2.8.** Anaerobic fermentation of vinasses as robust technology to produce green chemicals. *Greses S., Aboudi K., González-Fernández C.* IMDEA Energia and Institute of Sustainable Processes (ISP), University of Valladolid (Spain).

- **T2.10.** Fractionation of vine shoots to biosugars and lignin using an ionic liquid. *Duque A., Alonso G., Cañadas, R., Higueras I., Manzanares P.* CIEMAT and Universidad Complutense de Madrid (Spain)

- **T2.13.** Agricultural products from algal biomass grown in piggery wastewater. A techno economic analysis. *Rojo E.M., Filipigh A., Molinos-Senante M., Fernández-Sevilla J.M., Acién-Fernández F.G., Bolado S.* Institute of Sustainable Processes (ISP), University of Valladolid and Universidad de Almería (Spain)

- **T2.14.** Bioremoval of Cd, Hg, Pb and U by microalgae and bacteria grown in photobioreactors treating piggery wastewater. *Antolín-Puebla B., Moldes-Plaza D., Corchero-Quirce A., García-Encina P., Vega-Alegre M.* Institute of Sustainable Processes (ISP), University of Valladolid (Spain).

- **T2.15.** Co-production of microbial oil and carotenoids using biowaste by the oleaginous yeast *Rhodosporidium toruloides*. *Gallego-García M., Moreno A.D., Fernández J.L., Ballesteros I., Negro M.J.* CIEMAT (Spain)

- **T2.16.** Effects of temperature and bagasse addition on anaerobic codigestion of sludge with beer wastewater. *López R.A., Pérez M., Solera R.* University of Cádiz (Spain)

- **T2.18.** Improvement of sewage sludge treatment by anaerobic co-digestion with agri-food wastes (wine vinasse and poultry manure). *Sillero L., Solera R., Pérez M.* University of Cádiz (Spain)

- **T2.19.** Opuntia ficus-indica seed pomace processed by autohydrolysis. *Ferreira R.M., Flórez-Fernández N., Saraiva J.A., Cardoso S.M., Torres M.D., Domínguez H.* CINBIO-Universidade de Vigo (Spain) and LAQV-REQUIMTE-Universidade de Aveiro.

- **T2.21.** Recovery and purification of intermediate products of dicarboxylic acid esterification. *Sánchez F., Andreatta A., Pereda S.* PLAPIQUI-Universidad Nacional del Sur-CONICET, Universidad Tecnológica Nacional-CONICET (Argentina) and University of KwaZulu Natal (South-Africa).

- **T2.26.** Microwave-Assisted hydrolysis of triacetin to understand ester bond cleavage. *Maciel M.C., Cocero M.J., Mato R.B.* BioEcoUVa, Bioeconomy Research Institute of University of Valladolid (Spain).

- **T2.27.** Microwave pretreatment for supercritical carbon dioxide extraction of lipid fraction of shrimp shell. *de Souza Ribeiro M., Mato Chain R., Rodríguez-Rojo S.* BioEcoUVa, Bioeconomy Research Institute of University of Valladolid (Spain).

- **T2.28.** Understanding the behavior of chitin in Subcritical and Supercritical Water in a continuous reaction system. *Casas González A., Alonso E., Rodríguez Rojo S.* Bioeconomy Research Institute, Universidad de Valladolid - BioEcoUVa (Spain).

- **T2.30.** Hydrolysis of water-soluble protein from fish meal by subcritical water. Effect of pressurization gas agent. *Barea P., Melgosa R., Illera A.E, Alonso-Riaño P., Benito-Román O., Beltrán S., Sanz M.T.* University of Burgos (Spain)

- **T2.32.** Hydrothermal treatment of black liquor in search of biopolyols in supercritical water. *Demirkaya E., Cantero D., Cocero Alonso, M. J.* BioEcoUVa, Bioeconomy Research Institute of University of Valladolid (Spain).

- **T2.33.** Influence of acetate as main carbon source for lipid production via oleaginous yeast fermentation. *Sanz Martín J.M., Ramos Andrés M., Piñero Hernanz R., Barriuso Maicas J., García López J.L., Vlaeminck E., Quataert K., Atsonios K.* Centro Tecnológico Cartif (Spain), Centro de Investigaciones Biológicas-CIB-CSIC (Spain), Bio-based Europe Pilot Plant -BBEPP (Belgium) and Centre for Research & Technology Hellas (Greece).

- **T2.35.** Pretreatment of almond tree pruning for xylose production. *Romero-García J.M., Ruiz-Martínez M., Rojas-Chamorro J.A., Romero I., Ruiz E., Castro E.* University of Jaen (Spain).

- **T2.36.** Levulinic acid from olive stones: production optimization. *Romero-García J.M., Padilla-Rascón C., Rojas-Chamorro J.A., Romero I., Ruiz E., Castro E.* University of Jaen (Spain).

TOPIC 3

CO_2 CAPTURE AND UTILIZATION

Keynote Lecture

- **T3.17.** Converting CO_2 emissions from bio-based industries into sustainable chemicals to mitigate climate change. *Piñero-Hernanz R., Ramos-Andrés M., Sanz-Martín J.M., Balaguer-Ramírez M., Barriuso-Maicas J.* Centro Tecnológico Cartif (Spain), Instituto de Tecnología Química, ITQ-UPV-CSIC (Spain) and Centro de Investigaciones Biológicas, CIB-CSIC (Spain).

Oral Communications

- **T3.1.** Evaluating the potential of transforming CO_2 into value added products. biomethane and polyhydrohybutyrate. *Serna-García R., Collura F., Favaro L., Morosinotto T., Seco A., Bouzas A., Treu L., Campanaro S.* CALAGUA – Unidad Mixta Universitat de València-Universitat Politècnica de València (Spain) and University of Padua (Italy).

- **T3.5.** Hydrothermal reduction of CO_2 by using catalysts and biomass residues. *Chinchilla M.I., Chain F.A., Martín Á., Bermejo M.D.* BioEcoUVa, Bioeconomy Research Institute of University of Valladolid (Spain).

- **T3.7**. Sustainable formulations from CO_2 and orange peel waste. *Viciano M., Cumplido M.P. Aimplas* (Spain)

- **T3.10.** Catalytic hydrothermal conversion of carbon dioxide and organic waste under sub-critical conditions. *Konstantinova M., Quintana-Gomez L., Liu Y., Davies G., Nasir N., Muhammad, F., McGregor J.* University of Sheffield and UK Catalysis Hub (UK).

- **T3.13.** Cyclic carbonates production from CO_2 and epoxides using sustainable solvents. Quaternary ammonium based-ionic liquids versus -deep eutectic mixtures. *Paninho A. B., Branco L. C., Nunes A.V.M.* LAQV, REQUIMTE, Universidade NOVA de Lisboa (Portugal).

- **T3.14.** Evaluation of the potential of phosphonium-based ionic liquids for CO_2 absortion through soft-saft. *Rodríguez-Reartes S.B., Ouedghiri Ben Otmane F.E., Llovell F.* Universitat Rovira i Virgili (Spain), Universidad Nacional del Sur and PLAPIQUI-CONICET (Argentina).

- **T3.15.** Understanding the potential of des for GHG capture and separation: from thermodynamics to process design. *Alencar L.V.D., Rodriguez-Reartes S. B., González-Olmos R., Llovell F.* Universitat Rovira i Virgili (Spain), Universidade Federal de Río de Janeiro (Brazil), Universidad Nacional del Sur (Argentina), PLAPIQUI-CONICET (Argentina) and Universitat Ramon Llull (Spain).

Flash Oral Communications

- **T3.2.** Defossilization of the pretrochemical industry via renewable carbon to stay within planetary boundaries. *Galán-Martín A., Tulus V., Pérez-Ramírez J., Guillén-Gosálbez G.* University of Jaén (Spain) and ETH-Zürich (Switzerland).

- **T3.3.** Assessment of selected catalysts and reducing metals for the simultaneous conversion of captured CO_2 and hydrogen generation. *del Río J.I., Almarza M., Martín A.,* *Bermejo M.D*. BioEcoUVa, Bioeconomy Research Institute of University of Valladolid (Spain) and Universidad de Antioquia UdeA (Colombia).

- **T3.11.** Protic ionic liquids as electrolyte for electrochemical CO_2 reduction. *Messias S., Pires C., Paninho A.B., Rangel C.M., Branco L.C., Reis Machado A.S.* LAQV, REQUIMTE, Universidade NOVA de Lisboa (Portugal) and Laboratório Nacional de Energia e Geología (Portugal)

Poster Communications

- **T3.4.** Hydrothermal conversion of CO_2 captured in seawater into formate using metal-sourced hydrogen at mild reaction conditions. *Goicoechea A., Bermejo M.D., Martín Á.* BioEcoUVa, Bioeconomy Research Institute of University of Valladolid (Spain).

- **T3.6.** Anaerobic bioprocesses towards the conversion of carbon dioxide into bio-based products. *Zuliani A., Lo Coco R., Battista F., Bolzonella D., Frison N.* University of Verona (Italy).

- **T3.9.** Dry reforming of methane with CO_2 for syngas production over MgO-modified co/natural perlite catalysts. *Mahir H., Benzaouak A., Consentino L., Touach N., El Hamidi A., Kacimi M., EL Mahi M., Lotfi, EM., Liotta L.F.* Mohammed V University in Rabat (Morocco) and Istituto per lo Studio dei Materiali Nanostrutturati ISMN-CNR (Italy).

- **T3.12.** Biobased Aerogels as Nanoparticle Support for CO_2 Conversion Reactions. *Melo C.I., Paninho A.B., Carvalho J., Pires C., Machado B.F., Lopes J.C.B., Nunes A.V.M., Branco L.C.* LAQV-REQUIMTE Universidade NOVA de Lisboa (Portugal) and CoLAB Net4CO2 (Portugal).

- **T3.16.** Biotechnological platform to produce CO_2-derived intermediates and monomers. *Ramos-Andrés M., Sanz-Martín J.M. , Barriuso-Maicas J., García-López J.L., Verhoeven E., Quataert K., Piñero-Hernanz R.* Centro Tecnológico Cartif (Spain), Centro de Investigaciones Biológicas Margarita Salas-CIB-CSIC (Spain) and Bio-based Europe Pilot Plant -BBEPP (Belgium).

- **T3.18.** Nitrosamine formation during CO_2 and NO_x absorption. *Castro- Ferro, M., Vaquerizo- Martin, L.* BioEcoUVa, Bioeconomy Research Institute of University of Valladolid (Spain).

TOPIC 4

GREEN REACTION AND CATALYSIS

Keynote Lecture

- **T4.10.** CO_2-H_2O Based Green Engineering for Biomass Valorization. *Quitain A.T.* Kumamoto University (Japan).

Oral Communications

- **T4.2.** Microfluidic approaches for the sustainable and green synthesis. *Bondzic B*. University of Belgrade (Serbia).

- **T4.3.** Green method to functionalize melamine foams with silver nanoparticles in a single step. *Quilez Molina A.I., Barroso-Solares S., Rodríguez-Pérez M.A, and Pinto J.* BioEcoUVA Research Institute on Bioeconomy of University of Valladolid (Spain).

- **T4.7**. Green H_2 from water splitting: the critical role of the choice of electrodes. *de Sá M. H., Costa R., Sottomayor M. J., Pereira C.* Centro de Investigação em Química UP (CIQUP) - Instituto de Ciências Moleculares (IMS) da Universidade do Porto (Portugal).

- **T4.8.** Catalyst-free acetylation of starch using a green deep eutectic solvent as reaction promoter. *Portillo Perez G.A., Skov K.B., Martinez M.M.* Center for Innovative Food (CiFOOD), Aarhus University (Denmark).

- **T4.9.** Biocatalysis in deep eutectic solvents. designing safe and sustainable processes. *Cvjetko Bubalo M., Radović M., Panić M., Damjanović A., Radojčić Redovniković I.* University of Zagreb (Croatia)

Poster Communications

- **T4.1.** Application of ac-magnetic field activation for ferritization synthesis of magnetic materials**.** *Kochetov G., Samchenko D., Lastivka O., Derecha D.* Kyiv National University of Construction and Architecture (Ukraine) and Institute of Magnetism (Ukraine)

- **T4.4.** Bringing value-added to the NaOH-based CO_2 capture by generating green hydrogen at the same time in a semicontinuos facility. *del Río J.I, Hernáez C., Martín A., Bermejo M.D.* Bioeconomy Research Institute of University of Valladolid (Spain) and Universidad de Antioquia UdeA (Colombia).

- **T4.6.** Biobased furan chemicals production using deep eutectic solvents assisted with microwave system heating. *Braga C., Romaní A., Domingues L., Gullón B*. University of Minho (Portugal), LABBELS-Associate Laboratory (Portugal) and University of Vigo (Spain).

TOPIC 5

POLYMERS AND ADVANCE MATERIALS

Keynote Lecture

- **T5.10.** Advanced synthetic bone grafts by supercritical fluid technology. *García-González C.A., Diaz-Gomez L., Carracedo-Pérez M., Magariños B., Alvarez-Lorenzo C.* Universidade de Santiago de Compostela (Spain).

Oral Communications

- **T5.2.** Advanced functional polymeric nanocomposites for the remediation of nitrates-polluted water. *Barroso-Solares S., Hurtado-Garcia V., Merillas B., Rodríguez-Pérez M.A., and Pinto J.* Bioeconomy Research Institute of University of Valladolid (Spain).

- **T5.4.** Tröger's base network PIMs with tunable pore size for heterogeneous catalysis. *Carta M., Antonangelo A.R., Hawkins N.* Swansea University (UK).

- **T5.7.** Towards the production of green and advanced thermal insulators. *Martín-de León J., Sillero A., Baiochi A.G., Gomes V., Rodríguez-Pérez M.A.* Bioeconomy Research Institute of University of Valladolid (Spain) and Universidade Estadual de Campinas (Brazil).

- **T5.8.** Self-healing tire rubber composites: environmental implications of technical advances. *Alonso Pastor L.E., Núñez Carrero K., Araujo-Morera J., Hernández Santana M., Rodríguez Pérez M.A.* Universidad de Valladolid (Spain) and Institute of Polymer Science and Technology, ICTP-CSIC (Spain).

- **T5.11.** Effect of egg white protein and water content in the stabilization mechanisms of biobased rubber latex foams. *Amezúa-Arranz C., Salmazo L.O., López-Gil A., Rodríguez-Pérez, M.A.* BioEcoUVA Research Institute on Bioeconomy of University of Valladolid (Spain) and CellMat Technologies S.L. (Spain).

- **T5.12.** Preparation and characterisation of mycelium and lignocellulosic waste composites. *Kržišnik D., Kunstelj M., Gonçalves J., Humar M.* University of Ljubljana (Slovenia) and Institute of Sustainable Processes, University of Valladolid (Spain).

- **T5.15.** Closed-loop recycling of fiber-reinforced polymer composites waste from aeronautic industry. *Santiago-Calvo M., Guerrero J., Asensio M., Alonso C., Fernández M., Cañibano E.* Cidaut Foundation (Spain) and University of Valladolid (Spain).

- **T5.19.** Synthesis and applications of porphyrin based-MOFs using supercritical CO_2. *Lopez-Periago A., Kubovics M., Careta O., Ayllon J.A., Domingo C., and Nogues C.* Institute of Materials Science of Barcelona, ICMAB-CSIC (Spain) and Universtitat Autònoma de Barcelona (Spain).

- **T5.20.** Is there any suitable alternative solvent for membranes? *De la Viuda M. R., Soto C., San José E., Carmona F.J., Palacio L., Paniagua S., Prádanos P., Hernández A., Tena A.* Institute of Sustainable Processes, University of Valladolid (Spain).

- **T5.21.** Reducing thickness or inducing porous structure? A methodology to increase the permeance in gas separation membranes. *Cuadra-Rodríguez D., Soto C., Carmona J., Palacio L., Tena A., Rodríguez-Pérez M. Á., Pinto J.* Institute of Sustainable Processes, University of Valladolid (Spain) and Bioeconomy Research Institute of University of Valladolid (Spain).

- **T5.26.** Biodegradable packaging materials based on *Agaricus bisporus*. *Pérez-Bassart Z., Martínez-Abad A., Reyes A., López-Rubio A., Fabra M.J.* Institute of Agrochemistry and Food Technology IATA-CSIC (Spain) and CSIC Interdisciplinary Thematic Platform for Sustainable Plastics towards a Circular Economy. (PTI-SusPlast+)

- **T5.27.** Improving water resistance of rice straw cellulose-based aerogels. *Cabrera-Villamizar L., Campano C., Rivero-Buceta V., Fabra-Rovira M.J., López-Rubio A., Prieto M.A.* Institute of Agrochemistry and Food Technology, *IATA-CSIC (Spain) and Biological Research Centre Margarita Salas, CIB-CSIC (Spain)*.

Flash Oral Communications

- **T5.6.** Transparent polyurethane aerogels: promising materials to reduce CO2 emissions. *Merillas B., Martín-de-León J., Villafañe F., Rodríguez-Pérez M.A.* BioEcoUVA Research Institute on Bioeconomy and IU Cinquima, University of Valladolid (Spain).

- **T5.17.** Design and transformation of biodegradable composite materials with improved properties for the packaging industry. *Asensio M., González M., Santiago-Calvo M., Guerrero J., Fernández M., Cañibano E.* Cidaut Foundation (Spain) and University of Valladolid (Spain).

- **T5.29.** Dynamic chemistry in sustainable food packaging design. *M. Herrero, K. Núñez, S. Vallejo, J.C. Merino, J.M. García, M.A. Rodríguez, J.M. Pastor*. Dpto. de Física de la Materia Condensada, Universidad de Valladolid (Spain) and Dpto. de Química Orgánica, Universidad de Burgos (Spain)

Poster Communications

- **T5.1.** Copper nanoparticles-anchored PCL electrospun fibers with excellent capability to remove a dangerous pesticide. *Quilez-Molina A.I., Barroso-Solares S., Hurtado-García V., Heredia-Guerrero J.A., Rodríguez-Mendez M.L., Rodríguez-Pérez M.A. and Pinto J.* BioEcoUVA Research Institute on Bioeconomy of University of Valladolid (Spain) and Instituto de Hortofruticultura Subtropical y Mediterránea “La Mayora” IHSM-UMA-CSIC (Spain).

- **T5.3.** Development of nades-based injectable hydrogels through enzymatic crosslinking. *Meneses L., Bagaki D., Roda A., Paiva A., Duarte A.R.C.* LAQV, REQUIMTE, Universidade NOVA de Lisboa (Portugal).

- **T5.5.** Wood in 3D printing - from a sustainability point of view. *KrapeŽ Tomec D., Kariž M.* University of Ljubljana (Slovenia).

- **T5.9.** Transparent nanocellular polymers as insulating windows for zero-energy building. *Lizalde-Arroyo F., Martín-de León J., Bernardo V., Rodríguez-Pérez M.A.* BioEcoUVA Research Institute on Bioeconomy of University of Valladolid (Spain) and CellMat Technologies S.L. (Spain).

- **T5.13.** Revalorisation of high-performance thermoplastic composite waste. *Guerrero J., Santiago-Calvo M., Asensio M., Mazzeschi M., Rodriguez, A., Alonso C., Fernández M., Cañibano E.* Cidaut Foundation (Spain) and University of Valladolid.

- **T5.14.** Porous foams from gels for green insulation and filter. *Fernández-de la Fuente M., Martín-de León J., Rodríguez-Pérez M. A.* BioEcoUVA Research Institute on Bioeconomy of University of Valladolid (Spain).

- **T5.16.** Synergistic effect of the addition of environmentally friendly flame retardants to recycled ABS. *Rodríguez A., Asensio M., Santiago-Calvo M., Guerrero J., Cañibano E., Fernández M.T.* Foundation Cidaut (Spain) and University of Valladolid (Spain).

- **T5.22.** Click and de-click carbonyl-amino coupling for the stabilization and smart release of naturally-occurring antifungal volatiles from renewable polymers. *Esteve-Redondo P., Heras-Mozos R., Simo-Ramírez, E., López de Dicastillo C., Gavara R., Hernández-Muñoz P.* Instituto de Agroquímica y Tecnología de Alimentos, IATA-CSIC (Spain).

- **T5.23.** A green crosslinking strategy to improve functional properties of gliadin films. *Esteve-Redondo P., López de Dicastillo C., Gavara R., Hernández-Muñoz P.* Instituto de Agro-química y Tecnología de Alimentos, IATA-CSIC (Spain).

- **T5.24.** Valorization of post-consumer polypropylene through the reinforcement with amine and amine/silane modified clays for potential use in food packaging. *López de Dicastillo C., Velásquez E., Gavara, R., Hernández P., Galotto M.J., Guarda A.* Instituto de Agro-química y Tecnología de Alimentos, IATA-CSIC (Spain) and Universidad de Santiago de Chile (Chile).

- **T5.25.** Sustainable bio-based materials from minimally processed red seaweeds: effect of composition and cell wall structure. *Cebrián-Lloret V., Martínez-Abad A., López-Rubio A., Martínez-San, M.* Instituto de Agro-química y Tecnología de Alimentos, IATA-CSIC (Spain) and Instituto de Investigación en Ciencias de la Alimentación, CIAL-CSIC-UAM (Spain).

- **T5.28.** Influence of green high hydrostatic pressure pretreatments on the structure and functional properties of alginate extracts. *Bojorges H., Fabra M.J., Martínez-Abad A., López-Rubio A.* Institute of Agrochemistry and Food Technology, IATA-CSIC (Spain).

TOPIC 6

APPLICATIONS IN CARE AND HEALTH PRODUCTS, FOOD AND AGRICULTURE TECHNOLOGY

Keynote Lecture

- **T6.20.** Sterilization of PPE with supercritical carbon dioxide. *Ruiz-Saldaña H., Pepzcynska, M, Cabañas A., Gómez-Salazar, J.M., Calvo L.* Complutense University of Madrid (Spain).

Oral Communications

- **T6.8.** Green inhalers containing beclomethasone dipropionate-loaded aerogels. *Duong T., Kalmár J., Álvarez-Lorenzo C., García-González C.A.* Universidade de Santiago de Compostela (Spain) and University of Debrecen (Hungary).

- **T6.9.** Supercritical CO_2 applied on the production of quercetin-loaded liposomal dry powder formulations for the treatment of inflammatory lung diseases. *Costa C., Grenho L., Casimiro T., Sousa Gomes P., Fernandes M.H., Fernandes E., Corvo M.L., Aguiar-Ricardo A*. LAQV-REQUIMTE, Universidade NOVA de Lisboa and Universidade do Porto (Portugal), Instituto de Investigação do Medicamento (iMed.ULisboa),

- **T6.11.** A green approach for the development of chitosan hydrogels using olive leaf extract as dissolution and gelating agent. *Pitterou I., Nanou D. A., Chinni S., Ntirogianni A., Tzani A., Detsi A.* National Technical University of Athens (Greece).

- **T6.14.** Extraction and utilization of bioactives from agro- and food industrial wastes by green technologies. *Vági E., Horváth V., Molnár M., Tátraaljai D., Székely E.* Budapest University of Technology and Economics, BME(Hungary).

- **T6.15.** The separation of biologically active extracts from chamomile seeds. *Milovanovic S., Grzegorczyk A., Świątek Ł., Tyskiewicz K., Konkol M.* University of Belgrade (Serbia), Łukasiewicz Research Network (Poland) and Medical University of Lublin (Poland).

Flash Oral Communications

- **T6.2.** A new and green media for ocular drugs based on Natural Deep Eutectic Systems. *Jesus A. R., Sarmento C., Monteiro H., Paiva A., Duarte A.R.C.* LAQV-REQUIMTE Universidade NOVA de Lisboa (Portugal).

- **T6.21.** Impregnation of thymol in biofilms for active food packaging using supercritical carbon dioxide. *Cerhová M., Martín Á., López Gil A., Casas Gonzáles A. P., Rodríguez Pérez M. Á., Cocero M. J., Rodríguez-Rojo S.* BioEcoUVA Research Institute on Bioeconomy of University of Valladolid (Spain) and CellMat Technologies S.L. (Spain).

- **T6.22.** NADES GOODNESS liquid food supplements. *Panić M., Damjanović A., Bagović M., Radović M., Cvjetko Bubalo M., Radošević K., Radojčić Redovniković I.*NADES Design (Croatia) and University of Zagreb (Croatia).

Poster Communications

- **T6.1.** In vitro assessement of the performance of polymeric membranes encapsulated with lavender essential oil for wound healing. Cruz E., Pereira J., Oliveira F., Craveiro R., Paiva A., Duarte A. R. C. Universidad de Castilla La Mancha (Spain) and LAQV-REQUIMTE Universidade NOVA de Lisboa (Portugal).

- **T6.7.** Enantioselective supercritical fluid chromatography separation of chiral anticoagulant rodenticides. *Ares A.M., Valverde S., Toribio, L., Bernal J.* IU Cinquima, University of Valladolid (Spain).

- **T6.4.** VOC adsorption by means of activated carbons derived from wasted coffee grounds and olive stones. *Czerwińska N., Giosue C., Bernardo M., Matos I., Ruello M.L.* Università Politecnica delle Marche (Italy) and Universidade Nova de Lisboa.

- **T6.5.** Chemical composition, antioxidant and antibacterial potential of *Diplopolepsis rosae* galls. *Cvanić T., Šovljanski O., Tomić A., Aćimović M., Saveljić A., Vulić J., Čanadanović-Brunet J., Ćetković G.* University of Novi Sad (Serbia) and Institute of Field and Vegetable Crops Novi Sad (Serbia).

- **T6.6.** Effects of supercritical CO_2 sterilization on the physicochemical properties of bioaerogels. *Carracedo-Pérez M., Casares-Pérez M., Magariños B., García-González C.A.* Universidade de Santiago de Compostela (Spain).

- **T6.10.** Rheological properties and inhibitory effect on digestive enzymes of model beverages with saffron floral by-products. *Cerdá-Bernad D., Bordenave N., Frutos M.J.* CIAGRO – UMH, Miguel Hernández University (Spain) and University of Ottawa (Canada).

- **T6.12.** Thermal stability of chitosan coated packaging papers. *Todorova D., Yavorov N., Lasheva V., Vrabič Brodnjak U.* University of Chemical Technology and Metallurgy (Bulgaria) and University of Ljubljana (Slovenia).

- **T6.13.** To choose or not to choose hydrophobic deep eutectic solvents for pharmaceutical application. *Bagović M., Panić M., Jakopović, Ž., Juričić, H., Cvjetko Bubalo M., Radojčić Redovniković I., Radošević K.* University of Zagreb (Croatia)

- **T6.16.** Valorisation of orange peels using deep eutectic systems. *Marques M., Pereira J., Duarte A. R., Paiva A.* LAQV-REQUIMTE-Universidade NOVA de Lisboa (Portugal) and DES Solutio (Portugal)

- **T6.17.** *Chlorella vulgaris* and *Tetradesmus obliquus*. Impact of pretreatments on supercritical CO_2 extraction yield and cytotoxic activity of extracts. *Vladić J., Simić S., Pereira H., Stanojković T., Žižak Ž., Besu I., Ferreira A., Gouveia L.* Universidade NOVA de Lisboa (Portugal), University of Novi Sad (Serbia), GreenCoLab-Universidade do Algarve (Portugal), Institute of Oncology and Radiology of Serbia (Serbia) and Laboratório Nacional de Energia e Geología (Portugal).

- **T6.18.** Morphological control of Ciprofloxacin micronized by the Supercritical Antisolvent Technique (SAS). *Zahran F., Ruiz-Saldaña H., Pérez E., Calvo L. and Cabañas A.* Complutense University of Madrid (Spain) and Helwan University (Egypt).

- **T6.19.** Microbial inactivation of sanitary material with supercritical CO_2. *Ruiz M., Ruiz-Saldaña H., Cabañas A., Serrano, D.R., Calvo L.* Complutense University of Madrid (Spain).

- **T6.23.** (Re)valuation of wine industry by-products using ohmic heating as an emerging technology. *Ferreira-Santos P., Rodrigues R.M., Genisheva Z., Botelho C., Rocha C.M.R., Teixeira J.A.* University of Vigo (Spain), CEB - Centre of Biological Engineering, University of Minho (Portugal) and LABBELS - Associate Laboratory (Portugal).

- **T6.24.** Biodegradability assessment of choline choline-based protic ionic liquids and deep eutectic solvents. *Tzani A., Zampeti Z. Papadopoulos A., Detsi A.* National Technical University of Athens (Greece).

- **T6.25.** Preparation of drug parenteral formulations for the treatment of visceral leishmaniasis. *Echevarria L., Loe Sack Sioe L., Guillén A., Cabañas A., Serrano D.R., Calvo L.* Complutense University of Madrid (Spain).

TOPIC 7

SCALE-UP AND INDUSTRIAL APPLICATIONS

Oral Communications

- **T7.2.** Scale-up of a new flexible process for phosphorus and PHA recovery from sewage sludge and organic wastes treatment. *Frison N., Foglia A., Bernardi M., Insonne B., Eusebi A.L., Fatone F.* University of Verona (Italy), Marche Polytechnic University (Italy) and CAP Holding Spa (Italy).

- **T7.6.** Stirred extraction columns for industrial reaction processes. *Rudelstorfer G., Greil R., Siebenhofer M., Lux S., Grafschafter A.* Graz University of Technology (Austria).

Poster Communications

- **T7.3.** Determination of scale-up parameters to design an industrial microwave to extract pectin from Sugar Beet Pulp. *Fernández-Delgado M., del Amo-Mateos E., García-Cubero M.T., Coca M., Lucas S.* Institute of Sustainable Processes (ISP), University of Valladolid (Spain).

- **T7.4.** Mass transfer phenomena in liquid-liquid extraction of biobased carboxylic acids with TiOA. *Rudelstorfer G., Siebenhofer M., Grafschafter A.* Graz University of Technology (Austria).

- **T7.5.** Phase separation and settler design. *Bol P., Rudelstorfer G., Bol J.B., Siebenhofer M., Grafschafter A.* Graz University of Technology (Austria).

- **T7.7.** Natural deep eutectic solvents (NADES) as alternative media for the development of a greener leather dyeing process. *Tzani A., Loukaitis K., Hatzouli A., Detsi A.* National Technical University of Athens (Greece) and Chromatourgia Tripoleos S.A. (Greece).

- **T7.1.** Construction of a pilot plant for the reduction of CO_2 captured by amines. *Bermejo M.D., Goicoechea A., Quintana L., Almarza M., Martín Á.* Bioeconomy Research Institute of University of Valladolid (Spain).

ABSTRACTS

PLENARY LECTURES

DEEP EUTECTIC SYSTEMS TARGETING CURRENT CHALLENGES IN LIFE SCIENCE APPLICATIONS

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Abstract

The concept of green solvents was introduced by John Warner and Paul Anastas, in 1998, when they listed the 12 principles of green chemistry. One of these principles assumes that the use of solvents, should be as an auxiliary substances, in the synthesis and preparation processes, and emphasises that they should be made unnecessary wherever possible, and if used they should be innocuous[1].The sustainability of a process or a product is, hence, a result of the complex interaction between the product or process implemented and environment, technology and economy factors[2]. In the current scenario of a worldwide quest for sustainable and "greener" alternatives for current applications, in the past two decades the number of reports on NADES/DES applicability in various situations has rapidly grown. The tailor-made versatility of these eutectics, meaning in practical terms a wide range of chemical and physical properties, has resulted in promising studies applied in industry, biotechnology, cosmetics, pharmaceuticals, food, and health[3].

In life science applications, several challenges arise. In particular, the formulation of therapeutic deep eutectic systems (THEDES) revealed to be very promising to enhance the characteristics of existing drugs and optimize new formulations that could be easily administrated and more effective, providing higher dissolution rates of the API, enhancement of solubility, permeability and absorption through tissues, or they can be incorporated in suitable polymer to potentiate the efficiency of biomedical devices. The use of DES as stabilizing agents has also paved its way in the biomedical field, as additives for blood preservation and in the cryopreservation of cells. In this communication, these different examples will be presented and discussed.

Keywords: Life sciences, Pharmaceutics, Deep eutectic solvents, Therapeutic deep eutectic solvents, Green chemistry, Cryopreservation

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Acknowledgements:

This project has received funding from the European Union's Horizon 2020 (European Research Council) under grant agreement No ERC-2016-CoG 725034 and was supported by the Associate Laboratory for Green Chemistry-LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020).

SUSTAINABLE MEMBRANE TECHNOLOGY THROUGH POLYELECTROLYTE SELF ASSEMBLY

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Abstract

Polymeric membranes are ubiquitous in numerous applications including kidney dialysis, water treatment, filtration, gas separation, energy generation and storage. It is ironic that membranes that hold such great potential for sustainable solutions are usually produced using unsustainable and toxic organic solvents. New approaches are urgently needed to make the production of membranes as sustainable as their possible applications.

Polyelectrolytes and their complexes are an especially promising system to produce sustainable membranes, while at the same time imbuing them with advanced functionalities. Here, we discuss recent work where thin separation layers, but also complete membranes are produced using only water as the required solvent. This leads to membranes with highly tunable separation properties and with additional functionalities such as stimuli-responsiveness, fouling control, stability, specific selectivity, sustainability, and antimicrobial activity. Indeed, the unique materials properties of polyelectrolyte based membranes often lead to advantages that go well beyond their sustainable method of fabrication. Their combination of versatility, and high chemical stability, already leads to new separation processes that were simply not possible before. This includes, for example, a new and simple process to effectively remove micropollutants from drinking water and waste water, but also a simple coating process to produce recyclable oxygen barrier films for more sustainable packaging materials.

Keywords: Polyelectrolytes, Aqueous Phase Separation, Multilayer, Contaminants of emerging concern

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GREEN PROCESSES WITH SUPERCRITICAL FLUIDS

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Abstract

Supercritical fluids, especially carbon dioxide and water, are regarded as green solvents. Thus, supercritical fluid technology is expected to contribute to greener processes for separation, reaction, and material processing. Supercritical CO_2 has been used extensively for extraction and material processing. Subcritical water is also used as separation solvent, because the water property is close to organic solvent. We have been developing various separation processes using supercritical CO_2 or subcritical water. We proposed green solvent platform using CO_2 and water for natural materials processing.

Micronization process using supercritical fluids is useful to produce organic nanoparticles, encapsulated particles, and metal particles. Organic particles can be produced by various methods such as RESS, SAS, PGSS using supercritical CO_2. We have incorporated isomerization of carotenoids to improve the efficiency of extraction and micronization processes. Supercritical hydrothermal synthesis has been used to produce metal or metal oxide nanoparticles.

One of the important applications of supercritical fluids is chemical recycling of waste plastics. Subcritical water or supercritical alcohol is suitable solvent for depolymerization processes. We have developed PET depolymerization process to its monomers in supercritical methanol collaborated with industry. Fiber reinforced plastics were decomposed to recover fibers and decomposed organics in sub- or supercritical fluids.

We have launched spin-off company “Super Critical Technology Centre Co. Ltd. (http://www.sctc.co.jp/en/)” focusing on supercritical CO_2 extraction in 2013 with Dr. R. Fukuzato. It was certified as a university-launched venture company. Now we have various scales of extractors including pilot-scale and commercial-scale extraction plant. We also have lab-scale reactors for supercritical water. The business contents of the company are technical consulting, contract-based prototyping, pre-production, and contract-based production. Production of decaffeinate green coffee beans has started in 2019, since there was no decaffeination process in Japan. The decaffeination process was extended to green tea and black tea.

Keywords: Supercritical fluid, Subcritical fluid, Separation, Reaction, Material processing.

TOPIC 1

GREEN EXTRACTION, FRACTIONATION AND FORMULATION OF BIOACTIVES

SUPERCRITICAL CO_2 FRACTIONATION – A GREEN AND CONTINUOUS PROCESS FOR COMPLEX SEPARATIONS

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Abstract

Supercritical CO_2 fractionation is a high-pressure separation process applied to liquid mixtures or suspensions. It offers the advantages of being conducted continuously in counter-current packed columns, with a selective and GRAS solvent[1] and being generally performed under moderate pressures and at low temperatures, allowing to preserve thermosensitive compounds. These benefits open potential outlets for this process in many industries where the use of toxic organic solvents and high temperatures are not suitable anymore. However, supercritical CO_2 fractionation is not widely used in industry while very efficient when applied to complex mixtures. The main reason is that there is still a lack of knowledge (or data) for performing a reliable scale-up according to the system studied. Indeed, tools developed for absorption and liquid-liquid extraction can't be directly applied to supercritical fractionation.

The aim of this presentation is to demonstrate the great potential of supercritical CO_2 fractionation for industrial applications. The selectivity of the process will be illustrated through case studies. The first case study is a nice application in the field of perfume production with the obtention of a high content sclareol fraction from a concrete containing more than 100 compounds[2]. The supercritical CO_2 fractionation led to a separation efficiency higher than molecular distillation could perform. The second case study is about the dealcoholization of beverages with the processing of ethanol-water mixtures using supercritical CO_2[3]. Those results combined to the measurement and calculation of physicochemical properties of mixtures under pressurized CO_2[4] led to a better understanding of the phenomena occurring in counter-current packed columns under supercritical conditions[5].

Keywords: Supercritical CO_2, Fractionation, Separation, Flooding prediction

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NEW STRATEGY BASED ON HYDROPHOBIC NATURAL DEEP EUTECTIC SOLVENTS AND CYCLODEXTRINS FOR CAROTENOID EXTRACTION-ENCAPSULATION FROM PERSIMMON PEELS

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Nowadays, there is a growing interest in increasing the sustainability of the agrifood production chain and promoting the circular economy based on the generation of “zero waste”. This is because food processing produces large amounts of waste that contain high-value compounds that are underused. This work proposes to increase the value of waste from persimmon (*Diospyros kaki Thunb*) peel, by recovering bioactive lipidic compounds, such as carotenoids. This is why, a method was developed and optimized to extract carotenoids by a sustainable extraction technique, such as ultrasound-assisted extraction (UAE) combined with natural deep eutectic solvents (NaDES). Since solvent selection is one of the critical factors in carotenoid extraction, a NaDES screening was carried out to determine which of the seven selected NaDES allows obtaining extracts with high carotenoid contents and antioxidant capacity. The extraction process was optimized using an experimental design. The optimal extraction conditions were based on the use of thymol: menthol with a molar ratio 2:1, 33% ultrasound amplitude, and 13,8 min as the extraction time. The extracts obtained under the optimal extraction conditions were compared with those obtained under the same extraction conditions but using organic solvents instead of NaDES. In addition, the carotenoids present in the optimal extracts were determined using ultra-high-performance liquid chromatography (UHPLC). To recover the carotenoids from the extraction solvent, an encapsulation strategy based on the use of cyclodextrins was developed, which protects the bioactive carotenoids and improves their water solubility and their sustained compound releasing behavior. Carotenoid-cyclodextrin powder was characterized by scanning electron microscopy (SEM), Fourier transform infrared-attenuated total reflection (FTIR-ATR), and the encapsulation efficiency, cytotoxicity, and antioxidant capacity of the encapsulated were evaluated. Results indicated for the first time that the use of hydrophobic NaDES for achieving the extraction in combination with cyclodextrin encapsulation could be a sustainable alternative for the extraction of antioxidant carotenoids from persimmon peel for important applications in the food, pharmaceutical, agrochemical, and cosmetic fields.

Keywords: Carotenoids, Cyclodextrins, Extraction-encapsulation, Hydrophobic natural deep eutectic solvents, Persimmon peel.

Acknowledgments: This research work is part of the project TED2021-131011B-I00, funded by MCIN/AEI/10.13039/501100011033 and by the European Union “NextGenerationEU”/PRTR. Authors also thank the Comunidad of Madrid and European funding from FSE and FEDER programs (project S2018/BAA-4393, AVANSECAL-II-CM), the University of Alcalá (project PIUAH21/CC-007), and M. Romero and L. El Ouahabi for technical assistance.

USE OF BIOBASED SOLVENTS IN CAROTENOID EXTRACTIONS FROM RED YEAST *RHODOTORULA MUCILAGINOSA*

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Abstract

Carotenoids are important tetraterpenoids, famous mostly as liposoluble pigments used widely in the phytomedicine, chemical, pharmaceutical, cosmetic, food, and feed industries. Due to the ongoing growth of the market of natural pigments, carotenoids, and the ability of numerous microorganisms to synthesize carotenoids, biotechnology is considered the best alternative for their production. Red yeasts, such as *Rhodotorula mucilaginosa*, are proven producers of carotenoids. Until recently, volatile organic compounds were used to extract these valuable compounds because of their organic nature, and low miscibility with the aqueous medium. This research aimed to investigate the potential of biobased solvents in carotenoid extractions. Yeast cells were incubated at 30 °C centrifuged at 6000 rpm, and lyophilized for 48 h. For the cell disruption method, milling was used for 90 seconds (CryoMill). Then, in order to find greener solvents to use in extractions the screening was performed using 3 biobased solvents (D-limonene, 2-methyl tetrahydrofuran (2-MeTHF), and cyclopentyl methyl ether (CPME)) and acetone, as a reference solvent which has already proved to be suitable for carotenoid extractions. After cells diffusion in these solvents, extracts were centrifuged, and supernatants were collected and measured spectrophotometrically. These extracts were later evaporated using 12 position nitrogen evaporator and dissolved in 1 ml of acetonitrile-methanol (70:30) solution in order to identify obtained carotenoids on UHPLC chromatographic system with a PDA UV detector and mass spectrometer. Also, two different extractions were used (classical and ultrasound) and compared with all four solvents. Results show that four different carotenoids were extracted: torularhodin, β-carotene, torulene, and zeaxanthin. Compared to acetone, 2-MeTHF and CPME presented as good alternatives as green solvents, as opposed to limonene. The higher carotenoid yields were obtained using ultrasound extractions, with acetone (4.23 mg/100g), 2-MeTHF (3.49, 4.23 mg/100g), and CPME (3.58, 4.23 mg/100g). 2-MeTHF and CPME presented great potential as green solvents in the extractions of hydrophobic compounds like carotenoids, especially in novel, greener extraction methods, including ultrasound.

Keywords: green extractions, biobased solvents, extractions, carotenoids, Rhodotorula mucilaginosa

Acknowledgements: Authors would like to thank *COST Action CA18229 "Funded by the European Union" for support.*

INTEGRATION OF GREEN-BASED EXTRACTION APPROACHES IN THE ISOLATION OF VALUABLE MOLECULES FROM GINGER BY-PRODUCT

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Increased production of herbal tea generates increased amount of waste that remains during the first phase of filter tea processing (that includes grinding by a hummer mill and sieve fractionation). A certain quantity of plant material of particles lower than 0.315 mm is generated as fine powder i.e., herbal dust (approx. 10-40% of the total processed raw material). This fraction could not be used further for the filter tea production since its particle size is lower than the filter pore size. Therefore, this material is usually disposed and has no commercial value.

Therefore, this research was focused on the valorization of ginger (*Zingiber officinale*) herbal dust as a potential source of valuable bioactive molecules, such as gingerols and shogaols trough the establishment of an optimized, environmentally friendly and industrially appropriate sequential extraction process.

In order to investigate the content of phenolic compounds, pressurized liquid extraction (PLE) system was applied for the extraction of phenolic compounds from ginger herbal dust using - mixtures of water–ethanol (EtOH). The effects of operating conditions (% of ethanol in the solvent, temperature and extraction time) were obtained using the circumscribed central composite experimental design.

The study was also performed to the raw ginger herbal dust as well as to material previously deffated by supercritical carbon dioxide (SC-CO_2). The major phenolic compounds in ginger herbal dust as determined by RP-HPLC-DAD analysis of the extracts prepared under different extraction conditions were found to be 6-gingerol followed by 6-shogaol and 8-gingerol. The results obtained make a great advantage for potential application of ginger herbal dust extracts in food, pharmaceutical and cosmetic industry. In addition to this, the successful utilization of ginger herbal dust as a by-product of the filter tea industry will create benefit as a secondary income through decreased investments in necessary waste disposal.

Keywords: Ginger, herbal dust, waste valorization, pressurized liquid extraction, process integration

Acknowledgements: The article is based upon work from COST Action GREENERING, CA18224, supported by COST (European Cooperation in Science and Technology).

A GREEN STRATEGY TO IMPROVE THE RECOVERY OF FLAVANONES FROM ORANGE BYPRODUCTS BASED ON THE COMBINATION OF ULTRASOUND-ASSISTED EXTRACTION AND NATURAL DEEP EUTECTIC SOLVENTS

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Fruit and vegetable processing is one of the agro-food industries that generate more amount of waste. For instance, in the citrus industry, around 50-60% of the total weight of the fruit is discarded. However, the orange byproducts can constitute a source of products with high added value and energy. They contain a great amount of biologically active secondary metabolites such as phenolic compounds. Natural deep eutectic solvents (NaDES) have been considered an environmentally friendly and cheap alternative to conventional organic solvents. In this work, a green extraction methodology was developed using ultrasound-assisted extraction (UAE) and NaDES for the extraction of antioxidant flavanones from orange byproducts. Five NaDES were studied to search the best NaDES to extract flavanones. Antioxidant capacity and total proanthocyanidin contents were determined for the extracts. Experimental results showed that choline chloride–lactic acid (1:3) was the most efficient NaDES to recover the highest antioxidant proanthocyanidin and flavanones content in the extracts. A Box–Behnken experimental design was employed to optimize the main parameters in UAE with NaDES: water percentage, ultrasound amplitude, and extraction time. The optimal extraction conditions were 3% (v/v) water, 60% ultrasound amplitude, and 14 min as the extraction time. The flavanones present in the extracts were determined by high-performance liquid chromatography – diode array detector – quadrupole-time of flight mass spectrometry. Results showed that ultrasound amplitude and extraction time have a significant effect on the extraction of antioxidant flavanones from orange waste.

Keywords: Orange waste, flavanones, antioxidant capacity, natural deep eutectic solvent, ultrasound-assisted extraction.

Acknowledgments: Authors thank the Comunidad of Madrid and European funding from FSE and FEDER programs (project S2018/BAA-4393, AVANSECAL-II-CM) and the Comunidad of Madrid and the University of Alcalá (project CM/JIN/2021-023). Authors also thank L. Gil Parrales for technical assistance.

SUPERCRITICAL CO_2 EXTRACT OF *LAVANDULA STOECHAS* DISPERSED IN NATURAL DEEP EUTECTIC SOLVENTS: AROMA STABILISATION POTENTIAL

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Abstract

Aroma chemicals represent various volatile compounds with sensory characteristics. Their demand is on the constant rise in different industries including food, beverages, chemicals, cosmetics, perfume, and pharmaceutical industries. One challenge that significantly limits their use is their instability and susceptibility to changes caused by exposure to oxygen, light, and moisture during their attainment, storage, or application.

This work investigated the approach of obtaining and stabilizing volatile aroma compounds of *Lavandula stoechas* L. by using green solvents, supercritical carbon dioxide ($scCO_2$) and natural deep eutectic solvents (NADES). For obtaining the extracts, $scCO_2$ was used at 200 bar, 40 °C, and a CO_2 flow rate of 20 g/min, during 3 h. CO_2 extracts were then dispersed in different NADES mixtures (betaine:ethylene glycol (Bet:EG) (1:3), betaine:glycerol (Bet:Gly) (1:2), and glycerol:glucose (Gly:Glu) (4:1)) and their stability was monitored during 6 months of storage at room temperature by monitoring the headspace profile. CO_2 extract was used as the control.

It was initially determined that in the samples, there was a dominant presence of oxygenated monoterpenes (67.33-77.50%). During storage, significant changes occurred in the samples' headspace profile, such as the decrease in terpene hydrocarbons, which also affected the presence of oxygenated terpenes, which increased in certain cases. Moreover, the formation of new components was recorded which could be an indicator of decreased stability. The detected components include ethanol, furanones, and benzyl products and organic acids. Newly formed components were most present in the control, while in NADES-CO_2 samples, they were present in a significantly lower percent or not detected. The NADES-CO_2 were more stable than the CO_2 control and among them, Bet:EG stood out as the most adequate for maintaining the stability of *L. stoechas* headspace components. One explanation could be that the NADES acted as a stabilizing medium of headspace compounds *L. stoechas*, reducing the oxidative degradation of components. Additionally, due to the presence of components from different classes such as aldehydes, ketones, alcohols, esters, and hydrocarbons, it is possible that new NADES-extract intermolecular interactions were formed providing enhanced stability.

Keywords: Lavandula stoechas; volatile compounds, supercritical carbon dioxide; deep eutectic solvent;

Acknowledgements: This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 101003396.

SUPERCRITICAL CO_2 EXTRACTION OF NON-POLAR BIOACTIVE COMPOUNDS FROM TURMERIC *(Curcuma longa* L.*)*

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Abstract

Turmeric, the dry rhizome of the plant *Curcuma longa* L., is widely valued not only for its coloring and flavoring properties but also for its biological properties (e.g., anti-inflammatory, antitumor), that have been mainly attributed to a group of secondary metabolites, namely curcuminoids. Curcumin is the major curcuminoid of turmeric. These bioactive ingredients of turmeric can be isolated using various extraction techniques, one of which is supercritical CO_2 extraction (SC-CO_2). Supercritical fluids-based extraction is used for the recovery of non-polar to low or medium polar compounds from various plant materials and is in line with the ''Green Chemistry'' principles.

The purpose of the present study was the optimization of the extraction of curcuminoids from turmeric powder using SC-CO_2. Different pre-treatment techniques were also studied. The extraction yield (mass of the obtained extract) was evaluated in terms of CO_2 flow rate and pressure, whereas the extraction temperature remained constant at 40°C in all cases. After the optimization of extraction parameters, two different pre-treatment methods were examined. The first one included the enzymatic pre-treatment of turmeric powder using a cellulolytic enzyme mixture. In the second case, addition of hydroalcoholic solution prior to extraction was applied. The proposed method was also compared with conventional extraction and distillation methods, Soxhlet extraction using hexane as a solvent and conventional hydro-distillation, respectively. The obtained extracts were further analysed with HPLC for the quantitative determination of curcumin. Based on the results, SC-CO_2 extraction was found to be an efficient method for the recovery of bioactive compounds from turmeric. All the conditions tested affected the extraction yield, with the combination of the highest pressure and lowest flow rate resulting in the higher yield. Both pre-treatment methods were found to increase the extraction yield too. In addition, the yield of conventional Soxhlet extraction method was found to be lower compared to SC-CO_2 extraction, highlighting the efficiency of this green method for extracting non-polar compounds from turmeric powder. The findings of the present study could further pave the way for the valorization of turmeric extracts in nutraceutical or cosmeceutical formulations.

Keywords: Turmeric, Supercritical CO_2 extraction, Green Chemistry, Curcumin, Enzymatic pre-treatment

Acknowledgements: Stamatia Christaki would like to thank the COST Action CA18224 "Green Chemical Engineering Network towards upscaling sustainable processes – GREENERING'' for a Short Term Scientific Mission (STSM) at the University of Novi Sad (Serbia).

Caulerpa prolifera GREEN ALGA AS SOURCE OF HIGH VALUABLE COMPOUNDS

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Abstract

Green macroalgae are considered attractive sources of compounds with bioactive properties and potential biological activities. These natural compounds could present a relevant impact in different fields, including food, cosmetics or pharmaceuticals. In this context, this study is focused on the chemical characterization of the Tunisian green alga *Caulerpa prolifera* and the antioxidant potential of the recovered soluble fractions after hydrothermal treatment.

The alga used was manually collected in the Mediterranean coast of Tunisia. The chemical composition in terms of moisture, ash, carbohydrate, carbon, nitrogen, hydrogen and lipid content as well as the corresponding fatty acid profile, was determined. Microwave assisted hydrothermal treatment was conducted on a Anton Paar Monowave device operating at 850 W at different time (3-12 min) and temperature (120-210 °C) conditions. Liquid phases were separated by filtration before analyzing the antioxidant features (*i.e.* total phenolic content, TEAC, FRAP and DDPH).

Results indicated that the fundamental chemical composition in dry basis of the freeze-dried *C. prolifera* was about 5 % of moisture, 45 % of carbon, 4 % of protein, 10.5 % of ash and 1.5 % of crude lipids. Among the 11 identified fatty acids, the majority were the palmitic acid. Mineral content (g/kg) was represented by Ca (160) followed by Na (31), Mg (29), K (9.4) and P (8.1). The highest total phenolic content and antioxidant activities of the recovered soluble extracts treated by microwave were identified at the highest tested temperature independently of selected time.

Keywords: Antioxidants, Composition, Microwave assisted extraction, Seaweed

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CHARACTERIZATION OF VINE SHOOTS EXTRACT OBTAINED BY A GREEN METHODOLOGY

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Abstract

Winemaking constitutes an important engine of economic growth for many regions. As a result of the viticulture practices, vine shoots are generated, with an estimated yearly production of about 1–3 tons per hectare. This residue is discarded or burned in the vineyards with no revenue, but it has the potential to be a valuable bioresource for biochemical production in sustainable integrated biorefineries.[1] As a first processing step, solid-liquid extraction can be applied to recover stilbenes that find applications in a variety of fields, such as agriculture, cosmetics, functional foods, nutraceuticals, and medicine.[1,2] In this work, the extraction of these compounds was achieved using 80% ethanol and ultrasound-assisted extraction (probe-type with 80% amplitude for 5 min), which showed better performance in terms of total phenolic yield and energy consumption than conventional maceration aided by mechanical agitation (24 h, 150 rpm). The extract was characterized by high-performance liquid chromatography coupled to ultraviolet and mass spectrometry. A total of 27 phenolic compound were characterized. Among them, stilbenoids were the major phenolic class qualitatively (~74%) and quantitatively (~90%). Individually, resveratrol stood out in the extract, obtaining 1055 mg/kg dry biomass (or 27,189 mg/kg dry extract), followed by *trans*-ε-vitisin 393 mg/kg dry biomass (or 10,128 mg/kg dry extract), which is in the range of the values reported by other studies.[2] Moreover, the extract was further characterized showing that other compounds were co-extracted, e.g. organic acids, sugars (mono- and oligo-saccharides), alditols, nitrogenous and inorganic material. Overall, ultrasound is an interesting technology to be scaled-up for the green extraction of vine shoots, while further purification will be required to increase the purity of the extracts if required by the application.

Keywords: Green extraction, Resveratrol, Stilbenoids, Vine shoots

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Acknowledgements: Ministry of Science and Innovation (MCIN) and the European Social Fund for the Ramón y Cajal grant (RYC2020-030546-I/AEI/10.13039/501100011033), University of Jaén for the grant POSDPP/2022, and the projects PID2020-112594RB-C31 and TED2021-132614A-I00 funded by MCIN/AEI/10.13039/501100011033, by "ERDF A way of making Europe", and/or by the European Union NextGenerationEU/PRTR.

EVALUATION OF CHOLINE CHLORIDE/GLYCEROL AS A DEEP EUTECTIC SOLVENT ON RECOVERY OF PHENOLIC COMPOUNDS FROM AVOCADO SEEDS

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Abstract

Avocado seeds are the main waste produced in huge quantities by avocado processing industries, and its disposal causes serious environmental and economic impacts. However, these waste products present a wide range of bioactive compounds that can be used for the development of functional foods. In fact, avocado seeds are known as interesting sources of polyphenols with antioxidant properties[1].Traditionally, conventional methods based on organic solvents have been widely applied in the extraction of polyphenolic compounds from avocado seeds. However, these solvents present several disadvantages such as their toxicity, high volatility, and flammability which limits their application for the extraction of natural compounds[2]. In this context, Deep eutectic solvents (DESs) are a new class of green solvents that have been suggested as a safe and sustainable alternative to replace toxic organic solvents due to their excellent biocompatibility and low toxicity[2]. In this context, this work deals for the first time the use of a DES formulated with choline chloride and glycerol as an effective solvent for the extraction of polyphenols from avocado seeds. For this purpose, it was applied an experimental design based on response surface methodology for the optimization of process parameters (temperature, time, water content). The dependent variables evaluated were total phenolic (TPC) and flavonoid content (TFC), antioxidant capacity (measured as ABTS and FRAP). Under optimal conditions, TPC:19.71 mg GAE/g, TFC:33.41 mg RE/g, ABTS:20.91 mg TE/g, and FRAP:15.59 mg TE/g were obtained.

Keywords: Deep eutectic solvent, Phenolic compounds, avocado by-products, waste valorization

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Acknowledgements: Beatriz Gullón and Fernando Rodríguez Rebelo would like to express their gratitude to the Spanish Ministry of Science, Innovation and Universities for financial support (grant references RYC2018-026177-I and FPU20/02385, respectively). Pablo G. del Río would like to express gratitude to Consellería de Cultura, Educación, Formación Profesional e Universidades of Xunta de Galicia for his postdoctoral grant (ED481B-2022-020).

CHARACTERIZATION AND EXTRACTION OF BIOACTIVES FROM HALOPHYTE PLANTS

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Halophyte plants are high salinity tolerant plants, edible, and found all over the world, including in Portugal, along the coast. These plants have in their constitution phenolic compounds, which are natural antioxidants, that have been pointed out as responsible for some of the beneficial effects for the health of the human being. Given the increasingly important use of this type of plants, an in-depth study on its composition and possible health benefits is warranted. To increase this knowledge, there is a need to optimize extraction and analysis methodologies that allow obtaining detailed information about the composition of these plants. In this work, we present several extraction strategies to extract bioactive compounds from *Salicornia ramosissima*.

The volatile composition analysis showed that the plant had mainly alcohols (25%), alkanes (27%), menthol (9.55%) and camphor (2.90%). The fatty acid profile revealed that the major compounds were alpha-linolenic acid (C18:3, 34%), linoleic acid (C18:2, 17%) and palmitic acid (C16, 21%). Moreover, the carotenoid, $27\mu g_{lutein}/g$ and $27\mu g_{\beta\text{-carotene}}/g$, and chlorophyll contents, $12\ \mu g_{chlorophyll\text{-}a}/g$ and $151\ \mu g_{chlorophyll\text{-}b}/g$, were also analyzed in the dried plant. Regarding the phenolic composition, more than 10 different compounds were identified, and the most abundant ones were the chlorogenic acid and the quercetin-3-glucoside.

Different extraction techniques were used to extract bioactive compounds including conventional techniques (e.g., solid-liquid extraction with Soxhlet) and alternative methods (e.g. supercritical fluid extraction, ultrasound- and microwave-assisted extractions). Microwave-assisted extraction with ethanol and water resulted to be the best method for the recovery of phenolic compounds (56.69 % process yield, 30.76 mg GAE/g extract). Furthermore, it was the preferred extraction method since it is energy and time efficient.

Keywords: halophyte plants, Salicornia ramosissima, phenolic compounds, antioxidant activity.

Acknowledgements: This work was supported by FCT - Fundação para a Ciência e a Tecnologia, I.P., through ReHalAntiOx (EXPL/ASP-AGR/1655/2021), iNOVA4Health (UIDB/04462/2020, UIDP/04462/2020) and LS4FUTURE Associated Laboratory (LA/P/0087/2020).

SEMI-CONTINUOUS FLOW-THROUGH PRESSURIZED LIQUID EXTRACTION OF PHENOLIC COMPOUNDS FROM GRAPE PEEL

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Abstract

The design of sustainable processes for the valorization of agri-food by-products into value-added products is a worldwide growing demand. Grape peel is the main solid by-product generated during wine production, accounting for approximately 1.5 kg per liter of wine. In this study, a sustainable semi-continuous pressurized liquid extraction process was applied to recover phenolic compounds from the grape peel. For the extraction, 20 g of grape peel was loaded in the reactor and operated in semi-continuous mode, using hydroethanolic solution (70% ethanol and 30% water, v/v) as extraction solvent. The experiments were performed at 60 °C and 15 MPa, with a flow rate of 5 mL/min and a solvent-to-feed ratio of 7.5 $g_{water}/g_{grape\ peel}$. The extract was collected every 5 min to perform the extraction kinetics. The extract was characterized by high-resolution accurate mass coupled to a mass spectrometer (LC-MS/MS). The results on extraction kinetics showed that the highest concentration of phenolic compounds (72.11 ± 1.87 mg/mL) was obtained after 15 min of extraction, and after this extraction time the concentration of bioactive compounds decreased. In total, 29 phenolic compounds were identified and quantified by LC-MS/MS. The main phenolic compounds were kaempferol-3-glucoside (367.23 ± 25.88 µg/mL), prunin (270.23 ± 3.62 µg/mL), *p*-coumaric acid (236.43 ± 26.02 µg/mL), and procyanidin B1 (117.17 ± 7.29 µg/mL). In conclusion, the process designed can be adopted as a sustainable extraction technique for the valorization grape peel and production of bioactive compounds, which can be further applied in the food, pharmaceutical, and health industry.

Keywords: Bioactive compounds, LC-MS/MS, Value-added products, Bioproducts, Sustainable process.

Acknowledgements: This work was supported by the Brazilian Science and Research Foundation (CNPq, Brazil) (productivity grants 302451/2021-8); São Paulo Research Foundation (FAPESP, Brazil) (grant numbers 2019/14938-4, 2019/26925-7, 2021/04096-5, and 2020/16248-5).

COMPARATIVE CHEMICAL PROFILING OF UNDEREXPLOITED *CITRUS SINENSIS* L. HERBAL DUST EXTRACTS OBTAINED BY SUBCRITICAL WATER AND PRESSURIZED ETHANOL EXTRACTIONS

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Abstract

Extractions processess such as subcritical water extraction (SWE) or pressurized liquid extraction (PLE), that uses a liquid solvent under pressurized process conditions, enjoys a great deal of scientific interest. Among this group SWE is considered as the most promising. Safety, low price and green character of water, good yields of target compounds and reduced energy consumption, make this technique attractive for potential industrial applications. On the other hand, with PLE, it is also possible to use a mixture of water/ethanol and ethanol as solvents, because they are GRAS (generally recognized as safe) solvents. Therefore, the aim of this study was to compare SWE with pressurized ethanol extraction (PEE), to optimize the temperature as the most influential process parameter, and at the same time propose new streams for the valorization of waste from the filter tea industry - orange peel dust (OPD). OPD is the material left after the industrial processing of orange peel, containing particles lower than the pores of filter paper (<0.315 mm), and therefore cannot be used further in the final herbal filter tea production. But, it still contains a wide range of high value compounds that can be utilized. In order to determine the possibility of complete extraction of OPD, a series of experiments were performed, where the temperature was varied (120-220ºC), while the pressure and time were constant. After that, the obtained extracts were analyzed by LC-MS/MS. The comparison was made on the basis of total phenolic content (TPC), as well as chemical characterization of the obtained extracts. TPC in both techniques (SWE and PEE) increased with increasing temperature and the maximum value was 35.67 [mg GAE/g dry weight] and 70.56 [mg GAE/g dry weight], respectively. The most abundant compounds in the obtained extracts were hesperidin and naringin, where the highest concentration was reached at SWE (temperature 160 ºC) and was 662.82 [mg/L] for hesperidin, and 59.99 [mg/L] for naringin. Results described in this work show that SWE and PEE can significantly enhance extraction of valuable compounds from plant material, thus proving to be a value addition processes and potentially efficient techniques to be used at industrial level.

Keywords: Orange peel, herbal dust, subcritical water extraction, pressurized ethanol extraction, polyphenols, LC-MS/MS analysis.

Acknowledgements: This work has been supported by COST Action GREENERING, CA18224, funded by COST (European Cooperation in Science and Technology).

LOW ENERGY DEMANDING EXTRACTION OF TRITERPENIC ACIDS

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Abstract

The olive oil industry generates a huge quantity of byproducts and residues in the olive mill, which can be converted into valuable bioproducts through biorefinery processes. This includes the residual olive pulp, which derives from the recovery and cleaning of olive pits from the olive pomace.[1] While olive pits are currently used as a heating biofuel, the residual olive pulp has no industrial application. In this work, the extraction of bioactive triterpenic acids from this residue was considered as potential first step in a biorefinery. Microwave was used as intensification technology and the residual solid fraction was characterized for further cascading valorization. The operational parameters evaluated in the microwave-assisted extraction (MAE) were: ethanol concentration of ethanol/water solution (50−100%, v/v), extraction time (4−30 min), and temperature (50−120ºC). As response variables, the energy consumption, extraction yield and concentration of triterpenic acids were studied using the response surface methodology. Then, a multiple optimization was performed to minimize the former, while maximizing the rest of variables. At optimal extraction conditions (100% ethanol, 4 min, 99 ºC), maslinic acid (22.70 mg/g dry biomass) and oleanolic acid (9.97 mg/g dry biomass) were recovered in the ethanolic extract. It showed similar extraction performance than maceration with mechanical agitation but with lower energy consumption. Concerning the extracted solid after MAE, it contained 12.1% of cellulose, 10.9% of hemicellulose, and 40.5% of lignin, which can be subjected to further valorization. Overall, residual olive pulp is a rich source of triterpenic acids, which can be extracted under a biorefinery scheme to maximize the valorization of this bioresource.

Keywords: Green extraction, Microwave-assisted extraction, Residual olive pulp, Triterpenic acids

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PHASE EQUILIBRIUM ENGENEERING FOR WINTEREIZATION OF NATURAL EXTRACTS WITH CO_2

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Abstract

Supercritical CO2 extraction is a green technology that allows obtaining high quality products, free of any trace of organic solvent. However, a single supercritical extraction of a vegetable matter not only extracts the aromas or bioactive principles but also produces the co-extraction of other no-volatile compounds. For instance, supercritical CO2 also co-extracts cuticular waxes that are located on the surface of the solid matrix. Depending on the vegetable specie, these waxes comprise long chain paraffins and or fatty esters. In many cases, these compounds impair the product quality due to the appearance of precipitates that cause opacity of the natural extract. Therefore, their removal post-extraction is of interest, and is conventionally carried out by cooling the extract below -7ºC, a costly and inefficient process.

In this work, we investigate alternative processes to remove waxes, taking advantage of the presence of CO2 in the extract, by means of high-pressure separators or fractionation columns under feasible selective conditions. To design adequate operating windows that promote the precipitation of non-desired co-extracted solutes, a thorough understanding of the phase behavior of the extract with CO2 is essential. As a first approach, we assess the behavior of a simplified synthetic system comprising an allyl chain-substituted guaiacol (eugenol), paraffins (chain length between C28 and C32) and CO2. In particular, we measure phase equilibria of the binary system CO2 + eugenol and the solubility of synthetic mixtures of eugenol + paraffins in liquid and supercritical CO2. Since the selectivity in the near-critical region depicts highly non-ideal multiphase behavior, we test a wide range of conditions (263K – 333K and 64bar – 250 bar). The binary eugenol+CO2 system shows liquid-liquid-vapor equilibria at temperatures between 298 K and 308 K. Moreover, the multicomponent system formed by paraffins + eugenol + CO2 shows solid-liquid-vapor equilibria at 298 K and 64 bar. In this work, we also model the measured experimental data using the GCA-EOS. The group contribution approach of this equation of state allows assessing operating windows for different molecular weight waxes. Finally, the aim of this work is to understand the control of the phase behavior for the design of winterization units of guaiacol derivatives. In addition, the predictive character of GCA-EOS will allow the generalization of the design to natural products with waxes of different nature.

Keywords: winterization, natural products, GCA-EOS, supercritical CO2

IMPACT OF BIOPOLYMERS USE ON PHYSICO-CHEMICAL STABILITY OF BLUE MAIZE EXTRACT MICROENCAPSULATES

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Blue maize is a rich source of anthocyanins which could demonstrate many beneficial effects on human health and the prevention of various diseases associated with oxidative stress. Cereal processing could generate a large amount of anthocyanins-rich waste products. However, anthocyanins incorporation into food is a technological challenge due to their low stability. The stability of these extracted valuable bioactive compounds from harmful environmental influences (oxygen, light, water) can be preserved by the encapsulation technique, which could entrap them inside a coating material. Microencapsulation technique could improve bioavailability, mask undesirable organoleptic characteristics of polyphenols and anthocyanins, making them more usable and represented in diet foods and as nutraceuticals. Spray drying process is one of the most widely used microencapsulation technique due to its simplicity, efficiency, and low operational costs. Nowadays, the accent is on the utilization of novel carrier agents with unique properties, such as hydroxypropyl-β-cyclodextrin-(HPBCD). The aim of the present research was to develop and examine microencapsulation systems of blue maize extract using a conventional biopolymer as a maltodextrin, in combination with a novel one, HPBCD, in order to obtain powders with appropriate organoleptic and pharmacological characteristics. The waste product of blue maize processing was used for anthocyanins extraction. Liquid blue maize extract was spray dried with and without adding carrier agents: MD (30%), HPBCD (30 %), and a combination of both carriers (15% MD and 15% HPBCD). The obtained spray-dried maize extracts (SME) were analyzed by the physico-chemical powder properties, particle size, Fourier-transform infrared analysis (FTIR), and differential scanning calorimetry (DSC), in order to examine preservation of blue maize extract. The diameter of spray-dried microparticles varied from 2.22 (d_{10}) for SME+MD to 257.14 µm (d_{90}) for SME+MD+HPBCD, respectively, with the mean average diameter d_{50} ranged from 4.72 to 21.33 µm for all microencapsulated powders. The encapsulation of the blue maize extract with carriers such as MD and HPBCD did not create meaningful changes, which is according to the literature indication for a successful microencapsulation process. Therefore, spray drying process did not change the structure of the polymer matrix and extract according to the FTIR analysis, indicating that the anthocyanins microencapsulation was developed by physical incorporation. DSC analysis signified that spray drying technique developed powders with high thermal stability and up to 200˚C, related to the increasing stability with the addition of biopolymer material. The used biopolymers showed a good impact on the stability of microencapsulates of blue maize extract. Additionally, HPBCD provided an improvement in the physico-chemical characteristics of the powders.

Keywords: Blue maize, Waste, Microencapsulation, Spray drying, Characterization, Functional carriers.

MICROENCAPSULATED BIOACTIVE EXTRACTS FROM *DIPLOTAXIS ERUCOIDES* ISOLATED THROUGH GREEN STRATEGIES

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Abstract

Wild Edible Plants (WEP's) are plants that grow without the help of humans. These types of plants are considered weeds; however, they may have antioxidant compounds with potential applications. Therefore, the main objective of this research was the extraction of bioactive compounds from different parts of one wild edible plant, *Diplotaxis erucoides* (pods, leaves, stems), through environmental-friendly processes and their stabilization by microencapsulation. The extraction was carried out by ultrasound (US) in a cooperative extractor MW-US-ER-01/reactor. The alginate-based encapsulation was prepared using ionic gelation process by the Buchi encapsulator. Regarding the results, the pods of *Diplotaxis erucoides* showed the highest concentration in terms of total phenolic content (around 47 mg GAE/ g). Besides, the stems of *Diplotaxis erucoides* were the part that had the lowest total phenolic content (14.8 mg GAE/g). All encapsulated samples showed promising results regarding the release of bioactive compounds. Another important factor of the encapsulations for their practical applications is the swelling capacity, being the pods of *Diplotaxis erucoides* the sample that presented the highest percentage of swelling (217 %). However, the results of the stems of *Diplotaxis erucoides* were very different (87 %). In conclusion, these encapsulated plant extracts showed suitable properties, so they could be used as promising candidates to applicate in several fields, such as food, cosmetics or agriculture, among others.

Keywords: Wild Edible Plant, encapsulation, Total Phenolic Content, functional food, high-added value ingredients.

Acknowledgements: Thanks to Green Chemical Engineering Network towards upscaling sustainable processes (CA18224)-GREENERING funded by COST (European Cooperation in Science and Technology) for the STSM grant.

MICROENCAPSULATION BY SPRAY DRYING OF BIOACTIVE GREEN TEA EXTRACTS – CARRAGEENAN, ALGINATE AND STARCH AS CARRIERS

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Abstract

Nowadays, the cultivation of tea (*Camellia sinensis* (L.)) has been spread around the world. The biological properties as antioxidant, anticarcinogenic, and neuroprotective, among others associated to tea open a chance to incorporate vegetable by-products into nutraceuticals or cosmetics. Focused on the properties of this raw material, a green extraction technology is necessary to obtain these bioactive compounds. Ultrasound assisted extraction, microwave assisted extraction and subcritical critical water extraction are ecofriendly technologies suitable for processing vegetable raw materials. Besides, an extraction process based on the combination of two extraction technologies could achieve an increasing recovery of bioactive compounds. Another factor to take in account is the possibility to protect these bioactive compounds formulating microparticles using different green polymers. The main aim of this work was to evaluate three natural polymers (alginate, carrageenan and starch) to formulate polymeric particulate systems.

The results obtained show a high microencapsulation and loading efficiencies, 60–93% and 65–84%, respectively. The analyses of microparticles show a range of 32 to 46 g Trolox/100 g extract for the antioxidant capacity, and the total phenolic content a range of 10 to 13 g/100 g extract within different carrier-systems, besides the particle-size distribution, SEM-analysis and FTIR-analysis were also performed. Taking into account these results, the formulated polymer-coated microparticles could have a potential application in fields as nutraceutical or cosmeceutical.

Keywords: microparticles, tea extract, ultrasound-assisted extraction, subcritical water extraction, polymer.

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ENCAPSULATION OF RASPBERRY BY-PRODUCT EXTRACT USING PGSS PROCESS

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Polyphenols are secondary metabolites that are synthesized in plants and have biological activities such as antioxidant, anticancer, antimicrobial, and others. Polyphenols, however, show low stability under environmental conditions, such as exposure to light, oxygen, temperature, and enzymatic activities [1]. Therefore, encapsulation of polyphenols could be an alternative for stability and could increase their shelf life. The most widely used microencapsulation techniques include spray-drying, freeze-drying, fluidized bed coating, and coacervation phase separation [2]. One of the encapsulation techniques involving supercritical carbon dioxide is Particles from Gas Saturated Solutions (PGSS) process that shows several advantages for the encapsulation of bioactives such as microcapsules free from solvent traces with high encapsulation efficiencies. The aim of this study was to encapsulate polyphenols obtained from black raspberry press cake (BRPC) using emerging ultrasound-assisted extraction (UAE). UAE was performed using 30% ethanol as solvent at 100% sonication amplitude for 4 min. The extract was encapsulated using the PGSS method with glyceryl monostearate as a carrier under the following process conditions: temperature of 65°C, process time of 15 min, at different pressures (100, 150, and 200 bar) and mass ratios of extract and carrier (E:C) (1:11, 1:5, and 1:3). The encapsulation efficiency (EE) and quantitative HPLC analysis of the initial extract and obtained powders were determined. The results showed that by reducing the concentration of the carrier, the EE decreased. The highest EE of the process (66.76%) was recorded at 200 bar, the E:C 1:11. Also, it was concluded that the EEs were higher when the processes were carried out at higher pressures. The results of HPLC analysis showed that anthocyanins were the dominant compounds in the BRPC extract and powders. The highest concentrations of all compounds were measured when the E:C ratio was 1:3, and the most dominant was cyanidin-rutinoside (5.02 mg/g powder) followed by rutin, cyanidin-glucoside, gallic and ellagic acids. Eventually, BRPC proved to be a valuable source of polyphenolic compounds, while the PGSS encapsulation method proved to be promising for obtaining high-quality powders with preserved active compounds.

Keywords: raspberry press cake, ultrasound-assisted extraction, PGSS, anthocyanins, encapsulation.

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Acknowledgments: This publication is based upon work from COST Action GREENERING, CA18224, supported by COST (European Cooperation in Science and Technology).

PRESSURIZED FLUID EXTRACTION OF BIOACTIVE COMPOUNDS FROM PEANUT BY-PRODUCTS TO PROMOTE WASTE RECOVERY AND CIRCULAR ECONOMY

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Abstract

In recent years, significant research effort has been made to waste valorization and practices based on circular economy approaches. Therefore, it is worthwhile the development of a simple, green and effective strategy for extraction and determination of bioactive compounds in food waste. Polyphenols are important nutrients that are antioxidants and exhibit a wide variety of biochemical and pharmacological effects, including antimicrobial, anti-inflammatory, anticarcinogenic and other beneficial properties. Luteolin (3′,4′,5,7-tetrahydroxyflavone) is a flavonoid that has gained interest due to its promising results against the proliferation of certain cancer cells[1]. This compound is one of the most abundant flavonoids in peanut products. Most extraction methods for flavonoids are time-consuming as well as require a large amount of organic solvents and several sample treatments steps. The present work is focused on studying a green extraction technique, pressurized hot water extraction (PHWE), with the aim of obtaining extracts with the highest antioxidant activity from peanut shells. To optimize the extraction, a design of experiments (DoE) was carried out to obtain the best conditions that allow obtaining the richest extract in bioactive compounds. Other extraction procedure by using a green organic solvent as subcritical fluid was also tested to compare the results in relation to the total antioxidant capacity, and phenolic and flavonoid content. Moreover, an analytical method based on high-performance liquid chromatography with photodiode array detection was developed to evaluate the contribution of individual phenolic compounds. The green extraction techniques using pressurized fluids have turned out to be efficient and greener in extracting phenolic compounds as compared to the conventional methods.

Keywords: Subcritical Fluid, Bioactive compounds, DoE, Pressurized Extraction; Peanut shells

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Acknowledgements: C. Schumann-Pérez thank the Ministry Education for her grant for collaboration in University Departments.

VALORISATION OF SWEET CHERRY LEFTOVERS TO PRODUCE ANTIOXIDANT RICH EXTRACTS

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Abstract

Sweet cherries (*Prunus avium*) are a culture grown around the world. An amount of 2.6 million tons is produced per year, and it is estimated to be growing (FAO). Around 10% of the production is treated as waste, due to physical damage, excessive ripening, or microbial contamination. This fact causes huge losses of resources and time. Thus, it is essential to research new processes to valorize this product. In this study, the anthocyanins and polyphenols concentration, and the antioxidant activity of 13 varieties of cherry in three different stages: early, optimum and leftovers (or waste) was analyzed by spectrophotometry. The measurement was performed after maceration with methanol 90% + 0.1% HCl during 90 min at 37ºC and 450 rpm.

The early stage (Figure 1 in grey) had a significantly lower concentration of anthocyanins when compared to the other two stages. The varieties with the highest levels (≥ 0.5 mg/g) were Santina, Sandré Rose, Sonata, 4-84 and Sofía. The concentration of polyphenols followed the same trend. It was higher in the optimum stage and in leftovers, varying between 1.5-2.0 mg GAE/g. Consequently, so did the antioxidant capacity of the extracts.

Extracts rich in antioxidant compounds could be used in the development of new derivatives with higher added value contributing to the valorization of the cherry waste.

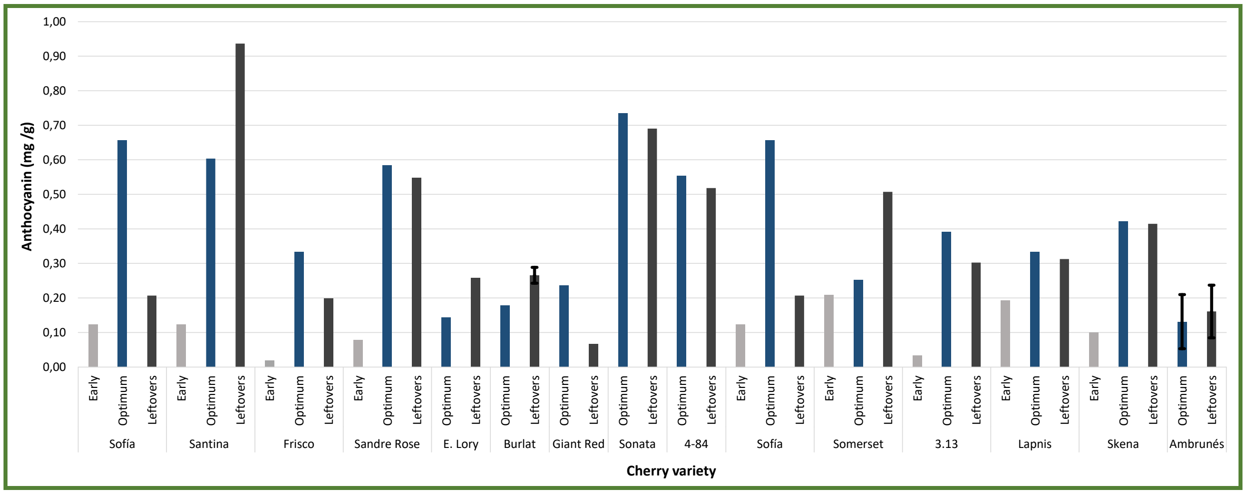

Figure 1. Concentration of anthocyanin in the methanolic extracts of thirteen cherry varieties in different stages.

Keywords: Anthocyanins, Antioxidants, Extraction, Food Waste, Valorization.

Acknowledgements: This work was financed by Campo y Tierra del Jerte, S.A. and by the UCM.

EXPLOITATION OF RICE HULLS AS SOURCES OF NATURAL PHENOLIC ANTIOXIDANTS FOR FOOD APPLICATIONS

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Abstract

The last few decades there is an increasing interest on the valorization of agro-industrial by products as sources for the recovery of functional ingredients, e.g. natural antioxidants, and particularly of phenolic compounds. Rice hulls, one of the main by-product of the rice milling industry (~20% of the grain weight), is produced in large amounts globally each year causing disposal issues. They are usually under-utilized as a fuel or a cementitious material. In the frame of the present study, rice hulls derived from Greek industries were investigated as a source of natural phenolic antioxidants with potential interest for food applications. Considering that the phenolic compounds present in rice hulls are mainly found in bound forms, their recovery requires the use of drastic conditions. In the present study, alkaline pretreatment was employed in combination with microwave-assisted extraction. The extraction parameters, namely duration, solvent:solid ratio and temperature was optimized using Response Surface Methodology. The effect of the examined conditions for the recovery of phenolic compounds was investigated by measuring total phenol content, *in vitro* antioxidant and reducing activity using various assays (i.e. DPPH, ABTS, CUPRAC), and by RP-HPLC-DAD analysis. Rice hulls were found to contain an appreciable amount of phenolic compounds with the major ones being p-coumaric and ferulic acids, which are bioactive. The results of the present study are expected to be of use to the local food industries in terms of by-product valorization for added-value applications.

Keywords: Rice hulls, bound phenolic compounds, microwave-assisted extraction, alkaline hydrolysis, natural phenolic antioxidants

Acknowledgements: This research has been funded by the Hellenic Foundation for Research and Innovation (HFRI) in the frame of the "2nd Call for H.F.R.I.'s Research Projects to Support Faculty Members & Researchers" under grant agreement No. 3308.

ANTIOXIDANTS RECOVERY FROM AVOCADO SEEDS USING MICROWAVES-ASSISTED AUTOHYDROLYSIS TREATMENT

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Abstract

The avocado processing industry generates substantial amounts of waste, such as peels and seeds, that can thus potentially be processed to produce value-added products with promising and significant applications in food industries. Microwave-assisted extraction is an environmentally friendly intensification technology that permits the selective solubilization of bioactive compounds in a short time with low energy consumption. In this context, the purpose of this work was to evaluate the suitability of microwave-assisted autohydrolysis extraction to recover antioxidant phenolic compounds from avocado seeds (AS). Microwave isothermal treatments (150-230 °C for 5 minutes) were performed, and extracts were evaluated by total phenolic (TPC) and flavonoid content (TFC), and antioxidant capacity (measured as ABTS, DPPH, FRAP and TAC). The effect of treatment severity on the recovery of phenolic compounds was assessed. Treatment at 230 °C enabled the maximum recovery of total phenolics (59.6 g GAE/g AS) accomplished with high antioxidant capacity (ABTS: 88.2 mg TE/g; DPPH: 50.7 mg TE/g; FRAP: 76.9 mg TE/g; TAC: 93.1 mg AAE/g AS). In addition, UHPLC-TOF-MS analysis of AS extract obtained at 230 ºC allowed the tentative identification of 10 phenolic compounds. Overall, the intensification of the autohydrolysis treatment by means of microwave technology enabled simultaneous and uniform heating of the sample allowing a faster and more efficient heat transfer, with a reduction in reaction times and energy consumption.

Keywords: Microwaves, Autohydrolysis, Phenolic compounds, Antioxidants, Avocado by-products.

Acknowledgements: Pedro Ferreira-Santos would like to express gratitude to the Spanish Ministry of Science, Innovation and Universities for financial support (FJC2021-046978-I), Beatriz Gullón expresses gratitude to the Spanish Ministry of Science, Innovation and Universities for financial support (RYC2018-026177-I), and Pablo G. del Río expresses gratitude to Consellería de Cultura, Educación, Formación Profesional e Universidades of Xunta de Galicia for his postdoctoral grant (ED481B-2022-020).

ULTRASOUND ASSISTED EXTRACTION AS A POSSIBLE SOLUTION FOR GINGER (*ZINGIBER OFFICINALE*) HERBAL DUST UTILIZATION

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Extensive filter tea production in the last decade has increased the amount of by-products and wastes generated by this industry. Due to the particle size (less than 0.315 mm), this material can't be packed into the filter tea bags, so it is discarded from the further processing. This kind of material, also known as "herbal dust", represents the useful material for further processing into the highly value products. Due to number of valuable bioactive constituents, ginger (*Zingiber officinale*) is commonly used for the treatment of digestive disorders, cough, cold and various health issues. In addition, ginger is the great antioxidant and possesses potential against inflammation and muscular pain. Therefore, the research of this study is focused on the valorization of ginger herbal dust as a potential source of valuable bioactive compounds through the establishment of an optimized, integrated and environmentally friendly extraction process.

The target of the research were primarily medium and high polar ginger bioactive constituents belonging to the group of phenolic compounds, and that is why the ultrasound assisted extraction (UAE) with ethanol solution was applied as the technique of the choice. For more efficient utilization of the ginger herbal dust the UAE was applied on the raw material, as well as material previously extracted and treated by supercritical carbon dioxide (SFE-CO_2), where mainly low-polar and non-polar bioactives were isolated. Ultimately, the extraction yield (EY), total phenols content (TP) and total flavonoids content (TF) were analysed, while the chemical characterization of the extracts was performed using RP-HPLC-DAD for detection and quantification of three most important bioactive compounds: 6-gingerol, 6-shogaol, 8-gingerol.

In the UAE investigation (for both investigated materials), the variable parameters were the sonification amplitude (20%, 60%, 100%) and the extraction time (2-20min), while the temperature (50°C) was the limiting factor. The highest EY (27.26%) was obtained using a sonification amplitude of 60%, in the raw material that was previously treated with SFE-CO_2 at a pressure of 20MPa. The highest TP (15.79±0.04 mg GAE/g) and TF (11.47±1.34 mg CAT/g) were obtained in the extract with raw ginger at amplitudes of 20% and 60%, respectively. Based on HPLC results the content 6-gingerol, 6-shogaol, 8-gingerol was significantly higher in the case of raw ginger herbal dust extracts produced using UAE generally.

Keywords: Ginger, herbal dust, valorization, pressurized liquid extraction

Acknowledgements: This work was supported through the STSM grant by the COST Action Greenering CA18224

TOPIC 2

BIOREFINERY:

BIOPRODUCTS AND BIOENERGY

KEY ELEMENTS FOR AGRICULTURAL RESIDUES-BASED BIOREFINERY DEVELOPMENT

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Abstract

Agricultural residues are considered as a relevant raw material for the production of biological compounds for different reasons. On the one hand, the economic aspects include the possibility of improving farm incomes, job creation in rural areas or the technological development associated with the conversion processes. Moreover, from an environmental point of view, the use of waste in the framework of a biorefinery represents important advantages, such as an alternative to the usual disposal methods (which usually consist of direct burning in the fields), the use of a renewable source of energy and products and the reduction of dependence on fossil energy sources.

Conversion of any kind of biomass into biobased products, particularly through a biochemical route, includes basically four steps: pretreatment, enzymatic hydrolysis, fermentation and separation. Pretreatment is needed to open up the lignocellulosic structure enabling the enzymes to hydrolyze sugar polymers to release single, monomeric sugars, which are in turn converted by microorganisms into the targeted bioproducts.

This talk reviews the most commonly used pretreatment methods applied to agricultural residues, describing the main parameters involved in pretreatment application, as well as other features such as the severity factor, the generation of inhibitors or the performance yield.

Keywords: Biorefinery, Pretreatment, Agricultural residues

RECOVERY OF BIO-BASED VOLATILE FATTY ACIDS BY PERTRACTION TECHNIQUES USING GREEN SOLVENTS

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Abstract

Recently, the chemical industry has suffered a significant detriment due to the energy crisis, which has led to a drop in production of more than 10%. In order to cope with the energy crisis, industries are pursuing virtuous strategies that are more resilient in the long run and decoupled from the supply of fossil-based raw materials and energy sources. For instance, bio-based Volatile Fatty Acids (VFAs) (eg., acetic, butyric, propionic acids, etc) from the acidogenic fermentation of organic waste have gained considerable attention as they represent a readily carbon source with several applications (eg., preservation, antimicrobials and acidity regulators) and biological precursors of biopolymer such as PHAs and bioenergy [2]. One of the recovery methods for VFAs is pertraction through liquid membranes is a widely studied approach for the recovery of low- concentration chemicals (such as VFAs) by exploiting the mass transfer that takes place between two aqueous phases of different pH (a feed solution and a adsorption solution) separated by an organic membrane layer [3]. The receiving phase is represented by an alkaline solution rich in volatile fatty acids that can be used as raw materials for several applications seen before. Traditionally, the organic solvents used in extraction processes have been environmentally unsustainable. Therefore, the ability to recover bio-based VFAs using alternative solvents was analyzed during this experiment. This work proposes to study the pertraction process from a real fermentation broth rich in volatile fatty acids, and to test three organic solvents (kerosene, Biodiesel and HDES) and three alkaline solutions (Na_2CO_3, $NaHCO_3$ and NaOH). This study aimed to determine the conditions that maximize the recovery and purity of VFAs. Recovery using kerosene and biodiesel lead to an overall VFA capture between 55 and 28,8 %. The transfer of short-chain fatty acids would seem to be more difficult ($0.21 < gCODtransfer\ L^{-1} < 2$). Instead, long-chain fatty acids, such as caproic acid, recorded the highest transfer ($gCOD\ L^{-1} = 9.02$), with a final purity of 45 %. The objective of this work was to test the feasibility of using a eutectic mixture (Menthol:Lauric acid) for the extraction of VFAs from real fermentation broth to evaluate its performance. HDES has a capture capacity that follows the lipophilicity trend of individual fatty acids, from acetic acid to caproic acid, with a capture rate from 31 to 92 %. Mass transfer to an alkaline solution was recorded for the first time in this work. A high mass transfer of caproic acid of 16 gCOD L^{-1} corresponding to 6.40 g(HCa) L^{-1} with an acid purity of approximately 50% was also found.

Keywords: HDES, Biodiesel, VFAs, Extraction, Purification

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GREEN EXTRACTION OF MICROALGAL PROTEINS WITH AQUEOUS TWO-PHASE SYSTEMS BASED ON DEEP EUTECTIC SOLVENTS

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Abstract

New sustainable protein sources must be found to meet the growing demand for this nutrient and the environmental concerns linked to animal protein production. Microalgae can be grown rapidly in wastewaters, converting nutrients and carbon into biomass rich in proteins and in other biomolecules of interest, such as carbohydrates. Traditional protein extraction methods involving chemical or enzymatic hydrolysis may cause protein degradation, are time-consuming, or use reagents harmful to the environment. Moreover, the coextraction of carbohydrates occurs, which hinders further applications of proteins. Therefore, sustainable, efficient, and selective methods for the separation of proteins from microalgae biomass are needed. Aqueous two-phase systems (ATPS) are environmentally friendly solvents standing as a promising tool for the recovery of biomolecules. In this work, extraction of proteins from green microalgae *Scenedesmus almeriensis* grown in photobioreactors treating pig slurry wastewater has been attempted using different ATPS based on a deep eutectic solvent, DES [choline chloride:urea (1:2) or betaine:levulinic acid (1:2)] and a saline aqueous solution (K_3PO_4 or K_2HPO_4). The binodal curves and tie-lines of the investigated systems were obtained, and the main factors influencing protein recovery were studied through a full factorial experimental design, with protein extraction yield and protein/carbohydrate partition as response variables. Good separation of proteins and carbohydrates from raw biomass was achieved, with proteins concentrating in the DES-rich phase and carbohydrates in the salt-rich phase. To check the efficiency of the tested ATPS for protein extraction, the experiment was also performed on a BSA (bovine serum albumin) control sample, achieving quantitative recovery of protein. To our knowledge, this is the first time that ATPS based on DES have been applied to the fractionation of proteins from microalgae. Although the procedure requires further optimization to increase the protein yield, this research opens a range of possibilities in the use of more sustainable and environmentally friendly solvent systems to attain protein separation from microalgae.

Keywords: Aqueous two-phase systems, Deep eutectic solvents, Microalgae biorefinery, Protein recovery.

Acknowledgements:

This research is funded by MICINN-FEDER (PID2020-113544RB-I00 and the Regional Government of Castilla y León and EU-FEDER (CL-EI-2021-07). D. Moldes acknowledges the "Ministerio de Universidades" for his FPU grant (FPU20/02086).

Recovery of pectin from sugar beet pulp using emerging extraction technologies

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Abstract

Sugar beet pulp (SBP) is a lignocellulosic waste produced in the sugar industry. The annual production of this residue in Europe[1] is $13 \cdot 10^6$ t. Since SBP is mainly composed of carbohydrates (55–80 %), it can be a source of high value-added products such as pectin. Microwave-assisted extraction (MAE) and ultrasound-assisted extraction (UAE) are considered eco-friendly emerging technologies that can be applied for pectin extraction. Moreover, surfactants are amphiphilic molecules that can increase pectin recovery due to its wide range of polarity[2]. The aim of this work was to compare the efficiency of MAE, UAE, and UAE using surfactants as solvent to recover pectin from SBP.

The temperature effect was evaluated on MAE, while pH, surfactant, and time effect were studied on UAE. The highest galacturonic acid recovery by MAE using a solid:liquid ratio of 10 % w/w was obtained at 150 °C for 5 min (51.2 %), while the highest by UAE using a solid:liquid ratio of 5 % was obtained using Tween 80 (4 g/L) in acidified water (pH 1) as solvent, amplitude of 90 % and 30 min reaction time (68.7 %). Comparing to MAE, UAE reached higher galacturonic acid recovery in the presence of surfactant but lower if water was used as solvent.

Keywords: galacturonic acid, ultrasound-assisted extraction, microwave-assisted extraction, surfactants

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CHANGING THE SUGAR-BASED PLATFORM BY THE CARBOXYLATES PLATFORM WHEN TARGETING AT MICROBIAL OILS PRODUCTIONS: LESSONS LEARNT

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Abstract

Oleochemicals are a green promising alternative to replace petroleum in the synthesis of chemicals and fuels. Alternatively to fossil oils, vegetable oils are conventionally used as a source of lipids for oleochemicals production. Nonetheless, microbial oils can overcome some of the drawbacks associated to vegetable oils such as the long cultivation periods and the higher surface area required for growth.

Some oleaginous yeasts are very good candidates for microbial oils production, accumulating more than 30% of lipids per dry weight and exhibiting high similarities with vegetable oils in terms of fatty acid composition. During the last years, sugars have been the most common carbon sources employed for lipid accumulation in yeasts and it is known that they assimilate these sugars through the *ex novo* pathway. Nevertheless, the actual price of these sugars in the market hampers the production of lipids at industrial level. To counteract this drawback, considerable efforts have been directed to find alternative low-cost substrates to build an economically-viable microbial oils production process. Short chain fatty acids (SCFAs), which are produced inanaerobic fermentation processes of organic wastes, offer an interesting possibility to replace the sugar-based platform. Although it has been proved that some yeast species can produce lipids by using SCFAs as carbon source, the available information about the metabolism involved in the assimilation of SCFAs by oleaginous yeasts is still scarce. Indeed, the little amount of information corresponds to fragmented research and thereby, some misleading conclusions were drawn. To through light on this topic, this work will review the new knowledge generated over the last 5 years. To elucidate the effect that SCFAs have on yeast growth and lipid production, the effect that the carbon-to-nitrogen ratio, as well as sulfate and phosphate limitation was tested. It can be stated that the results obtained over these 5 years open a new perspective for the utilization of SCFAs derived from low-cost substrates as alternative carbon sources to favor the economic viability of the lipid production process.

Keywords: Carboxylate platform, short-chain fatty acids, oleaginous yeast, Yarrowia lipolytica, lipid production

Acknowledgements:
The project BIOMIO+H2 (PID2020-119403RBC21) funded by MCIN/AEI/10.13039/501100011033, OLEOFERM (EraBoBiotech; PCI2021-121936) funded by MCIN/AEI/10.13039/501100011033 and "European Union NextGenerationEU/PRTR" supported this research. We also acknowledge the grants PRE2018-086477 and RYC2019-027773-I funded by "ESF Investing in your future" and by MCIN/AEI/10.13039/501100011033.

A TECHNO-ECONOMIC ANALYSIS AND LIFE CYCLE ASSESSMENT OF AN OLIVE-BASED MULTIPRODUCT BIOREFINERY COUPLED WITH CARBON, CAPTURE AND STORAGE

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Abstract

The ambition of reaching climate neutrality by 2050 as part of the European "Green Deal" requires incorporating new CO_2 removal strategies in the countries' agendas. Hence, coupling biomass conversion technologies with carbon capture and storage (BECCS concept) is receiving the most attention for its potential to remove CO_2 while delivering marketable products.

In this work, we conducted a techno-economic and environmental assessment of a multiproduct biorefinery coupled with CCS located in Andalusia (Spain) using olive tree pruning (OTP) as feedstock to produce bioethanol and antioxidants. The methodology consisted of two consecutive steps. First, the multiproduct biorefinery process was modeled and simulated in SuperPro Designer v9.0 to evaluate the technical feasibility and economic viability using standard economic metrics. Second, we use state-of-the-art Life Cycle Assessment (LCA) methodologies to quantify the environmental impacts of the biorefinery from cradle-to-gate, including the potential to deliver carbon dioxide removal. The model was built in SimaPro v9.0 software, the inventory was completed with data from the simulations, published literature, and the Ecoinvent database, and the impacts were evaluated using ReCiPe 2016 Midpoint (H).

The preliminary economic results were promising, with a positive net present value of 19.6 M € total, a payback time of 11.8 years, and an internal rate of return (IRR) of 7.5%. Notably, these results could be further improved if incentive schemes such as subsidies to remove CO_2 are provided. On the other hand, the LCA results demonstrated that reaching a net negative carbon footprint is possible, particularly when biomass is burned to power the heating needs of the processes (i.e., -530 kg CO_2-eq per 1 kg and 0.15 kg, of bioethanol and antioxidants respectively). However, the analysis of other impact categories reveals a severe burden-shifting, particularly in eutrophication and acidification. These collateral damages cannot be overlooked, and more in-depth research is required to understand the drivers and avoid undesired effects.

Overall, our work shows that the large-scale deployment of the multiproduct biorefinery is technically feasible. Marketable renewable bioethanol and antioxidants can be produced while simultaneously delivering permanent CO_2 removal, which is fundamental to meeting our climate goals.

Keywords: *bioenergy, carbon capture and storage, biorefinery, olive tree pruning, life cycle assessment.*

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 945413 and from the Universitat Rovira i Virgili (URV).

Hydrolization of Triacetin using Sub-supercritical water

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Abstract

Supercritical fluids have been intensively investigated in industry and science as a solvent and reaction medium for a variety of chemical applications over the last years[1]. Due to their advantages and physical chemical properties, this technology has given excellent results for the fractionation of lignocellulosic biomass used in different fields: hydrolyzation of cellulose and beet pulp [2], depolymerization of lignin[3] and generating new products from grape seeds[4]. From a chemical standpoint, the hydrolysis of an ester can be done using sub-SCW without the use of an acid or base[5]. This work presents a continuous hydrolysis system in sub - supercritical water that converts triacetin to diacetin, monoacetin, glycerol and acetic acid with total hydrolyzation yield and no byproducts formed. Investigations were done into the impacts of the reaction's time (0.6 - 20 s), temperature (250-400 °C), pressure (180-250 bar), inlet concentration, ionic product and density. Results show that at temperatures around 375 °C and 250 bar, it is possible to obtain 38.5% monoacetin, 52.3% diacetin, 7.6% glycerol and 1.6% of triacetin. Under subcritical water conditions, monoacetin, diacetin, and glycerol hydrolyzation is much lower respectively 7.2%, 35.2%, and 0.6%, respectively, while TA 57% is not hydrolyzed. Experimental data and kinetic study will be discussed in my presentation.

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Acknowledgements: This work was supported by Ministry of Science and Innovation & FEDER for funding the project PID2019-105975GB-I00 and the Regional Government of Castilla y León & FEDER for funding the program CLU-2019-0.

SUSTAINABLE BIOPROCESS FOR THE RECOVERY OF BIOBASED PRODUCTS AND BIOENERGY FROM BREWER'S SPENT GRAINS

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Abstract

In industrial brewing processing, brewer's spent grain (BSG) is the main lignocellulosic by-product generated, accounting for 20 kg per 100 L of beer. The hydrolysis of lignocellulosic biomass can be a limiting stage to the production of biobased products and bioenergy. In this study, a sustainable bioprocess combining subcritical water pretreatment (SWP) followed by methanogenic anaerobic fermentation was applied for the valorization brewer's spent grains (BSG). The SWP was carried out at 15 MPa, a water flow rate of 5 mL/min, 180 °C, and a solvent-to-feed ratio of 20 g_{water}/g_{BSG}. The hydrolysate obtained was characterized and applied as the substrate to determine the biochemical methane potential at pH 7.5 and mesophilic temperature (35 °C). The results revealed that SWP could produce sugars (47.76 $mg/g_{carbohydrates}$), where xylose (0.47 mg/mL) and arabinose (1.04 mg/mL) were the main monosaccharides. In addition, the SWP can be used to recover proteins (5.01 µg/mL). The application of the hydrolysate for anaerobic digestion could produce 71 L CH_4/kg_{TVS}, which can be used to produce electricity (0.702 kWh/kg_{TVS}) and heat (1.26 MJ/kg_{TVS}) in a co-generator. In addition, the anaerobic microorganisms could produce several short-chain fatty acids, such as propionic (2.07 mg/L), butyric (6.14 mg/L), and isovaleric (4.65 mg/L) acid. In conclusion, the sustainable bioprocess based on SWH of BSG followed by anaerobic fermentation can be a promising alternative for the recovery of biobased products (sugars, amino acids, short-chain fatty acids) and bioenergy (methane, electricity, and heat) in a biorefinery concept.

Keywords: Biobased products, Biorefinery, Sustainable process, Biorefinery.

Acknowledgements: This work was supported by the Brazilian Science and Research Foundation (CNPq, Brazil) (productivity grants 302451/2021-8); São Paulo Research Foundation (FAPESP, Brazil) (grant numbers 2019/14938-4 and 2019/26925-7).

Bio-polyesters from tomato peels, enabled by SCW

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Abstract

The chemistry based on the use of biodegradable and renewable resources has been on focus by several researchers in the last decades. Among the others bio-based high value compounds, polyesters stand out as one of the most important due to their wide application, like cosmetics and industrial materials.[1] One of the richest sources of polyesters is the plant cuticle. This is the outer membrane of the aerial parts of almost all land plants. The membrane plays important role in prevention of water loss, regulation of gas exchange and protection against mechanical injury, microorganisms, UV light.[2] This work focuses on obtaining bio-polyesters with a chemical structure similar to cutin from tomato peel. Tomato peels contain a significant amount of cutin, ~50% w/w, and then it is a promising source of polyesters. This work presents continuous extraction-reaction method using sub and supercritical water hydrolysis (SCW) as an efficient alternative to conventional cutin isolation with long reaction time and batch reactions.

The experiments were carried out in a continuous hydrolysis plant with sub and supercritical water and sudden – expansion tubular reactor. The extraction-reaction temperature were in the range of 300 – 400 °C and reaction time was below 10 s. The tomato peel was fed to the reactor as a suspension in water.

The product after SCW hydrolysis was obtained as a solid suspension in water. Liquid phase consists of hydrolyzed compounds and extracted during the process while, from the other side, solid fraction consists of the insoluble tomato peel fraction. Recovered solid fraction more than ~70% of cutin.

The SCW treatment was shown as a good alternative to conventional methods. During the process, the carbohydrates from the tomato peel were primarily hydrolyzed which builds on the previous experience of our group in working with lignocellulose biomass.[3] It is also shown that high value biopolyester can be made by SCW hydrolysis.

Keywords: tomato peel, subcritical and supercritical water, biopolyester, cutin.

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Acknowledgements: This work/project was supported by the Regional Government of Castilla y León and the EU-FEDER program (CLU-2019-04). Leontijevic V thanks to JCYL for predoct contract.

COMPUTATIONAL GENERATION OF MOLECULAR MODELS FOR ATOMISTIC SIMULATIONS OF BIOCRUDE OILS

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Abstract

In future biorefineries, processing biomass waste into biocrude oils is expected to provide several valorization routes with applications in asphalt additives or biofuel precursors, among others. Despite this potential, there is a lack of fundamental knowledge on the structure-property relationships of biocrude oils due to challenges associated to the experimental characterization of these complex fluids, and to the lack of molecular models that enable predictive computational simulations. Although some molecular models have been developed for algae-derived biocrude oils[1], and density functional theory (DFT) has been used to computationally characterize their reactivity, as well as the intermolecular interactions of biocrude oil derived from sewage sludge[2], a systematic method to generate molecular models from experimental characterization is needed. In this work, a novel computational method to generate accurate molecular models from GC-MS characterization of any biocrude oil has been developed. The method generates representative models that simplify the complexity of the biocrude in a limited group of molecules, but it captures the key chemical futures needed for computational chemistry calculations and large-scale molecular dynamics simulations. As case study, we have generated molecular models from the GC-MS characterization of different fractions of pine bark pyrolytic biocrude oils. Furthermore, DFT calculations have been performed to calculate a range of reactivity descriptors for both the complete list of compounds identified in the pine bark biocrude, and the newly generated average models. The DFT study validates the average models as representative of the total composition, and it provides deeper understanding of the eventual upgrading and oxidative processes the biocrude molecules can undergo. The computational framework developed here will provide a platform for the computational design of fit for purpose biocrude oils in the future, with a focus on self-healing asphalt for more sustainable pavements[3].

Keywords: molecular modeling, computational chemistry, biocrude oils, DFT, molecular dynamics

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Acknowledgements: Royal Society of Chemistry Enablement Grant (E21-7051491439), Supercomputing Wales, and Google Cloud Platform.

VALORIZATION OF ONION SKIN WASTES USING SUBCRITICAL WATER: FLAVONOIDS AND PECTIN RECOVERY

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Abstract

Onion skin wastes (OSW) represent around 10% of the total onion production and end up in landfills because they are not suitable for human consumption or animal feeding. Nevertheless, this non-edible brown skin and external layers of onions are rich in phenolic compounds, mainly flavonoids such as quercetin and derivatives [1], which are high-added value natural antioxidants. Additionally, onion skin has gained attention as a good source of pectin [2]. Pectin, a complex polysaccharide composed by uronic acids (66.4%) and neutral sugars (galactose, arabinose, xylose, mannose, glucose or rhamnose) in variable composition, is the major structural component onion cell walls (42.4%). Considering that according to FAO, 2020 onion worldwide production was 104 Mt, there is a great potential for the valorization of the OSW through the recovery of flavonoids and pectin.

In this work the valorization of OSW using subcritical water (subW) is studied in a semicontinuous extractor at temperatures up to 180 ºC. The extraction of flavonoids resulted to be fast (<30 min) and temperature sensitive (maximum at 145 °C; total flavonoids, 27.4±0.9 mg/g OSW). More specifically, quercetin (15.4±0.4 mg/g OSW) and quercetin-4'-glucoside (8.4±0.1 mg/g OSW) accounted for the 90% of the total flavonoids identified. Regarding pectin recovery, the extraction yield was close to 9%, being demonstrated that subW provided the recovery of the valuable RG-I regions compared to acid water extraction processes, which yielded the linear homogalacturonan region. The molecular weight of the pectin was mainly in the range from 50 to 100 kDa. High temperatures and long hydrolysis times led to the formation of organic acids (acetic, formic and levulinic) and degradation products such as furfural, as well as the reduction in the pectin molecular weight.

Keywords: onion; subcritical water; pectin; quercetin, valorization

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BIOHYDROGEN PRODUCTION FROM THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTE (OFMSW) VIA LACTATE-DRIVEN DARK FERMENTATION

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Hydrogen (H_2) is a promising energy source that can help reducing environmental issues caused by the overuse of fossil-derived fuels, as it can be produced through sustainable, mild biotechnologies using non-edible renewable feedstocks. These biotechnologies, which include dark fermentation (DF), photofermentation, biophotolysis and bioelectrochemical systems, aim at producing stably high H_2 yields and rates in the long run. The valorization of organic waste via biohydrogen (biogenic H_2) production embraces the circular concept of waste-to-energy.[1] DF makes use of simple designed reactors that operate in the absence of oxygen and light, hence the name adopted by the scientific community to this type of fermentation. In the DF of complex feedstocks by mixed cultures, microorganisms divide the labor to mainly break down and further ferment carbohydrates, an in a minor extent proteins, to produce H_2 with carbon dioxide, organic acids and alcohols as the side products.[2] In DF driven by mixed cultures, H_2-producing bacteria (HPB) such as *Clostridium*, *Enterobacter*, *Bacillus*, among many others, co-exist with other competitors/undesirable microorganisms. HPB outcompeted by lactic acid bacteria (LAB) like *Lactobacillus* has been regarded as the main bottleneck for efficient H_2 production. In this regard, lactate-driven DF has been proposed as a smart way to cope with this operational issue.[3] In steering this pathway LAB can help increasing H_2 production via syntrophic interactions with the H_2 producer that can metabolize lactate. [4]. However, a better understanding of the lactate-driven DF pathway is still needed for further optimizing waste-to-H_2 bioconversion. The aim of this work was to investigate the feasibility of producing H_2 from the organic fraction of municipal solid waste (OFMSW) via lactate-driven dark fermentation.

The experiments were conducted in triplicate in 1.4-L reactors operated in batch mode at constant pH of 6.5, temperature of 37 °C and stirring speed of 300 rpm. The profile of soluble byproducts (HPLC) and the production rate (wet gas counter) and composition (GC-TCD) of acidogenic off-gas were recorded throughout the test. It was observed that the concentration of lactate in the broth tended to increase during the first stage of fermentation but then it rapidly decreased. The lactate behavior matched well with the production of H_2, indicating the role of lactate as the main H_2 precursor. The lactate-driven DF allowed to achieve a H_2 yield of 3.2 NL-H_2/$L_{reactor}$ or 70 NmL-H_2/g-VS_{added}, with an associated volumetric H_2 production rate of 116 NmL-H_2/$L_{reactor}$-h.

Keywords: Bioenergy, Dark fermentation, Food waste, Hydrogen-producing bacteria, Lactic acid bacteria.

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Acknowledgements: This work was funded by ECLOSION (Misión 2, Plan Estatal I+D+I) and Next Generation EU.

A BIOREFINERY APPROACH FOR THE PRODUCTION OF PHAs

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Abstract

Agricultural waste amounts to more than 21 million tons/year in the European Union only. Instead of disposing this waste at high economic and environmental costs, we need to consider it as a resource and turn it into bio-based, high-value products in the context of biorefineries. Polyhydroxyalkanoates (PHAs) are biodegradable biopolymers synthesized by microorganisms, which can be assembled into bioplastic [2]. These can be produced in biorefineries by acidogenic fermentation of agro-waste followed by biomass selection and PHA-accumulation. However, their presence in the marked is currently limited because of the high cost for their extraction [3]. To make PHAs production affordable, the approach of our work has been to either avoid extraction and use whole PHA-containing microbial cells as the final product, or to make use of the nutrients-rich by-products obtained from the PHAs extraction products. Both pathways started with the fermentation of agro-waste, which was used to feed PHA-accumulating bacteria. The obtained biomass was analysed for its centesimal composition and nutritional value and was used to perform feeding trials with Zebrafish larvae (*Danio rerio*) to assess its suitability as protein source (MP = microbial proteins) for fish feed. As an alternative pathway, the biomass was hydrolysed to produce protein hydrolysates (PHs), while the PHAs were concentrated for their use as bioplastics; the PHs were further tested in growth trials with cucumber and tomato plants (*Cucumis sativus* and *Solanum lycopersicum*) to assess any effect on their growth and productivity. The MP to be used as fish feed resulted high in its protein content (61.8%) and containing all the essential amino acids for fish. The feeding trials showed that animals fed with a combination of commercial feed and MP (50:50) performed better than the control group, when fish oil or PHAs where added. This suggests that PHAs producing bacteria could be directly used as MP without the need of expensive extraction and purification procedures, probably due to the reported ability of PHAs to boost the immune system [4]. Tomato and cucumber plants treated with the PHs showed a biostimulant effect, either on the root or leaves development. PHAs were also recovered during the process, with different outcomes depending on the hydrolysis treatments used. These preliminary tests with fish and edible plants suggest that it is possible to biologically convert agricultural residues into products with high commercial value, such as fish-feed for pisciculture, biostimulants for agriculture and bioplastics. However, further research is needed to ascertain the best treatment for the simultaneous extractions of PHAs and PHs; fish trails should be performed with commercial fish species; plant trials should be repeated and standardised to confirm the results obtained to date.

Keywords: Biorefinery, fish-feed, biostimulants, microbial proteins, polyhydroxyalkanoates

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QUANTITATIVE ASSESSMENT OF CULTURE CONDITION CONTRIBUTIONS INTO CELL CONCENTRATIONS AND ASTAXANTHIN CONTENT IN ALGA *HAEMATOCOCCUS PLUVIALIS*

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Abstract

Haematococcus pluvialis Flotow is a unicellular alga that causes the red "bloom" of rain puddles. Most usually cultivated outdoors, *H. pluvialis* is used as a source of red pigment and antioxidant carotenoid astaxanthin for food and feed. We hypothesize that a limited number of factors exist which contribute the most to the culture growth and cellular astaxanthin accumulation and could be used for simple, efficient and feasible control of the outdoors culture of *H. pluvialis*.

The study was aimed at comparing light intensity and six medium components contributions into the cell yield and cellular carotenoid content after 42-day laboratory cultivation of *H. pluvialis* under the multifactorial experimental design and fed-batch nutrient supplementation.

By the effect sizes, limitation of nitrate and calcium were the most potent hinders of the culture growth of *H. pluvialis*; higher irradiance was the most potent stimulant of astaxanthin accumulation in the cells. Salt stress (10 g/L NaCl) appeared lethal for the strain of *H. pluvialis* studied. The severe limitation of iron (iron-limited inoculum transferred into iron-deficient medium) stimulated astaxanthin accumulation at moderate concentrations of nitrate. *H. pluvialis* was resistant to high doses of ferrous ions, 12 times as high as in the standard culture medium. Intense bicarbonate supplementation appeared lethal for *H. pluvialis* at low irradiance. Higher light intensity promoted survival of the algae and higher astaxanthin accumulation in the cells.

Nitrate and calcium fed-batch supply were recommended for culture growth stimulation on the first stage of the two-stage *H. pluvialis* culture to increase the yield of the biomass. The iron limitation may be applied to stimulate astaxanthin accumulation on the second stage. At that, the inoculum should be Fe-limited and nitrate must be supplied in moderate doses. Bicarbonate supplementation could be recommended to increase cellular astaxanthin, provided the light intensity is high enough.

Thus, the multifactorial experimental design allowed to identify the most powerful factors that determine cell concentrations and astaxanthin yield in the culture of alga *H. pluvialis*.

Keywords: Haematococcus pluvialis, astaxanthin, nutrient limitation, fed-batch culture, light intensity

Protein and carbohydrate recovery from secondary sludge biomass generated in urban wastewater treatment plants

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Abstract

Secondary sludge or WAS is an abundant and problematic waste biomass, which accumulates nutrients from wastewater in the form of proteins and carbohydrates, among others. In the last years, new processes have been developed with the objective of WAS valorization, mainly to produce energy from this waste. As alternative, recently, research is beginning to investigate the possibility of using this waste biomass as feedstock for new biorefinery processes through the fractionated valorization of its components. In this context, the present work evaluates different hydrolysis methods: chemical (acid, AC and alkaline, ALK), hydrothermal (HT), biological (autohydrolysis, AH), physical (ultrasound, US) and sequential (US-AH) and assisted (US+ALK, HT+ALK, HT+AC) combinations on the solubilization yield (SY) and recovery (RY) of the main components of this biomass: proteins as peptides or amino acids and carbohydrates as fermentable monosaccharides (glucose and xylose). The highest protein SYs (≈ 97.2 %) were obtained with alkali-assisted methods (US+ALK and HT+ALK). Alkali-assisted hydrolysis (US+ALK) also achieved the highest SY of carbohydrates (94.4%) although a low RY of monosaccharides (29%). The protein losses were lower than 25% for most of the experiments, with US+ALK achieving the highest peptide recoveries (75.1%) with sizes between 70-215 kDa and 40% of essential amino acid (EAA). Individual hydrolysis (ALK) also provided notable solubilization, reaching a protein SY of 75%. Increasing the alkali concentration reduced the SY of carbohydrates from 65.5% with 0.5 M NaOH to 56.8% with 1 M. The influence of temperature was also noticeable, mainly for proteins. The HT+ALK combination produced almost complete solubilization of proteins, but lower SY of carbohydrates (≈75%) and high loss factors (47%). HT+AC conditions, achieved high carbohydrate SY (94.2% 1M HCl), but lower protein SY (≈72%) with amino acid recoveries with predominance of non-essential ones. Addition of HCl increased carbohydrate SY by 130% (0.5 M) and 144% (1 M), and protein solubilization by 82% compared to HA under identical conditions, but at pH 6.5.

Keywords: pretreatment, peptides, monosaccharides, biorefinery, valorization.

Acknowledgements: This work was supported by "Ministerio de Ciencia, Innovación y Universidades", Spain (PID2020-113544RB-I00). The authors also thank the regional government of Castilla y León (UIC 338, CLU 2017-09) and the EU-FEDER (CLU 2017-09) for financial support of this work. Filipigh. A (PRE2021-10017) and Rojo. E (PRE2018-083845) would like to thank the "Ministerio de Ciencia, Innovación y Universidades" for their PhD scholarships.

Life Cycle Analysis of Pyrolysis by Using ZSM-5 and Zeolite Y catalysts

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Abstract

An effective measure to mitigate the environmental impacts is generating energy and value-added products from the residues such as bio-waste. Bio-waste valorization meets the expectations of the second generation of biofuels, in terms of environmental savings and revenue growth. One of the most known technological routes to convert bio-waste into bioproducts is pyrolysis, which may conduct with and without catalyst application.

This study aimed to investigate an early-stage life-cycle assessment (LCA) for catalytic pyrolysis to valorize rapeseed meal into bioproducts, split over the scenarios using two different catalysts. Based on a life cycle inventory analysis, four selected environmental impact categories were assessed by IMPACT 2002+ methodology in a gate-to-gate system boundary. The results demonstrate that the ZSM-5 pyrolysis process led to bigger environmental burdens than the process utilizing zeolite Y in all compared impact categories except global warming (GW). The bulk of GHG emissions within the conversion process comes from the electricity generation for running the process, which was provided by fossil resources. Given that catalysts can contribute significantly to biofuel life-cycle emissions, hence pyrolysis LCAs should consider the potential influence of catalysts in the valorization prosses. This study can provide an approach to foresee environmental hotspots in the very early stages of bio-waste valorization into bioproducts, and for highlighting drawbacks connected to the implementation of conversion processes at pilot and industrial scales.

Keywords: LCA, pyrolysis, zeolite catalyst, biochar, pyro-gas, bio-oil

UNDERSTANDING THE BEHAVIOR OF CHITIN IN SUBCRITICAL AND SUPERCRITICAL WATER IN A CONTINUOUS REACTION SYSTEM

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Abstract

After cellulose, chitin is the second most widespread biopolymer worldwide. Its best-known applications, thanks to its antibacterial, toxicological and biocompatibility properties, are oriented to the medical and pharmaceutical industry, cosmetics, agriculture, and water treatment, among others. Being a biopolymer, chitin is formed by [β-1,4-poly(n-acetyl-D-glucosamine)] units, which can be treated to obtain oligomers and monomers, N-acetylglucosamine (depolymerization) and glucosamine (deacetylation). These monomers constitute nitrogen containing building blocks that open the way to sea-waste biorefinery for obtaining molecules of interest, such as furan-based monomers or amines[1]. Studies have shown that chitin, like cellulose, can be dissolved and hydrolyzed in sub- and supercritical water; however, due to its high crystallinity, this process occurs less easily[2]. Processes studied have used sub- and supercritical technology in batch-type systems as pre-treatments in enzymatic processes, managing to dissolve and even obtain monomers in times of up to 1 minute[2]. However, degradation compounds have been obtained or even the prevalence of side reactions competing with hydrolysis has been observed (depending on the reaction conditions).

The present work shows the behavior of chitin in subcritical and supercritical media, seeking to understand the effect of water properties (density, viscosity, ionic product) at conditions surrounding the critical point; specifically, to investigate the reaction mechanism of chitin in SubCW and SCW media using ultrafast continuous reactors. Commercial chitin was characterized by elemental analysis, FT-IR, XRD to sketch a picture of the starting structure for the reaction process. The reaction process was carried out in sub and supercritical water (P= 250 bar, T= 350 °C to 390 °C) and short reactor residence times (0.3s to 12s). Unlikely the behavior of cellulose in sub/supercritical water in ultrafast reactors, the products obtained were solid suspension in all the experiments. Liquid fraction was characterized by Total Organic Carbon, Total Nitrogen and HPLC; and solid fraction was characterized by elemental analysis, FT-IR and XRD.

Keywords: Chitin, SCW Hydrolysis, N-acetyl glucosamine, Glucosamine, ultrafast reactors.

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Acknowledgements:

This work was supported by Spanish Ministry of Science and Innovation (project PID2020-119481RA-I00), the Regional Government of Castilla y León and FEDER-EU, program CLU-2019-04.

A sustainable strategy for the withdrawal of cellulose from eucalyptus tree wood waste using deep eutectic solvents and microwave-assisted extraction

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Abstract

The commonly used procedures for the extraction of cellulose from tree waste products are based on non-sustainable chemical and thermal approaches that normally includes as a first step an alkaline treatment[1,2]. In this work we describe a new sustainable process for the extraction of cellulose from eucalyptus waste products based on the use of deep eutectic solvents (DES) and microwave-assisted extraction (MAE) to replace the alkaline treatment. The process used in this work is easy, efficient, and eco-friendly. The MAE is faster, requires less energy and provides higher yields, when compared with traditional extraction techniques. DES have been considered as one of the most promising approaches for new pulping technologies due to their solubility capabilities. The possibility of using DES to fractionate biomass is very attractive, yet poorly explored[3].

In this work, 13 different DES were tested, in which each DES (aqueous solution, 25% v/v) was added to 250 mg of grounded wood and subjected to a microwave irradiation at 100ºC for 1 hour. Samples obtained from the extraction process were characterized by Fourier-transform Infrared (FTIR) spectroscopy, thermogravimetric (TGA) and Differential Scanning Calorimetry (DSC) and were compared to the starting material and with the commercially available microcrystalline cellulose. The results point out the applicability of the new approach as a sustainable strategy to replace the alkaline treatment in the extraction of cellulose from eucalyptus waste products.

Keywords: Sustainability, Deep eutectic solvents, Microwave extraction, Cellulose, Wood wastes

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Acknowledgements: M. Sarraguça and S. Vinhas thank FCT/MEC (DL 57/2016–Norma transitória and NORTE-08-5369-FSE-000050, respectively). T. Moniz also thanks FCT through project EXPL/QUI-QIN/0411/2021. Funding: Financial support from PT national funds (FCT/MCTES): UIDB/50006/2020 and UIDP/50006/2020.

PRODUCTION AND RECOVERY OF MEDIUM CHAIN FATTY ACIDS FROM *OPUNTIA FICUS-INDICA*

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Abstract

Medium-chain fatty acids (MCFAs) are saturated or unsaturated fatty acids having from 6 to 12 carbon atoms, which have different applications in food, pharma, chemical and biofuel industries. MCFAs are mainly synthetized from fossil-base compounds or from vegetable oils such as palm oil, coconut oil or castor oil. Even in this last case, the MCFAs production cannot be considered sustainable as their extraction involves the adoption of no green solvents. Moreover, the MCFAs content in the vegetable oils is low, the 5-15% w/w of the total compounds [1]. The investigation of sustainable processes for MCFAs production has been receiving great attention from scientific community in last decade. In particular, anaerobic fermentation is a well-known technology for the organic wastes conversion into valuable bioproducts, such as Volatile Fatty Acids (VFAs), and biogas, a gaseous blend rich in methane. But the higher energy densities and economic value than the traditional methane and VFAs, make MCFAs more interesting in a biorefinery scope [2]. The biological process that appears as the most promising for MCFAs synthesis is represented by the "chain elongation", where short chain VFAs, derived from the acidogenic fermentation of organic substrates, are converted into MCFAs through the addition in the reaction medium of electron donor-compounds, such as ethanol, lactate, methanol, n-propanol of biological origin. The present research will investigate the production of MCFAs, in particular caproic acid, from the fermentation of *Opuntia Ficus Indica's* cladodes. The chain elongation process will be optimized testing different Hydraulic Retention Times (HRT) in a range of 1 to 10 days. The challenge of this work is to select caproic acid producing microorganisms by reverse β-oxidation from Microbial Mixed Culture (MMC), whose presence was assured by an agricultural digestate as inoculum. Moreover, at the end of the chain elongation, three different methods for the recovery and concentration of the produced caproic acid will be tested: i) adsorption of solid matrices (ionic resins and powred activated carbons), ii) ultrafiltration and reverse osmosis and iii) liquid-liquid separation using biodiesel as solvent.

Keywords: Caproic acid, Opuntia Ficus Indica, Chain elongation, Volatile Fatty Acids

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ADSORPTIVE PRETREATMENT OF WASTE COOKING OIL USING QUICKLIME FOR TWO-STEP BIODIESEL PRODUCTION

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Abstract

Biodiesel, a mixture of fatty acid methyl esters (FAME), is an excellent non-toxic, and biodegradable substitute for mineral diesel fuels produced from crude oil. It is made from renewable sources by transesterification of triglycerides with methanol, or by a reaction usually defined as methanolysis. Usage of low-quality feedstock, such as waste cooking oil (WCO), is challenging due to the undesirable side reactions as a result of the presence of free fatty acids (FFA), and water, thus a pretreatment stage before subjecting it to the transesterification process is usually required. In the present study, a two-step approach based on an adsorptive pretreatment with quicklime in order to remove FFA from WCO, followed by methanolysis using CaO·ZnO as a heterogeneous catalyst was proposed. The first step was analyzed with the goal to define the optimal temperature of adsorption, the adsorbent particle size, calcination procedure, as well as the necessary amount of quicklime used. The analysis of adsorption kinetics was performed using pseudo-first and pseudo-second order kinetic models, and the efficiency of quicklime in the FFA removal from the WCO was also determined. The results showed that FFA from WCO could be successfully removed using quicklime as adsorbent at 30 °C for 1 h, with a removal efficiency of 72% and an adsorption capacity of 910 mg/g. The amount of Ca^{2+} ion present in the oil after the pretreatment was determined to be 12.64 mg/kg, showing that a very small amount of calcium from CaO was dissolved in treated WCO. The FTIR analysis of quicklime after the adsorption of FFA confirmed the interaction of the carboxyl group in FFA with the active site of the adsorbent. Adsorptive pretreatment had a positive effect on the rate of transesterification reaction with CaO·ZnO as a catalyst, enabling the achievement of over 96% of FAME yield in only 15 min at 60 °C. The present study showed that quicklime, being cheap, available, and efficient, has considerable potential for the removal of FFA from the WCO. Besides, both the adsorption and the heterogeneously catalyzed methanolysis are environmentally and economically acceptable processes.

Keywords: Biodiesel, Waste cooking oil; Adsorption; Quicklime; CaO·ZnO

Acknowledgements: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract No. 451-03-68/2022-14/200135). Work was carried out in the frame of the COST-Action "Green Chemical Engineering Network towards upscaling sustainable processes" (GREENERING, ref. CA18224) supported by COST (European Cooperation in Science and Technology).

ANAEROBIC FERMENTATION OF VINASSES AS ROBUST TECHNOLOGY TO PRODUCE GREEN CHEMICALS

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Abstract

The European Commission has launched several initiatives to boost technologies that enable the replacement of fossil-based fuels and chemicals by renewable and sustainable ones. In this context, anaerobic fermentation (AF) has emerged as sustainable technology to valorize organic residues into green chemicals, such as short-chain fatty acids (SCFAs). Nevertheless, the effect of the operational parameters on the product spectrum remains uncertain given the wide number of co-occurring metabolisms in an open-mixed culture. This study aimed at evaluating process robustness against operational parameter variations to assess SCFAs production stability. To this end, AF of vinasses was performed in continuous reactors subjected to a hydraulic retention time (HRT) of 15 days, 25 ºC and pH 5.5. Once the process exhibited stability, two perturbances were applied: (a) HRT increase from 15 to 20 days and (b) a temperature increase from 25 to 37 ºC. These perturbances were selected based on the unforeseen events that could be found at the industrial scale (deficient pumping or thermostat control).

The 25ºC-AF at 15 days HRT evidenced a clear methanogenic activity suppression that boosted SCFAs accumulation (35 gSCFAs/L), reaching a yield of 0.56 gSCFAs-COD/gVS_{in}. Nevertheless, the implemented perturbances did not provoke significant variations in SCFAs production yield or profile. The reactor showed extreme robustness by providing similar values to the control one. Although previous investigations determined temperature and HRT as critical parameters for SCFAs production, the waste composition also had a significant influence on process performance. Microbial community analysis revealed that the vinasses reshaped the microbiome present in the inoculum. The microbial population was enriched in lipid- and protein-degraders belonging to Firmicutes phylum. The high substrate affinity and the presence of redundant metabolisms among the bacterial population showed a robust microbiome that was able to deal with process perturbances, demonstrating the SCFAS production stability and thereby the promising behavior of this technology for scale-up.

Keywords: Anaerobic fermentation, Carboxylates, Green technology, Robust microbiome

Acknowledgments:

This work has been supported by MCIN/ AEI /10.13039/501100011033 through the project BIOMIO (PID2020-119403RB-C21) and UPGRES (PLEC2021-00776) with "NextGenerationEU"/PRTR, and the financial support from Comunidad de Madrid provided through project ALGATEC-CM (P2018/ BAA-4532), co-financed by the European Social Fund and the European Regional Development Fund.

FRACTIONATION OF VINE SHOOTS TO BIOSUGARS AND LIGNIN USING AN IONIC LIQUID

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Abstract

The world currently faces an inevitable transition from a fossil-based economy to a bio-based economy. Agricultural residues are an abundant source of non-edible and usually cheap biomass that can be valorized to produce bioenergy and bioproducts, within a biorefinery strategy [1]. In Spain, vineyards are one of the most important crops, taking up 957,856 ha of land in 2019 [2]. Vine pruning results in the generation of a huge amount of lignocellulosic residues (the vine shoots, VS) that could be used to obtain fermentable sugars and lignin. However, due to its heterogeneous composition and complex structure, lignocellulosic biomass need to undergo a fractionation process to extract and separate the interesting compounds. Among the variety of fractionation techniques that have been investigated, ionic liquids stand out by their extraordinary solvent properties, i.e. non-flammability, low vapor pressure, tenability, and recyclability [3].In the present work, VS were pretreated with the ionic liquid 1-ethyl, 3-methyl, imidazolium acetate (EmimAc) to remove part of the lignin and enhance the enzymatic digestibility of the pretreated pulp. Some exploratory experiments were carried out to determine the effect of several pretreatment conditions i.e: particle size, time, and temperature. Furthermore, the performance of different mixtures of EmimAc and water was tested. Finally, two alternative extraction and separation protocols were evaluated with the aim to improve the separation of the dissolved lignin and the recovery of the ionic liquid. The results showed that the variables studied had a significant effect on the enzymatic digestibility of the pulp. Moreover, the washing method was proved to be of capital importance for the production of sugars from the pretreated VS.

Keywords: lignocellulosic biomass, fractionation, ionic liquids, bio-sugars

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Acknowledgements:

Authors acknowledge MCIN/AEI/ (10.13039/501100011033) for funding this research work through PID2020-112594RB-C32 project.

AGRICULTURAL PRODUCTS FROM ALGAL BIOMASS GROWN IN PIGGERY WASTEWATER: A TECHNO-ECONOMIC ANALYSIS

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Abstract

The exponential growth of the world's population is increasing the demand for animal products, leading also to an increase in animal manure generation, highlighting pig manure which has become a huge source of environmental pollution. This residue is rich in nutrients for microalgae growth in a promising treatment process with biological photobioreactors. After the piggery wastewater treatment, a biomass formed by microalgae and bacteria with a high content of proteins and carbohydrates is obtained and can be employed as a feedstock to produce commercial products for agriculture like biostimulants or biopesticides.

This research is aimed at the techno-economic analysis of producing biostimulants and biopesticides by enzymatic hydrolysis and ultrasonication from a microalgal biomass grown in a thin-layer photobioreactor treating piggery wastewater, comparing different process alternatives. The harvesting methods were membranes in Scenario 1 and centrifugation in Scenario 2. Scenario 3 evaluated the co-production of biopesticides by acetone extraction. In each scenario, the biostimulant produced had a different nutrient composition (C, N and P), being more concentrated in Scenario 2 using a centrifuge for biomass harvesting (4.58% of C, 0.83% of N and 2.04% of P). The total investment cost (IC) was higher in Scenario 2 than in Scenario 1 due to the high cost of the centrifuge (contribution of 62.2%), although Scenario 3 resulted in the highest IC as it was a process with more equipment for the biostimulant and biopesticide production (contribution of 63%). Regarding operational and maintenances costs (OMC), energy requirements (electricity) were higher in Scenario 2 for centrifuge operation, while the energy requirement (heating) was higher in Scenario 3 for acetone removal. Finally, the biostimulant production cost was 76.41 €/m^3 in Scenario 1, 351.21 €/m^3 in Scenario 2 and the biopesticide production cost was 375.54 €/m^3 in Scenario 3. Comparing with commercial fertilizer, the annual cost to treat 1 ha of land was lower with the biostimulant produced in the three scenarios (35.1%, 12.1% and 38.2% respectively).

Keywords: Piggery wastewater, techno-economic assessment, biostimulant, biopesticide.

Acknowledgements: This work was supported by the "Ministerio de Ciencia, Innovación y Universidades" of Spain (PDC2021-121861-C22, PID2020-113544RB-I00). Elena M. Rojo and A. Alejandro Filipigh would like to thank the "Ministerio de Ciencia, Innovación y Universidades" for their doctorate scholarship (PRE2018-083845 and PRE2021-100176). The authors also thank the regional government of Castilla y León (UIC 338, CLU 2017-09, CL-EI-2021-07) for the financial support of this work.

BIOREMOVAL OF Cd, Hg, Pb AND U BY MICROALGAE AND BACTERIA GROWN IN PHOTOBIOREACTORS TREATING PIGGERY WASTEWATER

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Livestock farming is a relevant economic sector in Castilla y León which generates large quantities of highly polluting wastes causing serious environmental issues if not properly treated. The polluting potential of livestock waste, particularly pig slurry, is due to its high content of organic matter, nitrogen, and traces of toxic substances (heavy metals, pharmaceutical residues). Among the available technologies, pig slurry treatment in photobioreactors has shown great potential for nutrient recovery and removal of heavy metals. In this work, the removal capacity of trace elements by microalgae and bacteria grown in photobioreactors treating pig slurry is compared.

The effect of contact time and metal concentration on the biosorption of Cd(II), Hg(II), Pb(II) and U(VI) on green microalgae *Scenedesmus almeriensis*, and on bacteria from aerobic activated sludge collected from urban wastewater treatment plants were investigated, using batch photobioreactors feed with synthetic wastewater simulating the composition (C, N, P) of piggery wastewater and irradiated in 12:12 h photoperiods. Two concentration levels for each metal were assayed, equivalent to 2 and 5-fold the maximum allowable levels in drinking water according the EU Directive 2020/2184 and USEPA. Samples of the cultures were harvested periodically along 15 days and the remaining metal in the solution measured by ICP-MS.

Metal bioelimination resulted greater than 90% after few days of contact in the case of microalgae, and after a few hours in the case of bacteria. TOC RE% (removal efficiency) higher than 90% was reached within 1 and 3 days for microalgae and activated sludge, respectively, in the presence of Cd, Hg, Pb and U. For TN RE%, moderated values and longer removal times were observed.

The maximum biosorption capacity of both biomasses for each metal at 24 and 72 h contact time were obtained from the adsorption isotherms constructed at metal concentrations ranging from 1 to 200 $mg \cdot L^{-1}$. In general, metal biosorption capacities shown by aerobic bacteria were higher than those of microalgae. The isotherms indicate that adsorption occurs on specific homogeneous sites.

SEM-EDX and ATR-FTIR showed morphological changes in the microorganisms and that cell surface functional groups involved in the biosorption of these toxic trace metals are mainly carboxyl, hydroxyl, amino and amide groups.

Keywords: biosorption, heavy metals, Scenedesmus almeriensis, activated sludge, wastewater

Acknowledgements: This work was supported by MICINN – FEDER (CTQ2017-84006-C3-1-R, PID2020-113544RB-I00) and Junta de Castilla y León – FEDER (CLU 2017-09, CL-EI-2021-07). B. Antolín acknowledges the Junta de Castilla y León for her doctorate scholarship.

CO-PRODUCTION OF MICROBIAL OIL AND CAROTENOIDS USING BIOWASTE BY THE OLEAGINOUS YEAST *Rhodosporidium toruloides*

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Abstract

A commitment to the sustainability of industrial processes is crucial to contribute to a greener and more environmentally friendly Bioeconomy. This study used wastes as feedstock to contribute to this end. This avoids exploiting new resources and reintroducing materials that were considered waste into the production chain. The residues studied included discarded fruit and vegetable from the agricultural sector and rejected paper from the municipal solid waste. Theses raw materials are suitable to obtain sugar-rich streams to be used as culture media for microorganisms. The oleaginous yeast *Rhodosporidium toruloides* is capable of accumulating lipids up to 70-80 % of its total dry weight. In addition, this microorganism simultaneously syntheses other industrially valuable compounds such as carotenoids. However, nowadays, more than 90 % of commercial β-carotene is produced by chemical synthesis, which has been criticized for the use of highly toxic reagents that generates unwanted by-products[1]. The ultimate objective of this study is the co-production of microbial oil and carotenoids by using the aforementioned residual biomass to grow *R. toruloides* within a biorefinery perspective. A fed-batch strategy was designed to maximize lipid and carotenoid production on *R. toruloides*. For lipid production, 0.5L bioreactors (Minibio, Applikon) were used. The culture temperature was maintained at 30ºC and pH-controlled at 6, and aeration was maintained by adjusting agitation speed with an airflow rate of 1vvm (> 20% of air saturation). During fermentation assays, samples were regularly withdrawn to monitor cell growth, sugars consumption, and lipids and carotenoid production. After cultivation, a lipid accumulation of more than 50 % was obtained, with a fatty acid profile dominated by oleic, palmitic and linoleic acids. Concerning carotenoids, more than 1.5 mg/ g of dry cell was obtained, being torulene and torularhodin the main carotenoids compounds quantified. The simultaneous production of both fatty acids and carotenoids are of interest for several industries such as the transport and energy sector and/or the food, pharmaceutical and medical industry. Overall, the present biorefinery approach for the simultaneous production of these valuable products makes this process attractive from the economic and environmental point of view, thus offering possibilities to further scaling it up to the industry.

Keywords: lipids, biowaste, carotenoids compounds, yeast

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Effects of temperature and bagasse addition on anaerobic co-digestion of sludge with beer wastewater

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Abstract

Currently, one of the main environmental problems is the growing generation of organic waste and the consequent increase in pollution and gas emissions[1]. This problem has led to the emergence of the concept of circular economy. The circular economy is based on conserving the value of by-products by placing them back on the market for an extended period of time with reduced waste generation [2].

The main objective of the project is to study the feasibility of anaerobic co-digestion of three wastes with different characteristics. On the one hand, sludge from wastewater treatment plants (WWTP) is used and, on the other hand, two wastes from the brewing industry, namely wastewater and bagasse. This valorization is carried out by applying the single-stage anaerobic co-digestion process in two temperature ranges: mesophilic (35ºC) and thermophilic (55ºC). In this way, the efficiency of the process can be tested according to the operating temperature and the organic matter degradation yield and biogas (CH_4) production can be determined. The effect of bagasse addition on the above process at both operating temperatures is also studied.

To determine the anaerobic biodegradability of the tested substrates, standardized tests for calculating the biochemical methane potential (BMP) in the mesophilic and thermophilic temperature ranges are used for a sludge+brewery wastewater mixture and for the sludge+brewery wastewater+bagasse mixture.

The final results indicate that the mesophilic temperature conditions, at 35°C, are more efficient in all the studies addressed. Thus, for the mixture formed by sludge and wastewater, a yield of 102.2 mL CH_4 / g VS_{added} was achieved compared to 23.0 mL CH_4 / g VS_{added} for the thermophilic process. In the case of the mixture of sludge, wastewater and bagasse, a final yield of 138.5 mL CH_4 / g VS_{added} was obtained compared to 23.0 mL CH_4 / g VS_{added} for the thermophilic process.

Keywords: Anaerobic co-digestion of waste, mesophilic single-stage anaerobic digestion, thermophilic single-stage anaerobic digestion, biochemical methane potential tests.

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IMPROVEMENT OF SEWAGE SLUDGE TREATMENT BY ANAEROBIC CO-DIGESTION WITH AGRI-FOOD WASTES (WINE VINASSE AND POULTRY MANURE)

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Abstract

The work addressed in this research project focuses on the improvement of the conventional anaerobic digestion process by applying co- and tri-digestion of organic wastes of interest in our region, in a process with phase separation. Anaerobic co-digestion allows improving the effluent quality with a greater reduction in volatile solids and an increase in methane yield, increasing the stability and reliability of the process. On the other hand, the process with phase separation of microorganisms improves the stability of the overall process by optimizing the operating conditions of each stage while obtaining separate final products, hydrogen and methane. Specifically, the applied technology consists of two bioreactors connected in series: the first one operates at thermophilic temperatures (55ºC) and acid pH (5.5) and the second one has mesophilic temperatures (35ºC) and pH around 7.5. Thus, the first reactor favors the activity of acid-forming microorganisms and the second favors methanogenic bacteria. The final products are biohydrogen in the first stage and biomethane in the second stage, in addition to an effluent suitable to be classified as class A biosolid. For the development of the work, different optimization studies of the hydraulic retention time (HRT) of the thermophilic-acidogenic digesters were approached. In this way, the optimum conditions that maximize hydrogen production were selected. The effluent generated in this reactor is used to feed the mesophilic-methanogenic digesters. Similarly, and following the same HRT reduction procedure, the optimum of operation in terms of methane yield and purification efficiency was identified.

The results obtained show an optimum in hydrogen yield of 40.41mLH2/gVS for a THR of 5 days. The maximum methane yield in the second stage was obtained at a THR of 12 days, with average values of 391mLCH4/gVS. In terms of volatile solids scrubbing efficiency, 33% was achieved in the first stage and 56% in the second stage. Overall, the TPAcD system showed a volatile solids removal of more than 93% and a removal of volatile fatty acids in the effluent of 97%. In addition, the TPAcD system achieves a level of pathogen inactivation in the effluent that allows its classification as class A biosolids.

Keywords: anaerobic codigestión, TPAD, hydrogen, methane, biofertilizer

Acknowledgements: This study has been funded by the Project Management of agri-food waste and sludge in the framework of the circular economy: energy and fertilizer production by anaerobic co-digestion in pilot plant (P18-RT-1348) of the Andalusian Plan for Research, Development and Innovation (PAIDI 2020).

Opuntia ficus-indica SEED POMACE PROCESSED BY AUTOHYDROLYSIS

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Sustainable alternatives to recover high valuable compounds from underused natural sources have recently been gained attention in different industrial fields to cope the growing market demand within a biorefinery and circular bioeconomy framework[1]. In this context, this work deals with the valorization of *Opuntia ficus-indica* seed pomace after seed oil extraction using ecofriendly treatments.

The fundamental chemical composition of the *Opuntia ficus-indica* residues was studied. Autohydrolysis treatment of the pomace samples was carried out in non-isothermal mode up to 120 °C - 220 °C, using water as extractive agent in a fixed solid liquid ratio (1:8). The liquid phases were analyzed to estimate the carbohydrate content as well as the molecular weight distributions. The total phenolic content and the antioxidant activity (i.e. TEAC, FRAP, DDPH) of the soluble extracts was also determined.

The obtained outcomes indicated that total phenolic compounds of the soluble extracts increased from 7.7 to 13.7 g GAE/ 100 g extract with rising processing temperature over the tested range. The highest antioxidant capacity of the liquid phases was identified at 200 ºC with values of 68.5 g Trolox eq/ 100 g extract and 14.5 g BHT/100 g extract. The corresponding DPPH measurements exhibited EC_{50} values varying from 4.13 (140 ºC) to 1.14 (220 ºC) mg/mL. Overall, these results pointed out that there is an optimal temperature where the hydrothermal treatment promote the recovery of antioxidant fractions with potential interest in the cosmetic field. Further studies are ongoing developed to find the most adequate application.

Keywords: Antioxidant capacity, Hydrothermal treatment, Residue, Total phenolic content

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Acknowledgements:

Authors would like to thank the University of Aveiro, LAQV-REQUIMTE (UIDB/50006/2020), FCT for the PhD grant SFRH/BD/137057/2018 granted to Ricardo M. Ferreira. M.D.T. acknowledges to the Ministry of Science, Innovation and Universities of Spain for her postdoctoral grants (RYC2018-024454-I) and to the Consellería de Cultura, Educación e Universidade da Xunta de Galicia (ED431F 2020/01). N.F.F. thanks the Xunta de Galicia for her postdoctoral grant (ED481D-2022/018).

RECOVERY AND PURIFICATION OF INTERMEDIATE PRODUCTS OF DICARBOXYLIC ACID ESTERIFICATION

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Abstract

Carboxylic acids are present in a wide range of industrial processes, including the production of nylon, biodegradable plastics, soaps and detergents, and pharmaceuticals. In particular, dicarboxylic acids are versatile compounds and important ingredients in the manufacture of various commodity and specialty chemicals. Moreover, the increased interest in sustainable chemical products enhances the role of dicarboxylic acids derived from biomass, such as succinic, itaconic or adipic, as key building blocks for the chemical industry of the future.[1] In this context, the design and optimization of separation and purification units involved in their processing is needed, which in turn also require predictive thermodynamic models.

The esterification of dicarboxylic acids with *n*-alcohols is a reversible reaction, and therefore, the product is a mixture comprising unreacted diacid, monoester and diester products. Depending on the starting carboxylic acid and the alkyl chain length of the alcohols a wide variety of chemical products can be synthesized. The aim of this work is to assess the fractionation of mixtures comprising the products of dicarboxylic acid esterification with alcohols of different alkyl chain length. In particular, we investigate the process operating window, as well as the feasibility of using different solvents, classical and condensed fluids, in order to compare yields and select the best solvent. For this purpose, a group contribution approach not only allows predicting the phase behavior of systems for which experimental information is scarce or not available, but also is a convenient approach to describe different systems comprising many similar compounds. For this purpose, we extend the GCA-EOS[2] to model the phase equilibria in mixtures containing monocarboxylic and dicarboxylic acids with various organic compounds and water.

Keywords: Dicarboxylic acids, GCA-EOS, Chemical platforms.

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MICROWAVE -ASSISTED HYDROLYSIS OF TRIACETIN TO UNDERSTAND ESTER BOND CLEAVAGE

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Abstract

Biopolyesters are widely found in nature and their research is currently at the forefront. Cutin is one these interesting biopolyesters, and today there is still not enough information about its spatial arrangement. It is the main component of tomato peel, it has a complex tridimensional structure and it is mostly composed of C16 and C18 fatty hydroxy acids cross-linked by ester bonds[1]. As a first approach to analyze the structure of these links, this work studies the cleavage of triacetin ester bonds by microwave-assisted hydrolysis. Triacetin was selected as reference compound as it is the simplest triester of glycerol. The microwave-assisted hydrolysis is expected to improve the yield of treated biomass due to the volumetric heat generation into the material, which can lead to reduced reaction times and costs compared to conventional heating[2].

Microwave-assisted hydrolysis was performed using a single-mode microwave Monowave 300 (Anton Paar) equipped with an internal (fiber-optic) and external (infrared) temperature control and a built-in camera to observe the reaction and control the stirring. Borosilicate glass vials G30 with 20 ml of capacity were used. As for the reaction operating conditions, the temperature was varied between 125°C and 230°C, the reaction time between 10 and 30 min, and the stirrer speed was set at 600 rpm. After each reaction, the system was cooled with compressed air to 55°C. A 5% v/v solution of triacetin in water was used in each experiment.

Reaction kinetics obtained from these experiments showed that the ester bond is not easy to break under mild conditions, as the samples were only partially hydrolyzed. Under these conditions, but with longer reaction times, it was possible to completely hydrolyze triacetin to glycerol without showing selectivity in the different ester bonds. The use of microwaves means instantaneous, uniform, and selective heating leading to lower energy consumption and shorter reaction times compared to conventional heating.

Keywords: triacetin, hydrolysis, ester bounds.

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MICROWAVE PRETREATMENT FOR SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF LIPID FRACTION OF SHRIMP SHELL

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Abstract

According to the Food and Agriculture Organization of the United Nations[1], by the year 2022, crustacean production represented 10% of all global production from fisheries and aquaculture. The shell of the shrimp represents approximately 47% (w/w) of the animal[2]. It is therefore a potential source of pollution in the production (aquaculture) or processing (food industry) process, when not properly disposed. Currently, shrimp shell is partially used to produce chitin and chitosan by harsh acid and alkaline treatments[3], however, they pose an environmental threat and avoid the valorization of other compounds of industrial interest, such as the liposoluble compounds, with emphasis on carotenoids[2]. The application of the supercritical fluid extraction technique with the cooking and conventional drying of shrimp shells as a pretreatment for the extraction of carotenoids has already been studied[2]. Despite the advantages shown by this pretreatment to increase the extracted carotenoids by breaking their association with macromolecules[2], the process has the disadvantage of requiring long processing time and high energy consumption. However, for sustainable biorefining processes, faster and more efficient pretreatment processes are required. The microwave technique for pretreatment of the sample to increase the extraction yield has already been proven in the literature for other raw materials with shorter processing time compared to conventional methods[4]. Within this context, this work aimed to study the efficiency of the MW pretreatment for the combined cooking and drying process in relation to the conventional method, by comparing the kinetics of the process at different energy densities. To verify the potential increase in the lipid fraction extraction, afterwards the pretreated shrimp shell (MW and conventional) will be further processed by supercritical carbon dioxide extraction.

Keywords: Microwave, Supercritical carbon dioxide, Extraction, Shrimp molt shell, Astaxanthin.

Acknowledgements: This work was supported by Spanish Ministry of Science and Innovation (project PID2020-119481RA-I00), the Regional Government of Castilla y León and FEDER-EU, program CLU-2019-04. M.M.S.R thanks the Department of Education of the Regional Government of Castilla y León and the European Social Fund Plus (ESF+) for his doctoral grant.

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HYDROLYSIS OF WATER SOLUBLE PROTEIN FROM FISH MEAL BY SUBCRITICAL WATER: EFFECT OF PRESSURIZATION GAS AGENT

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Abstract

Production of small peptides and valuable free amino acids offers new opportunities to create new valuable products in the fishmeal production chain. The use of subcritical water (subW) as hydrolytic agent is a green alternative to the traditional hydrolytic methods. In this work, the hydrolysis of the water soluble protein (WSP) fraction of the fish meal, 28 % of the total protein fraction of the fish meal, was investigated by subW by using two different pressurization agents, nitrogen as inert gas and carbon dioxide as improvement agent for protein hydrolysis in the temperature range from 140 to 180 ºC at 50 bar.

The release of amino group was followed by the ninhydrin assay and no differences between nitrogen and carbon dioxide were observed. This was attributed to the high presence of non-protein nitrogen compounds that are generated during processing of fish products that can be also detected in the ninhydrin assay as primary amines.

Since determination of amino group release was overestimated by the ninhydrin assay, free amino acids were also determined by gas chromatography, previous derivatization. Total free amino acids, evaluated as the sum of the individual free amino acid, increased by increasing temperature due to an increase of the dissociation constant of water creating a more acidic medium. The amount of free amino acids in subW hydrolysates was higher in the presence of CO_2 compared with N_2. For instance, by working at 180 ºC, 275 ± 3 and 344 ± 5 mg of free aa/g WSP were obtained in N_2 and CO_2, respectively after 288 min of treatment time. This was attributed to the carbonate formation and the associated pH reduction in the subW treatment with CO_2.

A similar qualitative amino acid profile was obtained in both gases. The major free amino acids in the hydrolysates were alanine and glycine, followed by proline. These three amino acids accounted for 81 % and 74 % of the total free amino acids in N_2 and CO_2, respectively. The highest recovery yield was achieved by alanine followed by glycine, achieving more than 80 % of alanine recovery at 180ºC in the presence of CO_2 (more than 70 % in N_2).

Keywords: Water soluble protein, fish meal, hydrolysis, subcritical water, carbon dioxide.

Acknowledgements: Agencia Estatal de Investigación [grant numbers PID2019-104950RB-I00 / AEI / 10.13039/501100011033, PID2020-116716RJ-I00/ AEI /10.13039/501100011033, TED2021-129311B-I00, PDC2022-133443-I00] and the Junta de Castilla y León (JCyL) and the European Regional Development Fund (ERDF) [grant number BU050P20].

HYDROTHERMAL TREATMENT OF BLACK LIQUOR IN SEARCH OF BIOPOLYOLS IN SUPERCRITICAL WATER

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Abstract

Black liquor, that is a residual stream of pulp & paper industry, is generally used in traditional processes for energy recovery with a low efficiency[1]. However, it can be used as an important waste resource in production of aromatic monomers and biopolyols. The polyols (compounds that contain more than two hydroxyl group in one molecule) produced from black liquor or kraft lignin can be used for lubricant and/or polyurethane production replacing the petroleum-based polyols[1]. In this study, black liquor depolymerization into biopolyols and aromatics were investigated under ultrafast depolymerization in supercritical water.

The process was conducted at 385 ± 1 °C and 260 ± 5 bar, whereas the reaction time was between 0.36 and 0.40 s. Below 0.5 s reaction time was selected to prevent char-like formation from undesirable condensation reactions (repolymerization)[2]. Three refining methods were used to decide which one is best to follow. These can be named as: freeze drying, oven drying and biopolyol fractionation method. In freeze drying and oven drying methods, the product it is directly subjected to these drying techniques after acidification. Then, a solid liquid separation was done with ethyl acetate. In fractionation method, the product was separated to 2-phases via centrifuge after acidification and then, an ethyl acetate extraction was done for both phases. GC- MS, FTIR, TGA, GPC, Elemental Analysis were conducted for further characterization analysis.

Dissolved Solids analysis was performed to understand the pH evolution of both black liquor (BL) and its depolymerized product (SHP) see if there is any difference. The results showed that dissolved solids (DS) and suspended solids (SS) amount of BL and SHP are similar. However, the pH evolution slightly differs. Refining methods showed that freeze dried and oven dried particles were not being separated well from the complex material by using ethyl acetate and water. Hence, fractionation method was performed to separate the particles. The results showed that biopolyol fraction amount was increased 30 % at pH 2. Also it was observed that the separation still continues between phases until pH 2.

Keywords: Black Liquor, Kraft Lignin, Supercritical Water Depolymerization, Fractionation, Polyol.

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Acknowledgements: This work/project was supported by the Regional Government of Castilla y León and the EU-FEDER program (CLU-2019-04).

INFLUENCE OF ACETATE AS MAIN CARBON SOURCE FOR LIPID PRODUCTION VIA OLEAGINOUS YEAST FERMENTATION

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Abstract

Microbial oils are proposed as a suitable alternative to petroleum-based chemistry in terms of environmental preservation. These oils have traditionally been studied using sugar-based feedstock, which implies high costs, substrate limitation, and high contamination risks. In this sense, low-cost carbon sources such as acetate are envisaged as promising building blocks for lipid biosynthesis to produce oil-based bioproducts such as chemicals and drop-in biofuels. Acetate can be generated from a wide variety of biogenic residues and non-food bio-based feedstock through microbial fermentation and further converted into lipids by oleaginous yeasts. These microorganisms can accumulate in the form of lipid bodies, lipids of up to 60% w/w of their biomass.

Here, we investigated the use of acetate as main carbon source for the production of triacylglycerides (TAGs) using the oleaginous yeast *Yarrowia lipolytica*. In order to enhance TAGs production a genetic strategy was used to obtain recombinant obese strains of *Y. lipolytica* capable of accumulating a high amount of lipids. Subsequently, the most suitable metabolically engineered strains developed were tested and validated. For this purpose, not only batch and fed-batch fermentation processes but also continuous fermentations with cell recycle, fed with a diluted acetate solution, were carried out at lab scale using bench scale bioreactors of 1.5 L and 7 L. Fermentation conditions were studied at laboratory level to determine the most important parameters influencing lipid accumulation (pH, DO, C/N ratio) as well as alternative carbon sources to increase the yield of lipid production.

Impact of feed rates, growth rates and conversion rates (g/g), titers (g/L), volumetric productivity (g/L/h) as well as the fatty acid composition of TAGs produced were evaluated to select the most promising combinations in terms of economics and maximization of the performance of the overall process requirements.

Overall, the results obtained show that *Y. lipolytica* is a promising biotechnological tool for lipid generation using low-cost acetate media as substrates.

Keywords*: Lipids, oleaginous yeast, acetate fermentation, biogenic residues, biofuels.*

Acknowledgements*: This work was supported by the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 884208 (BIOfuels production from Syngas FERmentation for Aviation and maritime use - BioSFerA, https://biosfera-project.eu).*

LEVULINIC ACID FROM OLIVE STONES: PRODUCTION OPTIMIZATION

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Abstract

Olive stones constitute an important byproduct generated in the olive oil extraction process and in pitted table olive industries. The production of olive stones in Spain is more than 0.5 million tons/year[1]. The main use of this byproduct is as a fuel to produce electricity or heat. As a lignocellulosic material, whose main components are hemicellulose (mainly consisting of xylose), cellulose and lignin, olive stone has been proposed as raw material for the production of 2nd generation bioethanol and other bioproducts (xylitol, furfural, levulinic acid, etc.), particularly under the biorefinery concept. In addition, the low costs of manipulation and transport of this material make it attractive for biorefineries. The aim of this work was to study the optimal conditions to produce levulinic acid in the liquids; the remaining cellulose-rich solid could be subjected to a pretreatment or enzymatic hydrolysis to obtain glucose. Crushed olive stones were treated in a reactor (10 min, with liquid to solid ratio 40 %w/v) according to a central composite experimental design, temperature (170-210 ºC) and sulfuric acid concentration (1-4 %w/v) as variables. The analysis of results with Response Surface Methodology indicates that the maximum levulinic acid concentration in liquors was obtained at 210 ºC and 4% sulfuric acid concentration, with an estimated value greater than 25 g/l.

Keywords: biorefinery, levulinic acid, olive stone, optimization

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PRETREATMENT OF ALMOND TREE PRUNING FOR XYLOSE PRODUCTION

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Abstract

Almond tree pruning is generated annually by the necessary removal of the old branches of the almond trees. Its current disposal is performed burning it, which contributes to the global warming. The valorization of this lignocellulosic biomass could have important environmental and socioeconomic advantages with the development of a new industry. The production of this product in Spain is more than 0.8 million tons/year[1]. The Almond tree pruning as a lignocellulosic material, is a renewable raw material interesting for production of 2nd generation bioethanol and other added value compounds such as, oligosaccharides, antioxidants, xylitol, etc., under a biorefinery approach. The aim of this work was to study the optimal conditions to solubilize the xylose of almond tree pruning with the maximum concentration, which could be later fermented to produce ethanol using unconventional microorganisms capable of assimilating pentoses, or xylitol, or other products; leaving a cellulose-rich solid which could be subject to a pretreatment or enzymatic hydrolysis to obtain glucose. Crushed almond tree pruning were treated in a reactor (with liquid to solid ratio 20 %w/v) according to a central composite experimental design, temperature (170-200 ºC) and phosphoric acid concentration (0.5-1.5 %w/v) as variables. The analysis of results with Response Surface Methodology indicates that the maximum xylose concentration in liquors is obtained at 185 ºC and 1.5% phosphoric acid concentration, with an estimated value higher than 25 g/l.

Keywords: almond tree pruning, biorefinery, optimization, xylose

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TOPIC 3

CO_2 CAPTURE AND UTILIZATION

CONVERTING CO_2 EMISSIONS FROM BIO-BASED INDUSTRIES INTO SUSTAINABLE CHEMICALS TO MITIGATE CLIMATE CHANGE

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Abstract

The global production of chemicals requires a very large share of fossil feedstock and has a significant climate impact. Currently, Europe is producing a significant amount of CO_2 from different biogenic sources (biogas, bioethanol fermentation, etc.). Although several measurements have been already implemented for the reduction of CO_2 emissions, it is expected to encounter significant difficulties to meet the EU's reduction target of 55% by 2030, as planned in the European Green Deal. Additional measures and policies will be deployed in EU focused on the development of negative emissions technologies, as carbon capture, utilization and storage (CCUS). To that end, the utilization of the biogenic CO_2 streams along with renewable carbon feedstock, such as biomass, is a promising solution to produce low-carbon and long-life sustainable chemicals and biodegradable products. Thus, its implementation has a strategic importance for the future of European bio-based industries.

CO2SMOS project (www.co2smos.eu) is based on circular bioeconomy, a concept that address the full value chain: from the biofeedstock suppliers and CO2-emitters to the industrial potential end-users. It proposes a solution that combines a set of innovative biotechnological, electrochemical and catalytic conversion processes to produce added-value chemicals for their application into high-performance/biodegradable polymers and renewable (bio)chemicals. CO2SMOS concept include the production of seven added-value chemicals and biomaterials: polyhydroxyalkanoates, 2,3-butanediol, long chain dicarboxylic acids, BTEX, cyclic carbonates and hydroxycarboxylic acids using biogenic CO_2 as a carbon feedstock and renewable sources such as green H_2. The proposed technologies will be tested and validated from lab (TRL 3) to pilot scale (TRL 5), including the formulation of high-performance biomaterials.

Keywords: biogenic CO_2, biomaterials, bio-based industries (BBIs), electrochemical/catalytic conversion, gas-fermentation, biorefinery, bioacetate, polyhydroxyalkanoates, butanediol,organic acids.

Acknowledgements*: This work was supported by the European Union's Horizon 2020 research and innovation programme under grant agreement No 101000790.*

EVALUATING THE POTENTIAL OF TRANSFORMING CO_2 INTO VALUE ADDED PRODUCTS: BIOMETHANE AND POLYHYDROHYBUTYRATE

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Abstract

The reduction of the anthropogenic CO_2 released in the atmosphere is one of the main reasons that humanity has been facing in the last years trying to avoid an irreversible increase in the greenhouse effect. Reducing the emission sources is crucial, but also the production of valuable products from CO_2 is fundamental to help harness this issue. In this sense, the bacterium *Cupriavidus necator* and the cyanobacterium *Synechocystis* sp. are microorganisms known for their ability to naturally accumulate polyhydroxyalkanoates (PHAs), using CO_2 as a carbon source. PHAs are biodegradable polymers increasingly being used to replace plastics obtained from chemical compounds of fossil origin. PHAs accumulation, which can even reach 80% of cell dry weight in the case of *C. necator* occurs when the microorganisms grown in a standard medium are exposed to unfavorable growth conditions like major nutrient limitation (nitrogen or phosphorus), oxygen limitation or glucose exceeding. In the framework of using waste streams for PHB accumulation, like CO_2 from biogas or anaerobic digestate, several aspects are still unexplored. First of all, the toxicity of methane (CH_4) present in biogas for these microorganisms is unknown, and secondly, only a few experiments on their growth on anaerobic digestate can be found. The current study is focused on the evaluation of *C. necator DSM 545* and *Synechocystis* strain B12 growth on two cheap and renewable carbon sources: CO_2 from biogas streams and volatile fatty acids (VFA) present in anaerobic digestate checking also the conversion of carbon into PHA.

Both *C. necator* and *Synechocystis* cultivated at 30ºC were able to grow using CO_2 from biogas as carbon source. CH_4 was found not to be toxic for any of them. In the case of *C. necator*, biogas was fed with a minimum amount of H_2 and O_2 that act as electron donor and acceptor, respectively for CO_2 uptake. In the case of *Synechocystis,* CO_2 from biogas was consumed when the culture was exposed to light (35μmol of photons m^{-2} s^{-1}) while O_2 was being produced, so, a second step is required for removing the O_2 produced and obtaining biomethane. *C. necator* was also able to grow using anaerobic digestate. Polyhydroxybutyrate was being accumulated in both microorganisms when growing under stressed conditions. So, the process studied allows the removal of a greenhouse gas and the simultaneous production of two value-added products: upgraded biomethane, which can be directly used in the grid, and PHAs, while optimising a Carbon Capture, Storage and Utilization (CCUS) technology in a circular economy approach.

Keywords: *biogas upgrading, polyhydroxybutyrate, CO_2 capture, Synechocystis sp. Cupriavidus necator.*

Acknowledgements: *Work supported by ACT ERA-NET cofound under the European Union's Horizon 2020 Research and Innovation program (Project No 327331 CooCE) and Spanish Ministry of Universities via a postdoctoral Margarita Salas (MS21-046) grant to the first author financed by Next Generation EU.*

HYDROTHERMAL REDUCTION OF CO_2 BY USING CATALYSTS AND BIOMASS RESIDUES

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Abstract

This work aims to determine the best conditions for the hydrothermal reduction of CO_2 captured in basic solutions such as $NaHCO_3$, in the presence of metal catalysts (Pd/C 5%, Pd/C 10%, granular activated carbon, powdered activated carbon, Ru/C 5%), some already evaluated in a previous work[1], and various biomass residues (sugar cane, bagasse, beet, pine needles, vermicompost, cork, softwood and cellulose) acting as reducing agents. The experiments were performed in order to evaluate the possibility to obtain high value-added products such as formic acid (hydrogen vector).

The reactions were carried out in horizontal batch reactors. The highest yields of formic acid were obtained at 300 ºC and 2 hours of reaction, by using Pd/C 5% as catalysts and the residue of softwood or cellulose as reducing agents. The reaction provided yields of formic acid of about 12% (soft wood) and 18% (cellulose).

In the reduction of capture CO_2 with biomass, the formic acid produced can come from the oxidation of biomass or from the reduction of $NaHCO_3$. The origin of formic acid was investigated using NMR analysis with $NaH^{13}CO_3$ as carbon source. It was found that when using softwood residues, palladium on carbon 5% catalyst generates the highest amount of formic acid from $NaH^{13}CO_3$ (73% of the total yield of formic acid came from the captured CO_2 and 27% remained came from the biomass).

Key words: CO_2, Biomass, Hydrothermal conditions, Formic acid

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Acknowledgements: This project has been funded by the Ministry of Science and Universities through project RTI2018-097456-B-I00 and by the Junta de Castilla y León through project by FEDER FUNDS under the BioEcoUVa Strategic Program (CLU-2019-04).

CATALYTIC HYDROTHERMAL CONVERSION OF CARBON DIOXIDE AND ORGANIC WASTE UNDER SUB-CRITICAL CONDITIONS

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Abstract

This work will report novel insights into the reaction pathways in the hydrothermal processing of CO_2 and organic waste materials – both individually and concurrently. Catalytic hydrothermal conversion is a promising method of upgrading abundant resources to value-added products, however the nature of the reaction environment and competing and parallel reaction networks make elucidation of the reaction mechanisms challenging. In order to facilitate the design of appropriate catalysts and catalytic processes we have conducted mechanistic investigations into the hydrothermal conversion of CO_2 – introduced both as gas-phase CO_2 and as solid $NaHCO_3$ – and organic wastes and materials derived therefrom, *e.g.* plastics, spent grain, pine needles, glucose.[1-3,] We have further, under batch conditions, investigated the co-conversion of CO_2 and glucose to formate.

Considering the latter example, extensive analysis of aqueous, bio-oil and gas products, spiking reactions and studies using labelled reagents undertaken between 225–300°C revealed that formate formation occurred through glucose degradation *via* a pyruvaldehyde intermediate. Based on this, reactions employing Ni-based catalysts were shown to have remarkable activity in this reaction as compared to other metals. For example, formate concentration in the end product doubled to 1.240 $g\ l^{-1}$ *cf.* the non-catalysed reaction with both $NaHCO_3$ and glucose contributing to formate yield. Based on studies on the stand-alone conversion of CO_2, acetaldehyde was proposed to be a key intermediate in the formation of the ethanol by-product. Considering polymer conversion, contrasting decomposition mechanisms were observed between polypropene and nylon-6, with the latter converting *via* a radical mechanism to 2,4-dimethyl-1-heptene and the latter *via* an oxidative degradation process

These results provide the basis for the development of hydrothermal processing as a means for the upgrading, conversion and recycling of a wide range of waste or low-value materials.

Keywords: CO_2 utilisation, Biomass, Liquefaction, Polymers, Sub-critical water

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SUSTAINABLE FORMULATIONS FROM CO_2 AND ORANGE PEEL WASTE

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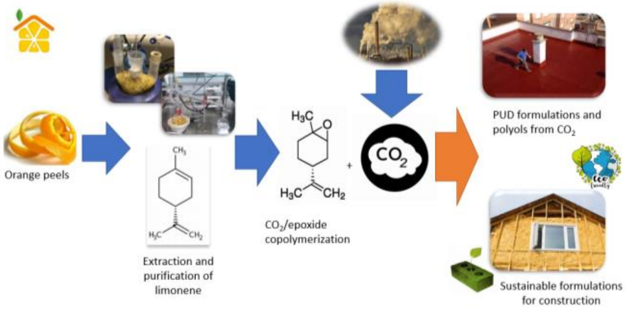
Abstract

Polycarbonates (PCs) can be divided into aromatic and aliphatic based in their chemical structure. However, the narrow mechanical and thermal properties of aliphatic PCs limit its applications. This scenario requires new monomers derived from renewable and non-toxic resources -or even from recycling wastes- as starting materials for new sustainable polymers and formulations[1].

Build Limonene project develops a new solution by extraction of sustainable limonene from different variations of orange peels employed as cyclic monoterpenes to be transformed into limonene oxide by improved epoxidation processes. Moreover, in this project a functional and sustainable bio-based and non-food-based polymer is obtained by copolymerization of limonene oxide with carbon dioxide. Poly(limonene carbonate) is stablished as a potential candidate for the replacement of toxic state-of-the-art polycarbonates. For this reaction commercial catalyst will be tested to obtain poly(limonene)carbonate with different degrees of molecular weight to be applied in the formulation of new polyurethane sustainable dispersions (PUD) for construction.



Keywords: limonene, CO_2 utilization, poly(limonene)carbonate, revalorization, sustainable formulations.

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Acknowledgements:

This work was performed under collaborative projects between Zuvamesa, ITQ-CSIC-UPV, Laurentia, AIMPLAS and Lamberti Iberia. The consortium thanks Agència Valenciana d’Innovació (AVI) the founding from the project.

CYCLIC CARBONATES PRODUCTION FROM CO_2 AND EPOXIDES USING SUSTAINABLE SOLVENTS: QUATERNARY AMMONIUM BASED-IONIC LIQUIDS VERSUS -DEEP EUTECTIC MIXTURES

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The production of cyclic carbonates from CO_2 and epoxides is one of the most investigated strategies for the chemical utilization of CO_2 as a renewable carbon source. In terms of green chemistry, the strategy is highly attractive since the CO_2 molecule is totally incorporated in the final product and though no waste is produced. Furthermore, CO_2 has the advantage of being abundant, economical, non-flammable, and non-toxic[1]. On the other hand, cyclic carbonates are valuable synthetic products with diverse applications such as polar aprotic solvents, electrolytes for lithium batteries, fuel additives, and intermediates in the manufacture of chemicals[2]. Recent developments comprise the replacement of metal based-catalysts by organic counterparts which can bring advantages in terms of process costs and greenness. Quaternary ammonium based-ionic liquids have been successfully explored as both catalysts and solvents for the cycloaddition reaction between CO_2 and epoxides[3,4]. A strategy to increase their catalytic activity is the addition of small quantities of hydrogen bond donors, mainly alcohols. The mixture of these two components, may or not form a deep eutectic mixture, depending on the molar ratios used. In this work different quaternary ammonium-based deep eutectic mixtures were prepared and tested as catalysts and solvents for the cycloaddition reaction between CO_2 and epoxides. The operating conditions (reaction temperature, CO_2 pressure, and salt:alcohol molar ratio) on cyclic carbonate formation were studied. Finally, the reusability of the catalytic eutectic phase was tested using supercritical CO_2 technology as a second step for product separation from the reaction mixture. Results obtained will be discussed and compared with experiments using a quaternary ammonium based-ionic liquid as the catalytic phase.

Keywords: CO_2 utilization; Epoxides; Cycloaddition; Cyclic carbonates; Deep eutectic solvents;

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Acknowledgments: This work was supported by FCT/MCTES through projects PTDC/EQU-EPQ/2195/2021, MIT-EXPL/CS/0052/2021, UIDB/50006/2020, UIDP/50006/2020 and LA/P/0008/2020 of the LAQV. The NMR spectrometers are part of The National NMR Facility, supported by FCT (ROTEIRO/0031/2013 - PINFRA/22161/2016) (co-financed by FEDER through COMPETE 2020, POCI, and PORL and FCT through PIDDAC).

EVALUATION OF THE POTENTIAL OF PHOSPHONIUM-BASED IONIC LIQUIDS FOR CO_2 ABSORPTION THROUGH SOFT-SAFT

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Abstract

Even though amines (i.e., MEA and MDEA) are commonly used for CO_2 absorption from flue gas streams, it is well known that they evaporate and degrade during process operation, with environmental and economic consequences. In the search for alternative solvents, the capture of CO_2 with Ionic Liquids (ILs) is a technology that has gained a lot of interest mainly due to their low vapor pressure and the possibility to "design" them by combining different cations and anions for each particular case, considering the flue stream composition and specific conditions. Particularly, some phosphonium cation/anion combinations have been studied in literature with promising results.Nonetheless, restricted and limited laboratory data are available and a complete characterization of these compounds is still required to select the most appropriate CO_2 absorber.

In this work, the potential of phosphonium based ILs as CO_2 absorbers at different operating conditions for industrial application is assessed through the use of an accurate statistical mechanics-based equation of state (EoS). Particularly, the soft-Statistical Association Fluid Theory (soft-SAFT) is found to provide a suitable description of ILs and their behavior in mixtures, and will be applied here, in combination with quantum-chemical approaches, such as Turbomole-COSMO, to obtain the charge distribution profiles and describe the key interactions in these compounds. The work departs from the trihexyltetradecylphosphonium cation $[P_{66614}]^+$, which is combined with different anions. The resulting ILs are characterized by a complete description of their pressure-temperature-density diagrams, and derivative properties. Transport properties, such as the viscosity, are also modeled using the Free-Volume theory coupled to soft-SAFT EoS. Then, CO_2 absorption isotherms are described and compared to experimental data when available. The CO_2 absorption capacity of the different ILs, considering both diluted and concentrated mixtures in CO_2, is assessed through the calculation of Henry's law constants and the solvation enthalpies and entropies at different conditions, proposing a preliminary list of potential compounds for different types of flue gases.

Keywords: ionic liquids, phosphonium, soft-SAFT, CO_2 absorption.

Acknowledgements: S. B. Rodriguez Reartes acknowledges the financial support of the "María Zambrano" grant awarded by Universitat Rovira i Virgili for the requalification of the Spanish university system for 2021-2023). This research is supported by project STOP-F-Gas (PID2019-108014RB-C21) funded by the Spanish Ministry of Science and Innovation.

UNDERSTANDING THE POTENTIAL OF *DES* FOR *GHG* CAPTURE AND SEPARATION: FROM THERMODYNAMICS TO PROCESS DESIGN

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Abstract

The potential of Deep Eutectic Solvents (DES) for industrial applications has been a matter of research in recent years [1]. Based on the combination of a Hydrogen Bonding Acceptor (HBA) compound, which is normally a halide salt, and a Hydrogen Bonding Donor (HBD), which typically is a neutral complexing agent, the hydrogen-bonding effect between both compounds causes a substantial decrease of the melting point compared to that of the individual components, becoming a eutectic mixture. This fact widens the range of the liquid state, while keeping a negligible volatility. In addition, DES are as tunable as ILs, as the HBA:HBD combination can be easily modified, changing the hydrogen-bonding dominance and the thermophysical properties. However, those mechanisms are still being investigated so as to better describe their thermophysical behaviour. In this regard, the use of multiscale simulation provides a useful path to obtain additional information to guide the experimental work into the right direction.

In this contribution, a practical methodology to thermophysically characterize DESs for greenhouse gas capture applications is described. For this purpose, the soft-SAFT equation of state has been used in combination with other modelling tools, such as COSMO-RS. Based either on molecular simulation data or charge analysis distribution, a rational choice of a molecular model and the number of dominating hydrogen bonds is proposed. An individual component approach, where each entity forming the DES is treated as an independent compound, is followed to describe density, heat capacity and viscosity of DESs, as well as the impact of water addition. Next, the solubility of CO_2 and fluorinated refrigerants in different DESs is provided, highlighting the impact of different variables (pressure, temperature) and structural characteristics of the DES (type of HBA, HBD, number of fluorine atoms, etc.) in the results [2,3,4]. Finally, variables, such as the selectivity to carry out a gas separation process, are predicted so as to provide a preliminary capture and separation simulation unit with ASPEN.

Keywords: deep eutectic solvents, choline chloride, soft-SAFT, greenhouse gas capture.

Acknowledgements: S. B. Rodriguez Reartes acknowledges the financial support of the "María Zambrano" grant for the requalification of the Spanish university system for 2021-2023). This research is supported by project PID2019-108014RB-C21 funded by the Spanish Ministry of Science and Innovation.

DEFOSSILIZATION OF THE PETROCHEMICAL INDUSTRY VIA RENEWABLE CARBON TO STAY WITHIN PLANETARY BOUNDARIES

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Abstract

The current petrochemical industry mainly relies on fossil resources for carbon feedstock and energy needs, making it one of the top carbon-intensive and hard-to-abate industries. Producing chemicals using renewable carbon from biomass or captured CO_2 and powering the processes with renewable energy is gaining momentum to make this industry more sustainable. However, although this alternative production is very appealing, the worldwide environmental implications of the transition beyond climate change remain unclear and unexplored.

This work fills this knowledge gap by thoroughly assessing the environmental footprints of entirely restructuring the chemical industry based on renewable carbon. The footprints are analyzed through the Planetary Boundaries (PBs) lens. This framework defines global thresholds in critical biophysical processes that should never be transgressed to operate safely on Earth. The methodology consists of a tailored Life Cycle Absolute Sustainability Assessment methodology that links chemical production's impacts with nine PBs, including climate change, freshwater use, biogeochemical flows, or biosphere integrity, among others. The footprints of the fossil-based petrochemical industry are compared with 50 alternative scenarios based on renewable carbon considering the main building blocks of the industry (methanol, ethylene, propylene, benzene, toluene, and xylenes) from which other chemicals can be derived. The results show that the current petrochemical production requires a quarter of an entire planetary budget for climate change to operate. Regardless of the scenario, using renewable carbon would alleviate this pressure, yet scenarios that decrease the carbon footprint the most could pose threats to biodiversity. Integrating routes based on biomass resources and captured CO_2 emerges as an appealing strategy to defossilize chemicals; however, resource availability and higher costs could hamper its large-scale deployment.

Keywords: chemical industry; renewable carbon; carbon capture and utilization; absolute life cycle sustainability assessment; Planetary boundaries.

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Acknowledgments: A.G-M. acknowledges the project TED2021-132614A-I00 funded by MCIN/AEI/10.13039/501100011033 by the European Union NextGenerationEU/PRTR

ASSESSMENT OF SELECTED CATALYSTS AND REDUCING METALS FOR THE SIMULTANEOUS CONVERSION OF CAPTURED CO_2 AND HYDROGEN GENERATION

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Abstract

Current changes in worldwide economic scenario are challenging the achievement of the past-decades objectives of cutting the CO_2 emissions and reducing oil and natural gas dependency. The increase of demand of fossil fuels to 2040 can increase to 30% [1], and the necessity of mitigating the subsequent CO_2 emissions is still on the table. In this context, one successful carbon capture and storage (CCS) technology is based on the absorption of CO_2 with aqueous solutions of ammonia, yielding equilibria of ammonia bicarbonate, carbonate and carbamate [2]. Hydrothermal catalytic reduction of captured CO_2 using reducing metals (as source of hydrogen) is one of the methods to obtain formic acid that remains on the research focus. In our most recent work, the endeavors laid the implementation of milder reactions conditions in batch reactor for ammonia-based CO_2 absorption derivatives, using only aluminum as reducing agent, and commercial Pd catalyst [3]. However, thorough the present work we wanted to extend the aforementioned study by assessing more materials, selecting Pd, Pt and Ru as catalysts, and aluminum and zinc as reducing metals. This study allowed concluding that aluminum was the most efficient metal for formate production, in combination with Pd-catalyst, given its lower affectation to the textural features of the catalyst in the solid mixing, with a formate yield as high as 22%; while, in terms of hydrogen generation, zinc in combination with Pt-catalyst presents the best performance with the highest H_2-yield of 20%.

Keywords: Catalysts screening, hydrogen evolution, formic acid production, metal-water splitting

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Acknowledgements: This project has been funded by the Ministry of Science and Universities through project RTI2018-097456-B-I00 and by the Junta de Castilla y León through project by FEDER FUNDS under the BioEcoUVa Strategic Program (CLU-2019-04).

PROTIC IONIC LIQUIDS AS ELECTROLYTE FOR ELECTROCHEMICAL CO_2 REDUCTION

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Ionic liquids have been considered a promising material under investigation for integration of CO_2 capture and electrochemical reduction, due to their recognized sustainability and tunable properties. During previous works, the development of an electrochemical process to produce syngas ($CO+H_2$) using electrolytes based on 1-ethyl-3-methyl-imidazolium trifluoromethanosulfate [EMIM][OTf] was reported[1,2]. A more recent work reported the effect of replacing the 1-ethyl-3-methyl-imidazolium cation [EMIM] by 1-ethyl-3-picolinium [C_2-3-pic] and 1-ethyl-4-picolinium [C_2-4-pic] cations as electrolyte for electrochemical reduction of CO_2 at pressures higher than atmospheric[3]. The objective of this work is to study the influence of protic ionic liquids-based electrolytes in electrochemical CO_2 reduction. In this context, protic ionic liquids prepared by direct protonation of different imidazolium compounds using suitable organic acids have been investigated. All electrolytes are characterized by cyclic voltammetry and electrochemical impedance spectroscopy to evaluate their electrochemistry behavior for CO_2 electroreduction processes. Produtivities of gaseous products resulting from the co-electrolysis of CO_2 and water together with their faradaic efficiencies have been also determined.

Keywords: Electrochemical, CO_2, Ionic Liquids.

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HYDROTHERMAL CONVERSION OF CO_2 CAPTURED IN SEAWATER INTO FORMATE USING METAL-SOURCED HYDROGEN AT MILD REACTION CONDITIONS

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Abstract

Mineral carbonation is a significant method for CO_2 sequestration and usage to solve climate change-related environmental challenges. Although several studies have investigated mineral carbonation using various solvents to increase the technical feasibility, seawater appears to be a promising contender as a carbonation solvent. Seawater makes up more than 97% of the world's water, being a renewable resource that is less expensive than other possible chemical solvents. Furthermore, seawater has an alkaline pH (8.0-8.2) and a high concentration of Ca^{2+}, Mg^{2+} and Na^{+1} ions, which can react with CO_2 via mineral carbonation to generate carbonated product[1].

This work presents a novel proposal consisting of on the transformation of this CO_2, found in seawater in the form of sodium bicarbonate, into formic acid by using metal reductants. The hydrothermal reduction using metals as reductant has shown to be a promising technology to convert concentrated sodium bicarbonate aqueous solutions in formic acid[2]. In this work, a series of batch experiments with real or synthetic seawater, at 0.2 g/L of bicarbonate, have been performed under hydrothermal conditions in order to study the influence of temperature, the molar ratio of metal and catalyst effects.

Keywords: Seawater, CO_2, Metals, Catalyst, Formic Acid.

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Acknowledgements: This project has been funded by the Ministry of Science and Universities through project RTI2018-097456-B-I00 and by the Junta de Castilla y León through project by FEDER FUNDS under the BioEcoUVa Strategic Program (CLU-2019-04).

ANAEROBIC BIOPROCESSES TOWARDS THE CONVERSION OF CARBON DIOXIDE INTO BIO-BASED PRODUCTS

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Greenhouse gases increased in the last 60 years due to anthropic activities. Carbon dioxide is present in major quantities at around 75%. [1] Thus arises the need to reduce GHGs; in fact, one of the objectives of the EU 2020 package on climate and energy is to reduce greenhouse gas emissions by 20% compared to 1990 levels.[2] In addition to mitigating carbon dioxide (CO_2) emissions into the atmosphere through more sustainable production processes, the trend is to further reduce them through systems that capture it; in this context, the driving force is the EU Emissions Trading System (ETS), which sets a price for carbon and reduces the upper limit applicable to emissions from certain economic sectors each year.[3] Therefore, climate neutrality is also achievable through the development of new carbon negative bioprocesses, which will allow the permanent removal of carbon dioxide (CO_2) and climate-altering gases from the ecosystem to balance the residual emissions from industrial production activities. There are various CO_2 capture and storage techniques (CCS) mainly based on chemical-physical methods, in particular chemical methods have the purpose of capturing carbon dioxide which can subsequently be stored in geological or marine cavities or can be converted or reused. However, biological methods of CO_2 sequestration using microorganisms as catalysts aim to utilize and then directly convert CO_2 into new bio-products (CCU).[4] The main research objective was to study the effect of applied potential on microbial growth by using a one- or two-chamber H-Type microbial electrosynthesis cell (MES) to fix dissolved CO_2 in photoautotrophic conditions using inorganic carbon as only carbon source in a synthetic medium with FeII in solution or FeIII coated to the cathode, In the first case FeII was used as an electron donor, in the second case FeIII was used as a redox mediator to grow purple phototropic bacteria. Two potentials were used for the experiments +400mV and -600mV. The recorded current consumption was lower (from 7 to 14C) if the iron was in solution in a single cell, both in biotic and abiotic conditions, it completely covered the electrode making it difficult for microorganisms to spread the current, led to a biomass growth of 15% or from 380mg/L to 440 mg/L. Using the electrode-coated iron in a single cell the current consumption in this case was the highest found at about 900 to 1200C, also the lowest microbial growth was obtained at 430mg/L to 450mg/L (5%). Using the FeIII coated electrode in a H-Type cell, the current consumption found was approximately 600C, furthermore the maximum microbial growth was obtained from 300mg/L to 500mg/L (86%). In conclusion, the cathode coated with FeIII in combination with the H-Type cell led to higher current utilization efficiency for the biomass growth.

Keywords: carbon dioxide; anaerobic process, circular economy, bio-based product

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DRY REFORMING OF METHANE WITH CO_2 FOR SYNGAS PRODUCTION OVER MgO-MODIFIED Co/NATURAL PERLITE CATALYSTS

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Abstract

The Dry reforming of methane (DRM) is a widely studied reaction because two greenhouse gases (CO_2 and methane) are used to produce synthesis gas (H_2 + CO) or high purity H_2 desirable, for example, for the fuel cell. Pure hydrogen can be recovered by separating the two gases produced, ($CO+H_2$) or the syngas can be used for the synthesis of hydrocarbons via the Fischer Tropsch process. Being both reagents produced from renewable resources such as biogas, fossil resources can be avoided. In this work, a Cobalt based catalyst supported on expanded natural perlite was synthesized using impregnation method, then, a portion of the prepared sample was modified by different amount of MgO (Co/Mg atomic ratio =1, 2 et 3). The prepared catalysts were characterized by XRD, SEM, N_2 adsorption/desorption technique and TPR analysis. Tests of methane dry reforming with CO_2 were carried out over pre-reduced catalysts flowing the reaction mixture at 700 °C during 120 min. Spent catalysts were characterized by TGA/DTA in order to evaluate the amount of coke formed during the reaction. The catalytic results show that the performances of Mg-promoted samples, especially for Co/Mg = 1, are notably improved in terms of both, CH_4 and CO_2, conversion compared to the corresponding unpromoted one. The CH_4 conversion values varied between 93% for Mg-promoted catalysts with Co/Mg ratio of 2 and 3 and 97% for the sample with Co/Mg = 1. A similar trend was observed for CO_2 conversion. Enhanced stability towards coke poisoning was observed for the MgO promoted catalysts with respect to the Co/perlite sample.

Keywords: Dry reforming, Methane, syngas, Co, perlite, MgO

Acknowledgements: The Projects "Capitale Naturale e Risorse per il Futuro dell'Italia (FOE 2020), CUP B85F21002120005, Programma di Ricerca e Innovazione dal titolo "NEST - Network 4 Energy Sustainable Transition", (Partenariato Esteso – PE0000021, CUP B53C22004060006) and (PNRR) - missione 2 "rivoluzione verde e transizione ecologica" – componente 2 "energia rinnovabile, idrogeno, rete e mobilità sostenibile" – investimento 3.5 "ricerca e sviluppo sull'idrogeno" – AdC ENEA-CNR (CUP B93C22000630006) are kindly acknowledged for financial support. The COST ACTION CA 18224 GREENERING "Green Chemical Engineering Network towards upscaling Sustainable Processes" is acknowledged for the opportunity to present such work.

Biobased Aerogels as Nanoparticle Support for CO_2 Conversion Reactions

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Abstract

CO_2 methanation can be achieved at relatively high selectivities and low temperatures using metal nanoparticles (NP) immobilized in ionic liquids (IL). The reaction mixture forms a biphasic high-pressure system composed by an excess $CO_2 + H_2$ gas phase and a liquid catalytic phase (NP/IL). The unique IL properties facilitate reactants dissolution, stabilization of highly active ruthenium-NPs and easy product recovery. Reaction optimization achieved a best result of 84% yield at 150ºC .[1-2] However reutilization studies show a drop in reaction yield with time, which is related to water accumulation and NP aggregation. Therefore, we have recently studied a series of new approaches to make this reaction more efficient and sustainable including the use of polymeric porous compounds as support for the Ru-NP/IL system. Aerogels are porous structures that have interesting properties such as large surface areas, high porosity and low bulk density, which make them very attractive for catalytic applications.[3] Their porous structure can be tuned in order to allow high dispersion of the active sites and facilitate reactants/products diffusion. In this work spheric alginate aerogel were impregnated and tested as catalytic supports for the CO_2 conversion into CH_4. The effect of the ILs applied, the composition of impregnation solution, time of immersion and the size of aerogel impregnated were some of the conditions explored to optimize our results.

Keywords: Aerogel, Ionic Liquid, Metal Nanoparticles, Methanation

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BIOTECHNOLOGICAL PLATFORM TO PRODUCE CO_2-DERIVED INTERMEDIATES AND MONOMERS

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Abstract

Europe generates a significant amount of CO_2 from different green sources e.g.: biogas, bioethanol, solid biomass combustion, and other fermentation processes. It is estimated that more than 506.7 MT/year of biogenic CO_2 are currently produced. This CO_2 from bio-based processes has been recycled/converted into sustainable chemicals. To do this, a set of six innovative cost-competitive fermentations have been studied with the aim of producing biopolymers and renewable chemicals: transformation of CO_2 (+ H_2) into acetate (1); transformation of CO_2 (bio-syngas) into 2,3-butanediol (2); and transformation of bio-acetate into mcl-PHA (3), PHB (4), 2,3-butanediol (5), and long-chain dicarboxylic acids (6). The proposed transformations will be optimized and validated from lab (TRL 3) to pilot scale (TRL 5). The bacteria and yeasts used in the fermentations are genetically modified in order to improve the productivity of the desired compounds. The fermentation variables are optimized, including high pressure to improve gas solubility and continuous operation with recirculation of microorganisms. The downstream purification processes of each biomolecule will also be optimized. The bioacetate obtained from CO_2 will be controlled to ensure that it meets the requirements to serve as substrate in the other fermentations. The CO_2-based monomers obtained stand out for their application in the biodegradable plastics industry.

Keywords: CO_2, biotechnology, polyhydroxyalkanoates, 2,3-butanediol, long-chain dicarboxylic acids

Acknowledgements: This work was supported by the European Union's Horizon 2020 research and innovation programme under grant agreement No 101000790.

NITROSAMINE FORMATION DURING CO_2 AND NO_x ABSORPTION

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Abstract

CO_2 is a greenhouse gas emitted mainly by human activities and is the most significant contributor to global warming. The combustion of fossil fuels for energy production generates 73.2% of the total CO_2[1]. Considering the negative impacts caused by CO_2 its emissions must be lowered when the gases are vented into the atmosphere. For the removal of CO_2, amine scrubbing is the most popular process, however, in the combustion stream are also NOx which are the precursor for the formation of nitrosamines[2,3]. Nitrosamines are hazardous byproducts that are strong carcinogens and produce cancer in tissues and organs[4]. To determine the nitrosamine yield formation from a stream containing CO_2 and NO_x under absorption parameters (40 – 80°C and 1-5 barg) parameters such as amine type, temperature, and pressure are evaluated. It is expected to have as a result that secondary amines have the highest yield of nitrosamine formation as they are formed from a secondary amine and a nitroso group, and their formation is not influenced by the temperature and pressure of absorption. Tertiary amines have the lowest nitrosamine formation rate as they do not form carbamates, which act as a catalyst for the formation of nitrosamines.

Keywords: greenhouse gas capture, CO_2, NOx, Amine scrubbing, nitrosamines

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Acknowledgements: This work/project was supported by the Regional Government of Castilla y León and the EU-FEDER program (CLU-2019-04 and CL-EI-2021-06).

TOPIC 4

GREEN REACTION AND CATALYSIS

CO_2-H_2O BASED GREEN ENGINEERING FOR BIOMASS VALORIZATION

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Abstract

The "Glasgow Climate Pact" agreed at the UN Climate Change Conference of the Parties (COP26) commits to accelerate global action this decade, by limiting global warming to 1.5°C over pre-industrial levels. To help achieve this ambitious goal, CO_2, the main contributor to the climate change, can be turned from a liability to an asset by mixing it with H_2O to produce an acidic condition suitable for many reactions. This opens new opportunities and challenges for researchers, process engineers and technologists. In this regard, this talk will showcase our recent works on the CO_2-H_2O synergy under elevated temperatures and pressures as applied to many reactions involving biomass valorization and natural products of pharmaceutical interests. One good example is the removal of sugar moieties (rhamnose, glucose and rutinose) from hesperidin (HPD), a citrus bioflavonoid, to obtain a more bioactive and bioavailable aglycone – hesperetin (HPT). The concept of reactive distillation, whereby HPT is simultaneously separated from the products will also be explained. The obtained sugar, like glucose, can be further converted into more useful chemicals such as 5-HMF taking advantage of the suitable balance of Bronsted base and acidities of the CO_2-H_2O mixture. The incorporation of the system in a microreactor for millisecond reactions, as well as the elucidation of the mechanism using Raman spectroscopy and quantum calculations will also be introduced. Furthermore, the positive effect of adding CO_2 to deamination to obtained high quality bio-oil by hydrothermal liquefaction of biomass will also be reported.

Keywords:

supercritical fluid, hydrothermal, biomass, reactive separation, microreactor, climate change, biofuels, natural products

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Acknowledgements:

The authors gratefully acknowledge the financial support from JSPS Grant-in-Aid for Scientific Research (Grant Numbers 17KK0118 and 18K05202), the Japan Science and Technology Agency via the e-ASIA joint research program in the field of Bioenergy (SICORP Grant Number JPMJSC18E2) and JSPS Bilateral Joint Research Program with UTP (Malaysia) and Valladolid University (Spain)

MICROFLUIDIC APPROACHES FOR THE SUSTAINABLE AND GREEN SYNTHESIS

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Abstract

Lately, the application of microfluidic devices has been a very promising strategy in organic chemistry, and one of the research fields in which microfluidics have shown great potential is visible light photochemistry. There are several advantages when conducting transformations in flow compared to the batch reactions, in particular: a more predictable reaction scale-up, decreased safety hazards, improved reproducibility and yields and thus lowered waste generation, shorter residence times leading to decreased energy consumption, higher reaction selectivity and product purity and lower catalyst loading leading to overall more sustainable and greener processes. In addition, for photochemical transformations, the high surface-area-to-volume ratios typical of flow reactors allow for improved light efficiency. Even though significant progress has been achieved, greener alternatives to many common industrial processes still remain elusive, especially in the fine chemicals industry. To render processes greener and cheaper, **catalysis** is a key tool to reduce energy consumption and to develop more atom-economical transformations. We have applied microfluidic chemistry and merger of photoredox and organocatalysis in the synthesis of the functionalized Tetrahydroisoquinolines, valuable fine chemicals with important biological and pharmaceutical effects. Use of microreactors allowed shorter reaction times, superb yields and decreased waste generation compared to standard batch conditions. All the tested microreactors were custom made and optimized to perform synthesis of desired materials in the most efficient manner.

Keywords: Organocatalysis, Microfluidic chemistry, Sustainable synthesis, Green synthesis

Acknowledgements: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-9/2021-14/200026) and the Proof of Concept project of Innovation Fund of Republic of Serbia No 5183.

GREEN METHOD TO FUNCTIONALIZE MELAMINE FOAMS WITH SILVER NANOPARTICLES IN A SINGLE STEP

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Abstract

Silver nanoparticles (AgNPs) display unique physicochemical properties, including high stability, biocompatibility, and catalytic and bactericide activity[1]. The emerging polymer functionalization approach has result into the fabrication of new active materials with a broad application in multiple fields, such as water cleaning, medicine, and food packaging. However, the activity performance of the silver composites is highly dependent on the exposure, concentration, morphology, and distribution of the metallic nanoparticles[1]. Therefore, the employment of suitable synthesis and functionalization strategies is critical for developing powerful materials. Most of the composite fabrication methods comprise many time-consuming, complex steps, and toxic reagents, contrary to the current environmental trend, which promotes the use of environmental-friendly chemicals[1]. This work presents a green method to phase out the 100 % of the polluting and organic solvent (tetrahydrofuran, THF) previously employed to obtain Ag-doped melamine foams in a single step[2]. The effect of the solvent ratio (water:THF), the reaction conditions, and the time of the reaction were evaluated to obtain a high degree of functionalization and an uniform distribution of silver nanoparticles. The functionalization yields in foams fabricated with water overcame the Ag content in samples fabricated with THF by increasing the temperature of the reaction solution, from room to mild conditions (40 ºC and 60 ºC). Among them, 40 ºC exhibited the best features, displaying anchored AgNPs with an ultrafine size (< 10 nm) and spherical morphology with a proper dispersion throughout the porous structure.

Keywords: Polymer foams, Green synthesis, Silver reduction, Reaction conditions.

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CATALYST-FREE ACETYLATION OF STARCH USING A GREEN DEEP EUTECTIC SOLVENT AS REACTION PROMOTER

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Abstract

Starch is widely regarded as a promising polymer for bio-based materials due to its polymeric and green nature, as well as its abundance. Starch modification and functionalization for the improvement of its physical properties (e.g., mechanical properties and water resistivity) has become a focus of research in the past years. Nevertheless, if starch derivatives are to be widely adopted as a sustainable alternative, their production needs to be sustainable, both environmentally and financially. Herein, a sustainable, catalyst-free acetylation reaction is presented, using choline chloride/urea deep eutectic solvent (DES) as reaction promoter. Substitution degrees (DS) of the materials were calculated via ^{1}H NMR and further confirmed by ^{13}C solid state NMR. Thermal properties were analyzed using TGA and DSC. The system proved to be highly efficient, achieving DS=2.2 only after one hour of reaction. However, under certain conditions, reactions between solvent and reagents took place, resulting in either acetyl urea or starch amides. The reaction conditions were analyzed by response surface methodology and optimized to reduce reaction times, obtaining DS=2,87 only after 30 min, and substrate loads of 20 wt%. This reaction was further optimized for continuous reactive extrusion, which further enhanced the efficiency and sustainability of the process.

Keywords: Starch acetylation, bio-based materials, deep eutectic solvents

Acknowledgements: The authors acknowledge Independent Research Fund Denmark - Danmarks Frie Forskningsfond (project number 1032-00491B) for funding this research.

BIOCATALYSIS IN DEEP EUTECTIC SOLVENTS: DESIGNING SAFE AND SUSTAINABLE PROCESSES

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Abstract

During the last decade, deep eutectic solvents (DESs) have emerged as a promising alternative to traditional organic solvents, from both environmental and technological perspectives. DESs' properties are a function of their composition, which makes them highly versatile and easily tunable solvents, meaning that, by changing the forming compounds (raw materials for their preparations) and the molar ratio of the latter, it is possible to design an optimal DES for a certain application[1]. The synergistic use of deep eutectic solvents (DES) and biocatalyst logically fits the efficient and sustainable production of various commercially interesting products. Namely, biocatalysis ensures that otherwise difficult transformations are catalysed in a highly regio-, chemo- and enantioselective manner at mild and economic conditions, where DES can serve as a strong green support for modulating/guiding the reaction route to obtain the desired product. In (bio)catalytic processes, a DES can serve as solvent/co-solvent, as an extractive reagent for an enzymatic product, and as a pretreatment solvent of enzymatic biomass[2].

In the following, the design and implementation of DESs as solvents or co-solvents in enzyme-catalysed reactions, using either isolated enzymes or whole cells as biocatalysts, is illustrated by the following examples: (i) *S. cerevisiae*-catalysed mediated asymmetric reduction of ethyl-3-oxobutanoate and acetophenones; (ii) plant cell-mediated asymmetric reduction of 1-(3,4-dimethylphenyl)ethanone and kinetic resolution (hydrolysis) of (±)-1-phenylethyl acetate; (iii) lipase-catalysed synthesis of butyl-acetate (esterification); and (iv) laccase-mediated oxidation of dehydroepiandrosterone (oxidation). In the case of plant-catalysed kinetic resolution (hydrolysis) of (±)-1-phenylethyl acetate, the chemical reaction is discussed in the context of integrated biorefinery approach (valorisation of orange peel waste). The presented results imply that DES can be considered as excellent medium for obtaining high yields and, more importantly, high enantiomeric purity. The ability of DES to stabilize isolated enzymes (e.g. lipases and dehydrogenases) is stressed and discussed as well.

Keywords: deep eutectic solvents, biocatalysis, enzyme selectivity and stability

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GREEN H_2 FROM WATER SPLITTING: THE CRITICAL ROLE OF THE CHOICE OF ELECTRODES

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Electrochemical water splitting is a promising approach for the hydrogen production, with zero emissions (green H_2) when using renewable electricity (from sources like the sun and the wind). This allows direct water decomposition in its elements; namely, the oxygen evolution at the anode, whereas the hydrogen evolution reaction takes place at the cathode. However, the widespread commercialization of this technology has been hindered by the fact that overall, it is a strongly uphill process with a large overpotential (theoretical minimum value of 1.23 V) and sluggish kinetics. Therefore, the electrodes choice, as well as the development of efficient, abundant, and economical catalysts, have been subject to intense innovation[1].

Herein, we present the framework and main results of the current research efforts we are developing in order to characterize alternative carbon-based working electrodes/substrates. Given that their different structure and properties, play a critical role in condition the catalyst performance and influence the reactions rates. Thus, the ultimate goal is to overcome the large water-splitting overpotentials, together with development of substitute critical raw materials, and make the whole process more energy-efficient and sustainable.

Keywords: Carbonaceous electrodes, Electrochemical impact. Green hydrogen (H_2), Water splitting.

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Acknowledgements:

This work was supported by funding from the European Regional Development Fund (FEDER) through Program NORTE 2020, within the Project NORTE-01-0145-FEDER-000076 "Development of Sustainable Materials for Water Splitting: an integrated study from cradle to grave", and by the Portuguese Science Foundation (FCT/MCTES), under projects UIDB/00081/2020 (CIQUP) and LA/P/0056/2020 (IMS-Institute of Molecular Sciences). RC thanks to FCT for funding through program DL 57/2016 – Norma transitória SFRH/BPD/89752/2012. M.H. de Sá also acknowledges the support from EU COST Actions CA20126 (2021-2025) - Network for research, innovation and product development on porous semiconductors and oxides (NETPORE) and CA18224 (2019-2023) - Green Chemical Engineering Network towards upscaling sustainable processes (GREENERING).

APPLICATION OF AC-MAGNETIC FIELD ACTIVATION FOR FERRITIZATION SYNTHESIS OF MAGNETIC MATERIALS

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Abstract

This study is intended to develop a new cost-efficient method for production of oxides-based magnetic materials. Traditional methods for production of these materials are characterized by significant energy and resource consumption. One of the promising economic methods of synthesis is hydrophase ferritization, that makes it possible to obtain magnetic materials by processing of industrial waste containing heavy metals. Essentially, the method is based on condensation of micro-sized iron-containing particles as a result of chemical reaction of co-precipitation of heavy metal ions in alkaline medium. Disadvantages of hydrophase ferritization are associated with its conducting at temperatures above 75 °C.

The work objective is to improve the technology for production of ferrite materials by development of scientific and technological basis for use of variable magnetic fields to activate processing of the ferritization waste - exhausted technological solutions and electroplating sludges, ensuring rational process modes and parameters with minimal energy consumption.

An alternative to the thermal ferritization, the AC-magnetic field activation of the process at ambient temperatures was proposed. In comparison to thermal one, application of magnetic activation of the process does not impair both the degree of removal of heavy metals ions from the reaction mixture and the crystalline structure of the precipitate. The qualitative and quantitative composition of ferritization sediments the was investigated using x-ray, infrared spectroscopy and scanning electron microscopy. The phases with magnetic properties: magnetite Fe_3O_4, iron monohydrate δ – FeOOH and heavy metal ferrites were detected.

Designed electromagnetic activation installation is constructed and a computer software for controlling the process parameters determined are developed. The efficiency of energy-saving application of AC-magnetic field activation for ferritization process with amplitude of magnetic induction of 0.3 T and frequency from 0.5 to 10 Hz is established. The consumption of electricity for AC-magnetic field activation in comparison with thermal one is reduced by 65 %. In addition, it is expedient to replace the ferrous sulfate with galvanic liquid waste. That makes possible to reduce the cost of this technique, and thus make it attractive for industrial applications.

It was shown that iron-containing industrial waste can serve as a production input for the energy-efficient synthesis. The developed method also provides implementation of wastewater treatment with closed circle resource management systems. Application of the obtained oxides-based magnetic materials in products capable of shielding electromagnetic radiation is proposed.

Keywords: synthesis, magnetic materials, ferritization, magnetic activation

BRINGING VALUE-ADDED TO THE NaOH-BASED CO_2 CAPTURE BY GENERATING GREEN HYDROGEN AT THE SAME TIME IN A SEMICONTINUOS FACILITY.

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Abstract

The search for efficient capture and storage (CCS) and utilization (CCU) technologies is a great concern nowadays [1]. One of the most mature technologies to capture CO_2 consists of absorbing it in basic solutions, such as NaOH [2]. For its part, hydrogen, as the future energy vector, can be generated by reaction of common metals and metallic residues with water [3]. The present work aims at integrating, for the first time, the NaOH-based CO_2 capture processes with the hydrogen generation from the aluminum-water splitting reaction. To do so, the CO_2 Capture-NaOH Lean stream (CO2LS) was used for the generation of hydrogen in a novel semicontinuous facility of self-construction, at temperature ranging from room-80ºC, concentration: 1-2 wt% of NaOH, and flow: 0.5-1.0 mL/min. These conditions are set based on the typical values employed in the NaOH-based CO_2 capture process [4]. A relative yield of hydrogen up to 70% was obtained at the highest level of conditions. A factorial design of experiments, along with a techno-economical assessment, will be presented in order to determine the profitability of the process.

Keywords: Green hydrogen, H_2-economy, CO_2-economy, metal-water splitting, semicontinuous facility

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Acknowledgements: This project has been funded by the Ministry of Science and Universities through project RTI2018-097456-B-I00 and by the Junta de Castilla y León through project by FEDER FUNDS under the BioEcoUVa Strategic Program (CLU-2019-04).

BIOBASED FURAN CHEMICALS PRODUCTION USING DEEP EUTECTIC SOLVENTS ASSISTED WITH MICROWAVE SYSTEM HEATING

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Abstract

Currently, society is facing environmental challenges as a consequence of the depletion of fossil resources and their impact on the environment. In this sense, the search for renewable resources for the production of bioproducts is essential to attain sustainable development based on a circular economy[1]. Residues generated in the food industry are composed of high content of polysaccharides and soluble sugars. The suitable conversion of these C6 sugars into value-added chemicals is shown as an attractive alternative to the petroleum-based refinery. Hydroxymethylfurfural (HMF) is one of the most important and versatile molecules that can be obtained from hexose sugars and converted by oxidation-reduction reactions into relevant products with interest in the pharmaceutical, textile, and plastic industries[1]. Traditional methods for HMF production from glucose and/or fructose normally use high temperatures coupled with strong mineral acids as catalysts, causing environmental issues. Recently, employing avant-garde solvents such as deep eutectic mixtures has emerged as an interesting alternative to be used as sustainable solvents for the processing of biomass. Taking this into account, the aim of this work was the evaluation of apple residue streams generated in the cider industry for the production of HMF. For that, the variables studied were different molar ratios of mixtures of choline chloride: lactic acid, temperature, and time using microwave technology for sugar dehydration to obtain HMF. Under the conditions selected, 4-13 g/L of HMF were produced corresponding to up to 93 % of the conversion of consumed sugars in the reaction. Overall, the extracted sugars from apple residue can be considered a suitable source for the sustainable production of HMF.

Keywords: Hydroxymethylfurfural, apple pomace, sugars platform

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Acknowledgements: B. Gullón and A. Romaní would like to express their gratitude to the Spanish Ministry of Science, Innovation, and Universities for financial support (grant references RYC2018-026177 and RYC2020-030690, respectively).

TOPIC 5

POLYMERS AND ADVANCE MATERIALS

ADVANCED SYNTHETIC BONE GRAFTS BY SUPERCRITICAL FLUID TECHNOLOGY

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Abstract

Advanced polymer foams, the so-called scaffolds, are under engineering development to replace biological grafts in promoting the self-healing capacity of the tissue patients. Scaffolds are usually 3D-porous structures made of biodegradable polymers with morphological and mechanical properties similar to those of the damaged tissue[1]. Supercritical (sc)CO_2 technology offers a broad portfolio of possibilities ranging from the production of drug-loaded polymeric scaffolds to the sterilization of implantable medical devices[2]. In this work, foams of poly(ε-caprolactone) and poly(lactic-co-glycolic acid) blends were subjected to an integrated scCO_2 sterilization-plus-foaming process patented by the research team. Sterilization efficacy was tested using *Bacillus pumilus* as bioindicator. The polymeric scaffolds were evaluated regarding physicochemical and mechanical properties. Finally, previous *in vitro* tests with cells encouraged to undergo *in vivo* tests in critical bone defects of Sprague-Dawley rat and Manchega sheep models to evaluate bone regeneration. Negative (void defects) and positive (autograft) controls were used. Scaffold performance after 16 weeks of implantation were effective in regenerating bone tissue in critical size defects. Overall, this work highlights the advantages of scCO_2 technology for sterile polymers processing from economical (single-step, reduced duration) and environmental perspective (CO_2 valorization), with promising performances in relevant *in vivo* models. The technological transfer and valorization of these scaffolds within the clinical area is currently ongoing.

Keywords: Biopolymers, synthetic bone scaffolds, supercritical fluids, process integration, in vivo tests

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ADVANCED FUNCTIONAL POLYMERIC NANOCOMPOSITES FOR THE REMEDIATION OF NITRATES-POLLUTED WATER

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Abstract

Providing access to potable water to the entire population is a global issue of utmost relevance. The United Nations (UN) prevision is that about half of the entire world population will live in water-stressed areas by 2025[1]. The intensive use of nitrogenate fertilizers, irrigation of crops with domestic residual waters, urban or industrial organic waste, and, above all, the use of manure and slurry derived from livestock activities as fertilizers cause nitrates to release into open waters. In particular, Spain is dramatically affected by nitrates pollution, directly related to the relevance of the livestock sector in several regions. Sepiolite, which is a fibrous magnesium silicate mineral, has been successfully tested as a sustainable absorbent for removing nitrates from water. However, the recovery of the nanoparticles from the water after the nitrates adsorption requires of additional filtration steps, while their accidental release or incomplete recovery could cause additional damage to the environment. Herein, a new approach is proposed, combining the enhancing of sepiolite by chemical modification with their incorporation in different porous polymeric substrates. This approach allows reaching a high nitrates adsorption performance (up to 23 mg/g) without requiring controlling the pH or temperature and overcomes the difficulties to manipulate and recover the sepiolite, avoiding any accidental release of the sepiolite to the environment[2]. The developed nanocomposites were tested in an aqueous solution of nitrates with a concentration of 100 mg/L at different contact times, as well as in actual polluted waters. The evolution of the nitrates' concentration was analyzed using UV-Visible spectroscopy, finding that the kinetics of the reaction can be accelerated by proper tuning of the polymeric substrate morphology. Remarkably, this strategy allowed overcoming the performance of the sepiolite in powder form, as well as reaching adsorption rates compatible with common gravity-driven filtration devices.

Keywords: Nitrate removal, Polymeric substrates, Water Remediation, sepiolite.

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Tröger's base network PIMs with tunable pore size for heterogeneous catalysis

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Abstract

Polymers of Intrinsic Microporosity (PIMs) are materials which microporosity is due to the rigidity of the monomers used in their synthesis that cannot pack space efficiently, leaving pores of nano-dimension.[1] A new class of PIMs, prepared via the *in-situ* formation of the Tröger's Base (TB), was recently introduced,[2] which combine a high porosity with the presence of two basic nitrogens that can be used as ***heterogeneous catalyst***.[3] The active site (the TB core) is an integral part of the polymer backbone, which is one of the main advantage of these materials over other catalysts as it facilitates their recycling and reutilisation.[4] PIMs are relatively new in catalysis and, despite recent improvements, their often small pore size can pose a problem when reacting large substrates, as they cannot enter into the pores.[4] To work around this issue, we herein report the synthesis of novel TB-PIMs composed of ***rigid monomers*** and slightly more flexible "***side-arms***". The introduction of the latter confers a higher degree of flexibility of the molecular chains that leads to the expansion of the pores, enhancing the accessibility of the catalytic sites. These conformational changes improve the swelling of the material in the presence of solvent, which enhances the catalytic performance. In addition, the recyclability tests proved that these materials can be readily recovered from the reaction and reused without any significant loss of activity for at least six catalytic cycles. The result of this work not only shows that the design of amorphous materials can be tailored to improve their catalytic performance, but also introduces a new concept for PIMs in catalysis.[5]

Keywords: Polymers of intrinsic microporosity, Heterogeneous catalysis, Materials

Acknowledgements: Engineering and Physical Sciences Research Council (EPSRC), Grant number: EP/T007362/1 "Novel polymers of intrinsic microporosity for heterogeneous base-catalyzed reactions (HBC-PIMs)"

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TOWARDS THE PRODUCTION OF GREEN AND ADVANCED THERMAL INSULATORS

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Abstract

One of the biggest challenges in our society is to prevent climatic change. The building sector in Europe is the most energy-consuming one and therefore the main responsible for the total CO_2 emissions to the atmosphere. Therefore, the European Union proposes restrictive legislation leading to the construction of only “nearly zero energy building” at the end of the decade.

Current insulators present so high thermal conductivity to fulfill the requirements. The solution lies in producing superthermal insulators, materials with a thermal conductivity lower than air. Solutions such as the use of Vacuum Insulation Panels or aerogels have been proposed, however, they present some important drawbacks, among them, high-cost production, poor mechanical properties, and an environmentally hazardous production process, especially aerogels.

Nanocellular polymers are one alternative to substitute previous materials due to their reduced gaseous thermal conductivity. However, it was recently proven that they are not able to block infrared radiation, increasing the final thermal conductivity[2]. In this work, we propose the production of nanocellular PMMA with infrared blockers such as Graphene Nanoparticles (GnP) through a green production process. The scalable route is studied together with a Life Cycle Analysis where their real impact is compared to other insulators.

Keywords: Superinsulator, IR Blocker, Nanocellular Polymer

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Acknowledgements: Financiado por los Fondos del Mecanismo de Recuperación y Resiliencia –Fondos NextGeneration EU- y los Fondos de la Comunidad de Castilla y León. Planes Complementarios de Investigación y Desarrollo con las Comunidades Autónomas en acciones de I+D+I, de la Componente 17. Inversión 1. (C17. I1), del Plan de Recuperación, Transformación y Resiliencia.

SELF-HEALING TIRE RUBBER COMPOSITES: ENVIRONMENTAL IMPLICATIONS OF TECHNICAL ADVANCES

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Nowadays society is undergoing a necessary ecological transformation. The circular economy (CE) is the new social and economic system globally adopted. It promotes the circularity of products and resources, extending their useful life and minimizing the environmental cost. Emerging technologies such as the development of self-healing elastomers, can be seen as an innovative pathway to sustainable applications. Self-healing materials are characterized by their ability to repair autonomously or upon exposure to stimuli. The main objective of these smart materials is to increase their useful lifespan and, therefore, help to reduce the ecological and economic costs. Although this field of research is growing and getting worldwide attention, self-healing rubbers are still far from satisfactory, especially because of their lower mechanical strength. One strategy reported by the authors is the inclusion of ground tire rubber (GTR) as a sustainable alternative to traditional reinforcing filler in styrene-butadiene rubber (SBR). GTR comes from end-of-life tires (ELTs), a waste that grown dramatically every year. The authors previously studied the technical aspects of physical and chemical modifications of GTR and their effect on the properties of self-healing SBR [1,2]. As a continuation, the environmental aspects were assessed. In this sense, life cycle assessment (LCA) stands out as a robust, science-based and very valuable tool for the analysis of the environmental impact, and to evaluate new innovative materials that can contribute to the CE model. Until now, little information is available about the environmental implications of self-healing rubbers. The aim of this pioneering work, therefore, was to determine the environmental implications arising from the technical advances developed on self-healing tire rubber composites. LCA was implemented according to ISO 14040 and 14044, using GaBi software and its database, as well as scientist literature. Results show a reduction of environmental impact, moreover, a self-healing SBR reinforced with a chemically modified GTR showed an environmental impact comparable to conventional scenario. These results encourage further research to improve mechanical and healing behaviour.

Keywords: Life-cycle assessment, Self-healing, End-of-life tire, Sustainable, Circular economy

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Acknowledgements: The authors are grateful to University of Valladolid for Postdoctoral Contract CONVOCATORIA 2020 (K.C.N.C), to State Research Agency of Spain (AEI) for grants RYC2017-22837 (M.H.S.) and PRE2018-084732 (L.E.A.P.). All authors would also like to thank Manuel González from CIDAUT for his contributions to LCA.

EFFECT OF EGG WHITE PROTEIN AND WATER CONTENT IN THE STABILIZATION MECHANISMS OF BIOBASED RUBBER LATEX FOAMS

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Abstract

Natural rubber latex foams (NRLFs) are flexible foams that are used in comfort products such as mattresses and pillows, among other applications [1]. The chemistry involved in the synthesis of NRLFs needs the use of vulcanizing agents to cross-link the polymeric matrix, and thus, promote the stability of the solid phase of the foams [2]. Therefore, in spite of the bioderived character of the initial raw material, natural latex, the final foam is neither fully biobased nor compostable. Nowadays, the industrial and academic interest in looking for more sustainable alternatives encourages the development of new formulations and synthesis routes for these foams.

In this work, we develop fully biobased NRLFs using egg white powder as a biobased stabilizer additive, which is usually used as foaming agent in edible foams. The foams are produced by a two-stage foaming process in which the liquid blend natural latex-protein is firstly aerated with a whipping machine and secondly dehydrated via microwave radiation, which is able to promote rapid heating and water evaporation and save more energy than the conventional heating methods used in the manufacturing of conventional crosslinked NRLF foams [3].

The density and the main structural parameters of both the liquid and solid foams are studied in this work to understand the effects of the protein in the stabilization mechanisms involved in the synthesis of these foams. Furthermore, the initial water content of natural latex is varied to understand how this factor affect the stabilizations mechanisms of these foams in the presence of egg white protein.

Biofoams, Latex, Egg white protein, Bioderived, Sustainability.

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PREPARATION AND CHARACTERISATION OF MYCELIUM AND LIGNOCELLULOSIC WASTE COMPOSITES

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Abstract

The development of new, more environmentally friendly materials has accelerated in the last decade[1]. New ecological building materials such as mycelium composites are being introduced. Mycelium is a vegetative tissue of fungi that grows on a nutrient-rich substrate. Fungi are among the oldest, largest, and most widespread organisms on the planet[2]. We can use lignocellulosic by-products or waste in such composites[3]. Because of these natural compounds, these composites are both environmentally friendly and cost-effective. Since these composites are still relatively new, there is not much data on their properties. In this study, we produced six different mycelium composites. A distinction was made between substrate fractions size and fungal species. We have evaluated their manufacture and compared their physical and mechanical properties with those of commercially available wood fibre insulation materials. We determined the density of all these materials using three different methods. We subjected them to compression, water absorption, surface energy and fire resistance tests. We found that the mycelium composites are comparable to the reference materials in all areas. The average density is 0.274 g/cm^3 and the contact angle of water after 15 seconds is 120°. The best composite was made from the fungus *Schizophyllum commune* and rough substrate; it had a water content of 175% after 24 hours of soaking, the lowest weight loss on exposure to fire (2.4 g) and the highest modulus of elasticity in the compression test (0.71 MPa).

Keywords: Mycelium, Composite, Insulation, Wood-waste

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CLOSED-LOOP RECYCLING OF FIBER-REINFORCED POLYMER COMPOSITES WASTE FROM AERONAUTIC INDUSTRY

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Abstract

Polymer composites reinforced with glass or carbon fibers are widely used in automotive, aeronautic and civil engineering industries; in which lightweight high-strength parts are required [1]. In particular, engineering polymers such as polyetherimide (PEI), polyphenylene sulphide (PPS) and polyetheretheretheretherketone (PEEK), among others, are often used in these sectors due to their high performance. Thus, the recycling and revaluation of these polymer composites are of particular interest due to their increasing demand and the high economic value [1,2]. Yet, this is a very recent topic with a low degree of maturity in comparison with the recycling of thermoset composites [3]. So far, most studies have focused on the mechanical recycling, leaving aside chemical or thermal processes that consume more energy and produce chemical waste [3]. However, the mechanical recycling technology has difficulty in maintaining fiber length and thus it reduces the mechanical properties of the recycled materials, typically leading to downcycling.

Therefore, the present study aims to demonstrate that it is maintained the quality of the recycled material obtained by the mechanical recycling of short glass fiber reinforced PEI waste from injected parts designed to replace the metal parts of the aeronautical sector. From the mechanically recycled material, injected samples with different contents of recycled and virgin materials are prepared to evaluate their mechanical properties and also their fibers content and length. The results show that the injected sample with 100% recycled material maintains the fibers content and length; consequently its mechanical properties are hardly affected. This means that the recycled material could be used again for the production of injection moulded products for the aeronautic sector or even other sectors, thus achieving a closed-loop recycling.

Keywords: Engineering polymers, Polyetherimide, Glass fibers, Recycling, Aerospace materials

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Acknowledgements: This investigation is framed within the framework of grants for Technological Centres of Excellence "Cervera" funded by the CDTI (OSIRIS Project, CER-20211009). The authors acknowledge the financial support of the Ministry of Economy and Competitiveness (MINECO) of Spain through the PTQ2020-010968 project (M. Asensio) and the PTQ2021-011628 project (M. Santiago-Calvo).

SYNTHESIS AND APPLICATIONS OF PORPHYRIN BASED-MOFs USING SUPERCRITICAL CO_2

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Abstract

For the last few years, our research group developed increased expertise in the synthesis of the metal-organic frameworks (MOFs) using a green technology based on supercritical CO_2 ($scCO_2$) assisted processes. [1-3]

Following these lines, in this work, we investigated the possibilities of precipitating MOFs using H_2TPyP porphyrin linker using $scCO_2$. We focused on porphyrins, as they are key building block precursors in many areas of synthetic chemistry. In particular, the preparation of MOFs containing porphyrin linkers is currently of great interest, since they can form coordination networks with applications in a large variety of fields. Among these, we focused our interest in their potential use in photodynamic therapy (PDT) for cancer treatment. Thus, four metal hexafluoroacetylacetonate complexes ($M(hfac)_2$, M= Cu, Zn, Co, Ni) were used as metal clusters for preparing metalorganic materials using $scCO_2$. Among all samples obtained, the $scCO_2$ precipitated Zn(II) MOF was successfully tested as a potential photosensitizer in PDT therapy in SKBR-3 tumoral cell line showing outstanding performance.

Keywords: Porphyrin, MOFs, supercritical CO_2, PDT

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IS THERE ANY SUITABLE ALTERNATIVE SOLVENT FOR MEMBRANES?

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Membranes are widely used in common industrial processes such as water desalination, reverse osmosis, dialysis, fuel cells, air enrichment, natural gas and biogas upgrading, and many more. The characteristics of this technology are easy handling, low energy consumption, simplicity, flexible design, low maintenance, compact process equipment and it can be considered an environmentally friendly process. However, the vast majority of the conventional membrane formation processes use polymeric solutions based on a mixture of polymer and an aprotic solvent such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAC) or, *N*-methyl pyrrolidone (NMP) as a main solvent. For instance, the NMP is reprotoxic, provokes serious eye, skin and respiratory irritation. DMF is a hepatotoxic and reprotoxic solvent and DMAC is a reprotoxic solvent. These undesirable characteristics motivated the presence these solvents in the REACH list (1). This will force to renovate the membrane production process.

In order to minimize toxicity and find a replacement, the solvent have to meet some requirements which are inherent to the process. The alternative solvent, among being less harmful and more sustainable, should be: able to dissolved the high-performance polymers such as polyamides and polyimides; present a high boiling temperature to minimize: the explosion risks, an extra safety investment, and changes in the production lines of the membrane producers; show complete miscibility with water which is the non-solvent in the phase inversion process; and should maintain the performances of the materials.

In this work, we employee three alternative and greener solvents for the processing of the films, and analyze their effect on the gas separation performances of four different polyimides. The solvents are γ-Butyrolactone (GVL), 3-methoxy-*N,N*-dimethylpropanamide (KJCMPA-100), Dihydrolevoglucosenone (Cyrene) which are compared with the often use solvents (NMP and THF). The polyimides have been selected has a function of their gas permeation performances. In this sense, we analyze the range from polyimides presenting very low to very high gas fluxes which is related to their fractional free volume (FFV). We show the correlation between FFV, type of solvent and separation performances.

Keywords: Membrane, alternative solvent, gas separation, polyimide, sustainable

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Acknowledgements: Acknowledgements: Authors would like to thank the "Ministerio de Ciencia e Innovación" for the financial support through the research project PID2019-109403RB-C21/AEI/10.13039/501100011033

REDUCING THICKNESS OR INDUCING POROUS STRUCTURE? A METHODOLOGY TO INCREASE THE PERMEANCE IN GAS SEPARATION MEMBRANES

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Abstract

In the conversion into a more sustainable and circular economic model, membrane-based processes are presented as a key-enabling technology, allowing industries to retain competitiveness and replacing conventional energy-intensive techniques. Membranes can remove selectively an undesired element, i.e., from the emitting source, preventing the emission of this component. For instance, the capture or separation of the CO_2 from other gases in power plans or biogas upgrading. However, these industrial separations are ruled by the cost and always demand for increasing the effectiveness and productivity of the membranes, generally aiming for increasing CO_2 fluxes. Therefore, the increase on the gas flux through the membrane without losing selectivity has been recognized to be a key factor in industrial scenarios [1,2].

Usually, the permeance is raised by reducing the membrane thickness to nanometer scale and profit from a permeance increase. However, the fabrication of thin films with thicknesses below the micron employs expensive and environmentally unfriendly methods. Membranes usually are composed of multilayer devices with at least a porous support layer, a gutter layer, and a selective layer. In a different approximation, all layers of the membrane should fabricate in a single, straightforward, and green step, by taking advantage of a thin selective layer.

This work aims to present a new methodology to fabricate porous membranes with desired thickness of the selective layers without compromising the total thickness of the membrane by employing environmentally respectful fabrication techniques. The idea is based on the production of an open-cell porous structure where the selective layer is located in one or both borders. These membranes are fabricated by gas dissolution foaming obtaining both features in a facile and environmentally friendly one-step process. By introducing porosity into the membrane, the permeance, inversely proportional to the transport time, is enhanced by keeping similar selectivities without needing membranes with extremely thin thickness. Additionally, the structure showed extremely high stability at very elevated feed pressures showing the stability and roughness of the method.

Keywords: Gas separation, CO_2 capture, Nanocellular polymers, Gas dissolution foaming

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Acknowledgements: Ministry of Science (Spain) (PRE2019-088820)

BIODEGRADABLE PACKAGING MATERIALS BASED ON *Agaricus bisporus*

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Abstract

The consumption of mushrooms has increased in recent years resulting in the generation of large amount of mushroom waste each year such as the misshapen mushroom and mushroom stems. The aim of this work was to valorize the biomass of two of the most consumed *Agaricus bisporus* varieties worldwide, *Agaricus bisporus brunescens* (Abb) and *Agaricus bisporus hortensis* (Abh), for the production of bio-based and biodegradable films. The two varieties were initially characterized and then, fungal based films were formed by extrusion followed by compression-molding. Abh formed films with better mechanical and barrier performance than Abb, so it was selected to optimize its production in terms of energy consumption and cost-effectiveness. Abh films could be also produced at lower temperatures without modifying the physicochemical properties of the films. Furthermore, barrier properties and wettability of Abh films were successfully improved by coating them with a beeswax layer with the additional advantages of easy processing and easy disintegration according to ISO 20200.

Keywords: Valorisation, food packaging, films, mushrooms biomass

IMPROVING WATER RESISTANCE OF RICE STRAW CELLULOSE-BASED AEROGELS

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Abstract

Annually, about 760 million tons of rice are produced worldwide. This results in agricultural residues such as rice straw. For 1 kg of rice grain, about 1.5 kg of rice straw is produced[1]. Therefore, some management strategies have been studied to extract value-added compounds from this abundant residue and convert it into commodities. In this context, cellulose is one of the compounds studied that can be used for various applications, such as the development of materials and food packaging. Recently, cellulose-based aerogels have become the focus of research as a substitute for absorbent materials. However, using cellulose to absorb aqueous solutions is challenging because the material usually loses its integrity due to its hydrophilic nature. Therefore, stabilization methods should be proposed to maintain the integrity of the material under high humidity conditions to solve this problem.

The aim of this work was to produce water stable cellulose-based aerogels from rice straw. Two strategies were investigated: first, TEMPO mediated oxidation followed by high pressure homogenization (HPH) and second, regeneration of cellulose by solubilization with ionic liquids. Briefly, rice straw cellulose was suspended in water by sonicating it at high intensity. Then, the suspension was oxidized and passed through HPH 2, 4 and 8 cycles at 600 bar. On the other hand, BMIM-Cl ionic liquid (IL) was used to dissolve the cellulose at 90 ºC. Then, the suspensions were poured off and freeze-dried. Both methods allowed the preparation of cellulose aerogels with improved water resistance. In addition, this work proposes a novel method to study the internal structure of the porous aerogel using confocal laser scanning microscopy (CLSM). The images acquired by CLSM showed differences in the size and distribution of microfibers in the aerogels at the different HPH cycles tested. In addition, the materials obtained by the regeneration method had different porosity/density than those produced by HPH. Therefore, HPH and regeneration by IL are valuable tools in the fabrication of materials with stable aerogel structure from rice straw. These advances mark a starting point for the development of cellulose-based aerogels without the need for compatibilization with other polymers.

Keywords: rice straw, cellulose, aerogels, ionic liquid, high pressure homogenization

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Acknowledgements: Spanish Ministry of Science and Innovation under the research grant PID2020-112766RB-C21, and Santiago Grisolia aid of Laura Cabrera-Villamizar (GRISOLIA/2021/050).

TRANSPARENT POLYURETHANE AEROGELS: PROMISING MATERIALS TO REDUCE CO_2 EMISSIONS

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Abstract

CO_2 emissions contribute to one of the main concerns of the current population: the well-known climate change. In the recent years, the European Commission has strengthened the Energy Performance of Buildings Directive (EPBD) [1] aiming to reduce a 36 % the total energy consumption by 2030. Nowadays, polyurethane foams, having thermal conductivity values between 25 and 33 mW/mK [2], are widely used for thermal insulation. Nevertheless, there is a large room for improvement in these thermal conductivity values which is essential to reach the settled goals. Therefore, the development of advanced thermal insulators that enhance the energy efficiency of buildings is of utmost relevance.

Aerogels are highly nanoporous materials combining excellent properties such as low density, huge surface areas, and thermal and sound insulation. Although most research is focused on silica aerogels, one usual drawback of these materials is their brittleness. Thus, herein, a novel synthesis of polyurethane aerogels showing thermal superinsulation in combination with good mechanical performance and transparency is described. Through changes in their nanostructure, their thermal insulation, mechanical properties, and transparency can be tailored, and the structure-properties relationship analyzed [3]. Thermal conductivities as low as 12 mW/mK, much lower than that of conventional thermal insulators, for densities ca. 160 kg/m^3 were reached, opening a broad spectrum of potential applications in the building sector such as glazing windows, or insulating walls.

Keywords: aerogels, thermal superinsulation, transparency, polyurethane.

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Acknowledgements: Financial support from the FPU17/03299 grant (Ministerio de Ciencia, Innovación y Universidades) is grateful acknowledged. Activities funded by the EU NextGeneration and Castille and Leon. Complementary plans of research and development with the autonomous regions in actions of R&D. Component 17. Investment 1. (C17. I1), of the recovery, transformation and resilience plan.

DESIGN AND TRANSFORMATION OF BIODEGRADABLE COMPOSITE MATERIALS WITH IMPROVED PROPERTIES FOR THE PACKAGING INDUSTRY

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Abstract

Nowadays, the packaging market is one of the industrial sectors that uses the most plastic and, consequently, generates the most plastic waste. The high level of contamination derived from this waste has driven the demand for biobased packaging products as a potential solution, especially for single-use packaging[1]. In this sense, the most environmentally friendly polymeric materials are those capable of being degraded under ambient conditions such as biopolyesters[2]. However, these materials have not yet been implemented in the packaging sector due to their fragility mechanical properties[3].

This work aims on the modification of biopolyesters by incorporating natural reinforcements to improve the physical and mechanical properties making easier the incorporation of these materials in the general industry, and particularly in the packaging sector.

Keywords: Biocomposites, biodegradable, Mechanical properties, Recycling, Packaging materials

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Acknowledgements: This work is part of the European project Bionanopolys GA: 953206 project funded by Horizon 2020 (H2020).The authors acknowledge the financial support of the Ministry of Economy and Competitiveness (MINECO) of Spain through the PTQ2020-010968 project (M. Asensio) and the PTQ2021-011628 project (M. Santiago-Calvo).

DYNAMIC CHEMISTRY FOR SUSTAINABLE FOOD PACKAGING DESIGNING

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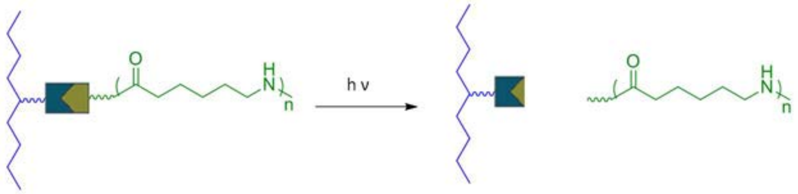
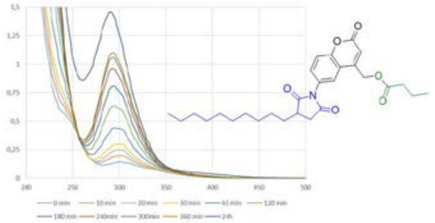
Abstract

It is well known that food packaging plastic represents one of the main players in the generation of polymeric waste due to its massive use, its short useful life and its single-use model. In addition, the current consumption trend requires complex multilayer packaging designs for transport and keeping the products in good conditions for longer [1]. These designs can contain up to 11 layers of different materials, with very low thicknesses. The heterogeneity and geometry make it extremely difficult its recycling process.

To face the recycling problem, research trends are mainly focused on different layer separation techniques. Among the different systems, the use of photosensitive adhesives based on dynamic chemistry is a new road to be explored [2]. This approach consists of the use of photolabile molecules that allow layer separation under an external stimulus. The preliminary studies of the synthesize photosensitive molecule show its ability to be used as an effective interface between different material layers and significant sensitivity to release the formed bonds when the complex is radiated with UV light.





Keywords: multilayer packaging, photolabile molecules, synthesis, modeling.

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Acknowledgements: The authors are grateful to the Recovery and Resilience Mechanism Funds -Next Generation EU Funds- and the Community of Castilla y León Funds. Complementary Research and Development Plans with the Autonomous Communities in R&D&I actions, of the Component 17. Investment 1. The authors also acknowledges the University of Valladolid for the Postdoctoral Contract CONVOCATORIA 2020 (K.C.N.C) and National Project (MINECO) ECOLAYER TED2021-129419B-C22

COPPER NANOPARTICLES-ANCHORED PCL ELECTROSPUN FIBERS WITH EXCELLENT CAPABILITY TO REMOVE A DANGEROUS PESTICIDE

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Abstract

The uncontrolled management of toxic pesticides have led to the contamination of water and food, putting in risk the population health and environment preservation. In particular, the pesticide Chlorpyrifos (CP) is acutely toxic for the aquatic ecosystem, birds, and mammals, including humans, causing a very harmful effect in the environment. Moreover, CP is highly recalcitrant, reaching several km from the used area. All these aspects have increased the social concerns about removing this toxic substance from the environment. Copper nanoparticles (CuNPs) have shown a high efficiency to catalyze the elimination of this pesticide[1]. However, the use of Cu is strongly limited by its tendency to oxidize, showing low stability and a variable response with time[1]. In this work, CuNPs were immobilized in polycaprolactone (PCL) polymer through electrospinning, obtaining an active mat that degrades CP. The best catalytic result was obtained with the mat containing 2.5 wt.% of CuNPs, degrading 40 mg/L of CP within 96 hours. Interestingly, PCL showed to slow down the oxidation of Cu maintaining the oxidation state (+1) for months. Moreover, the catalytic properties were independent on the light environmental conditions, and the great catalytic response was maintained for at least 5 cycles, with an intermediate washing step between each cycle. These reusability properties of the Cu-PCL mats resulted in an overall CP removal capacity up to 100 mg/L.

Keywords: Chlorpyrifos, Copper oxide, catalysis, electrospinning, reusability.

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Acknowledgements:
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DEVELOPMENT OF NADES-BASED INJECTABLE HYDROGELS THROUGH ENZYMATIC CROSSLINKING

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Abstract

Hydrogels are crosslinked polymeric networks capable of retaining water, that emerged as one of the main classes of biomaterials for tissue engineering and drug delivery systems (DDS). Injectable hydrogels have been extensively studied due to their minimally invasive properties, ease of application, and void-filling property. Several drugs can be incorporated into these matrixes, depending on the envisaged application, namely anti-tumor drugs, proteins, growth factors and non-steroidal anti-inflammatory drugs (NSAIDs). In this work, natural deep eutectic systems (NADES) based hydrogels were prepared using horseradish peroxidase (HRP) mediated crosslinking reaction. HRP is an oxidoreductase enzyme that offers structural stability and biocatalytic activity, having various industrial applications. This enzyme is also used as a catalyst in the crosslinking reaction to produce injectable hydrogels, formed *in situ*. Additionally, it has been proved in previous studies, that NADES promote an increase in the thermal and structural stability of HRP and improve its activity. Moreover, NADES are known to increase the solubility and delivery of low-water-soluble molecules, such as anti-inflammatory drugs, in aqueous media. Herein, gelatin was used as a natural polymer and gelatin-phenol (Gt-Ph) conjugates were prepared so that the reaction with HRP could occur. The hydrogel preparation, gelation time, long term stability at 37 °C and mechanical properties were investigated. Moreover, the feasibility of using these hydrogels as DDS was assessed by studying the compatibility of several NSAID’s with the NADES at study. Finally, the drug release profile of the NSAIDs, as well as the biocompatibility of the hydrogels, were studied.

Keywords: Hydrogels, Natural deep eutectic systems, Horseradish peroxidase, Drug delivery systems, non-steroidal anti-inflammatory drugs.

Acknowledgements: The authors thank the funding from European Union Horizon 2020 Programme under grant agreement number ERC-2016-CoG 725034 (ERC Consolidator Grant Des.solve). The authors also thank Laboratory for Green Chemistry - LAQV (UIDB/50006/2020), and the PhD grant SFRH/BD/148510/2019 financed by national funds from FCT/MCTES.

WOOD IN 3D PRINTING - FROM A SUSTAINABILITY POINT OF VIEW

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Additive manufacturing (AM), unlike traditional subtractive manufacturing, enables more automated fabrication of products or functional components with complex shapes at low manufacturing costs and low residues. Transportation costs, production-related energy demand and CO_2 emissions are reduced by shortened processes and more direct manufacturing, as 3D digital models can be sent via digital connections and produced on-site or nearby. The need for tooling, handling is minimized, and indirect material-related energy demand is lowered.

Polymer composites filled with natural-based fillers have gained interest in recent years, including in additive manufacturing. Consumers, industry and governments are increasingly demanding products made from renewable and sustainable resources that are biodegradable, non-petroleum based, carbon-neutral and pose low risks to the environment, human health and safety. Polylactic acid (PLA) is one of the fastest growing bioplastics in the bio-composite industry due to its good properties such as renewability, biodegradability, biocompatibility, easy processability, and high modulus [1]. To improve mechanical properties or to reduce costs (depends on the particles size, shape and ratio) wood or other lignocellulosic particles are added to polymers to form wood-plastic composites.

Our research focuses on the possibilities of using wood in additive technologies and their potential in the industry as well as for regular users. The integration of wood materials into additive manufacturing is of interest due to their positive environmental impact and improved properties [2]. Its reinforcing ability, biodegradability, availability as a waste material from other industries, ability to be used in different forms or only in partial components, recycling options, or even the use of its undesirable hydromorph-induced dimensional instability for 4D printing. Recently, we were investigating the use of wood-plastic composites for 4D printing and how we can predict shape changes with knowledge of the material properties and numerical simulations.

Products made with 3D printing need to be evaluated over the long term to assess their behavior in long-term use, not only in terms of mechanical properties, but also in terms of their environmental impact. We believe that greater use of wood and its positive impact on the environment could be achieved.

Keywords: 3D printing, wood, additive manufacturing, wood-PLA composites

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Acknowledgements: The authors acknowledge the support of the Slovenian Research Agency (ARRS) within the framework of research program No. P4-0015 "Wood and lignocellulosic composites".

TRANSPARENT NANOCELLULAR POLYMERS AS INSULATING WINDOWS FOR ZERO-ENERGY BUILDING

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Abstract

The world is currently immersed in an environmental crisis, which The United Nations calls "The Triple Planetary Crisis" in reference to air pollution, climate change, and biodiversity loss, that humanity must face[1]. One of the tools to fight against this is to reduce energy consumption in buildings. For this reason, the EU proposes to only built what is known as nearly Zero Energy Buildings at the end of this decade. To this end, the focus has been defined on improving the thermal insulation of walls and roofs; however, more than 15% of energy is lost through the windows. Therefore, window insulation will be also essential to solve the problem.

One recently proposed solution is to use transparent nanocellular polymers as thermal insulating windows[2]. It was proved that by reducing the cell size of cellular polymers below 50 nm transparency and high thermal insulation could be combined, that is, the possibility to have a transparent insulating window. However, so far this material has been only produced with polymethylmethacrylate (PMMA), a polymer with medium performance, and the process is still not suitable for the industry.

This work proposes the use of a high-performance polymer, polyetherimide (PEI), to produce transparent nanocellular materials, to turn such materials into an industrial reality. The production process is optimized at a laboratory scale and the first steps for industrialization are explored. These materials have the potential to become the transparent materials of the future, for windows in the building and automotive sectors, protective layers for mobile phones, electronic device screens, facemasks, contact lenses, etc. This is the way to a greener future.

Keywords: Polyetherimide, thermal insulation, transparent, nanocellular.

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REVALORISATION OF HIGH PERFORMANCE THERMOPLASTIC COMPOSITE WASTE

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Abstract

The introduction of high performance thermoplastic composites (HPTPC) to replace metals or thermoset composites in industry is a fact. This evolution has been driven, firstly, by the need **to reduce processing times and costs;** and secondly**, to contribute to decarbonisation and minimisation of environmental impact**. The pioneering sector in the introduction of these materials was the aeronautical sector and their use has been spreading to other sectors with lower profit margins where, in most cases, the leap from metals to thermoset composites had not yet been made. These sectors include automotive, wind energy, farming and leisure.

However, these advantages are accompanied by a new problem, the **generation of new waste** (resulting from manufacturing processes and components after their useful life) that recycling plants do not know how to recycle efficiently. This is due to several factors: **the lack of market demand for recycled products, the high cost of the recycling process, the high energy consumption and the low quality of the products compared to virgin raw material**. For this reason, most HPTPCs end up in landfill or incinerated after their useful life, thus becoming a new environmental and economic problem for society.

To address this situation, the present work has investigated about **an efficient, close to industry and environmentally friendly recycling route capable of transforming HPTPC waste into new products with high added value**. To this end, work has been carried out along two main lines: the waste and its processing.

The importance of working on the waste lies in the fact that this material, as it arrives at the recycling plants, is very heterogeneous and its processing generates a mixture of reinforced polymers with low performance. For this reason, this research has evaluated **different ways to maximise the properties of this material through a combination of thermo-mechanical and chemical treatments, thus obtaining a new raw material capable of replacing virgin materials in alternative products for composite-consuming sectors**. Furthermore, by working on the different processing routes and optimising the parameters, it was possible to define an efficient and environmentally friendly recycling and reuse process.

Keywords: High Performance Thermoplastic Composites, Recycling, Aerospace materials

Acknowledgements: This investigation is framed within the framework of grants for Technological Centres of Excellence "Cervera" funded by the CDTI (OSIRIS Project, CER-20211009).

POROUS FOAMS FROM GELS FOR GREEN INSULATION AND FILTERS

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Abstract

The search for materials that help mitigate the environmental problems in which we are immersed is a necessity. In this search, nanocellular polymers have gained strength in recent years. Nanocellular polymers are cellular materials with cell size on the nanometer scale. This reduction in pore size gives them interesting properties such as low thermal insulation, high surface-to-volume ratio, weight reduction, or even transparency. That is why they have been proposed as solutions in different applications, but many of them are unattainable if the pores are not interconnected with each other, which is called open-cell structure.

Open cell nanocellular materials would be the ideal solution for two applications, insulation, and the manufacture of filters for micro and ultrafiltration processes; but up to now, they are complex and expensive materials to produce. The insulation sector is focused on reducing emissions and energy consumption due to heating and air cooling[1]. A proper solution is to use of Vacuum Insulation Panels (VIP) that need an open cell material inside to make vacuum, current solutions are expensive and nothing green. On the other hand, the filter industry needs smaller and smaller cells to filter particles that are harmful to the environment and humans.

In this work, the fabrication of open cell nanocellular foams from PMMA gels is proposed. Starting from a gel allows obtaining open cells in a very simple way, with a reduction in cycle time by 90% [2]; and therefore in energy consumption through an environmentally friendly process.

Keywords: Nanocellular polymeric gel, PMMA, thermal insulator, open cell, filter.

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SYNERGISTIC EFFECT OF THE ADDITION OF ENVIRONMENTALLY FRIENDLY FLAME RETARDANTS TO RECYCLED ABS

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Abstract

The European Plastics Distributors Association claims that the industry is investing in the development of materials that further reduce the flammability risk of plastic products to help save lives and protect property. With the increasing use of composite materials in demanding applications, improving knowledge of their fire performance is becoming a critical safety issue, particularly in construction and transport applications. It is therefore common for composite manufacturers to incorporate flame retardant (FR) additives into materials that reduce or delay the combustion process. The global demand for flame retardants market was 2.49 million tonnes in 2015 and is expected to exceed 4.0 million tonnes by 2025, growing at a CAGR of 4.9% from 2016 to 2025.

The nature of these additives varies depending on the application in question and the relevant regulatory requirements. Different types of additives are used to provide flame retardant functionality to plastic materials, among which two main types of FRs stand out: halogenated and non-halogenated. For years, halogenated FRs (HFRs) containing mainly bromine or chlorine have been the most widely used in plastics applications due to their higher efficiency. However, HFRs have disadvantages such as the release of large amounts of toxic gases and smoke that cause environmental pollution.

In the present work, the addition of environmentally friendly flame retardant additives in recycled composite materials has been investigated. The main mechanisms against fire were analysed: water release and protective coating. And it was observed that the addition of FR additives modified the final properties of the composites improving their mechanical-thermal behaviour, as well as improving the flammability parameters of the final recycled materials.

With this study, it can be concluded that environmentally friendly options have been found that represent an alternative to eliminate the use of halogenated FRs.

Keywords: Acrylonitrile-butadiene-styrene; recycling; flame retardant; mechanical properties

Acknowledgements: The work is framed within the CREATOR PROJECT (European Union's Horizon 2020 Research and Innovation Programme under the Grant Agreement no. 820477).

CLICK AND DECLICK CARBONYL-AMINO COUPLING FOR THE STABILIZATION AND SMART RELEASE OF NATURALLY-OCCURRING ANTIFUNGAL VOLATILES FROM RENEWABLE POLYMERS

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Abstract

Chitosan is a biopolymer which has been widely employed to carry and release several antimicrobial volatiles by means of their physical entrapping in the polymer matrix. A novel approach for the employment of chitosan as a carrier of active volatiles is to employ reversible covalent linkages based on click chemistry. The “click” reactions allow to develop relatively fast reactions with high yields using mild conditions. These kinds of bonds allow active molecules to be covalently incorporated to the polymer matrix, whereas their release is provoked by the cleavable of the bond when is required.

The objective of this research has been the application of reversible imine linkages for the stabilization and smart release of food grade naturally-occurring antimicrobial trans-2-hexenal using chitosan in the form of films. Imine links can be hydrolysed under mildly acidic conditions allowing the release of the volatile. Therefore, trans-2-hexenal was covalently attached to primary amine groups of chitosan films by means of the formation of imine bonds. The reaction was carried out in solid/liquid medium, and main reaction parameters such as trans-2-hexenal:chitosan film ratio, temperature and the use of HCl as catalyst were optimized by employing response surface methodology (RSM) in order to obtain films with adequate antimicrobial activity. The release of trans-2-hexenal from the films was also studied in different acidic media, and their antifungal activity evaluated against *Penicillium expansum.*

It was conversely observed that reaction without catalyst and temperatures below 25 °C resulted in films with high volatile release and therefore, great antifungal properties. Whereas, mild reaction temperatures and the presence of a catalyst gave rise to crosslinked chitosan films and low release of the volatile. Additional conjugated Michael addition of amino groups of chitosan to the α,β-unsaturation of trans-2-hexenal together with formation of imines led to a highly crosslinked structure under specific reaction parameters.

Keywords: biopolymer, click chemistry, antifungal, natural aldehydes, imine reversibility

Acknowledgements: The authors want to thank the Spanish Ministry of Science and Innovation for financial support project PID2021-123077OB-I00 founded by MCIN/AEI/10.13039/501100011033 and by ERDF A way of making Europe.

A GREEN CROSSLINKING STRATEGY TO IMPROVE FUNCTIONAL PROPERTIES OF GLIADIN FILMS

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Gliadins are considered promising vegetal proteins for the design of biomaterials due to their abundance as a agro-industrial by-product of wheat industry. They present several properties such as biodegradability, low cost, film-forming capacity, solubility in ethanol aqueous solutions, control-release, viscoelastic and adhesive properties, which makes gliadins attractive proteins to be used with different non-edible purposes[1]. Several studies have developed transparent and flexible films from gliadins, but they have poor mechanical properties and lack of stability in water which makes films difficult to be used for packaging purposes. In that sense, chemical crosslinking provides a way to improve the aforementioned properties. Commonly, glutaraldehyde and formaldehyde have been widely used as crosslinkers of proteins; however, these compound have some toxicity and more natural alternatives need to be explored[2].

In this work, the potential of trans-2-hexenal as a covalent crosslinking agent for gliadins has been explored. Trans-2-hexenal is classified as safe for human consumption by the FAO/WHO Expert Committee on Food Additives (JECFA)[3]. The proposed crosslinking mechanism of this α,β-unsaturated aldehyde is based on its ability to react by Schiff base and Michael addition with side-chain groups (-NH2, -SH, -OH) found in the amino acids of gliadin backbone.

The mechanical properties and water resistance of gliadin films modified with trans-2-hexenal were evaluated. The results showed that films treated with trans-2-hexenal maintained their integrity after immersion in aqueous solution. In addition, the molecular weight profile of treated gliadins was analysed by SDS-PAGE, which corroborated that gliadins were cross-linked with trans-2-hexenal. These results showed the possible formation of intermolecular covalent bonds between gliadins, leading to a crosslinked network. Therefore, this aldehyde could be a natural alternative to improve properties of gliadin films for its use in different applications.

Keywords: Biomaterials, gliadins, trans-2-hexenal, crosslinking, Schiff base

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Acknowledgements: The authors want to thank the Spanish Ministry of Science and Innovation for financial support project PID2021-123077OB-I00 founded by MCIN/AEI/10.13039/501100011033 and by ERDF A way of making Europe.

VALORIZATION OF POST-CONSUMER POLYPROPYLENE THROUGH THE REINFORCEMENT WITH AMINE AND AMINE/SILANE MODIFIED CLAYS FOR POTENTIAL USE IN FOOD PACKAGING

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Abstract

The mechanical recycling of polymers allows the reduction of pollution caused by the accumulation of plastic waste in the environment and contributes the development towards its sustainability and a circular economy. However, the recycling of polymers involves the deterioration of their properties, which varies depending mainly on the processing conditions and the chemical structure of each polymer, and negatively impacts its processability and physical-mechanical performance [1,2]. Nanocomposites based on flexible post-consumer polypropylene and clays were obtained with varied physical-mechanical performance, depending on the type of organic modifier of the incorporated clays, amine (I.44P) or amine/silane (I.31PS). Clays reduced the water vapor permeability of the post-consumer polypropylene, and interestingly, this effect was more significant by the presence of aminopropyltriethoxysilane as a coupling agent in the clay due to its possible interactions with the oxidized groups of the polymer, which were produced by the thermal-oxidative degradation during recycling. Conversely, oxygen permeability was increased with NI.31PS clay incorporation but was greatly reduced by 1 wt% of NI.44P. The nanocomposite with 3% of NI.31PS presented the higher increase of Young's modulus and tensile strength but its ductility was significantly reduced. The nanocomposites complied with the overall migration limit towards aqueous and fatty simulants. Migration values were lower in 10% ethanol and 3% acetic acid than in olive oil.

Keywords: Recycling, Post-consumer polypropylene, nanoclay, migration

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Acknowledgements: The authors acknowledge the "Ramon y Cajal" Fellowship RYC2020-029874-I financed by the Spanish Ministry of Science and Innovation, and the financial support of "Programa de Financiamiento Basal para Centros Científicos y Tecnológicos de Excelencia" (Project AFB180001).

SUSTAINABLE BIO-BASED MATERIALS FROM MINIMALLY PROCESSED RED SEAWEEDS: EFFECT OF COMPOSITION AND CELL WALL STRUCTURE

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Abstract

The industrial process for the extraction of both agar and cellulose is time and energy consuming so in order to obtain biopolymeric materials for food packaging applications in a more energy efficient way, this study evaluated the use of the whole seaweed biomass to obtain bio-based films. To this end, four different species of agar-producing red seaweeds (*Gelidium sesquipedale*, *Gracilaria chilensis*, *Gracilaria tenuistipitata* and *Gracilaria verrucosa*) were minimally processed using the melt blending technique combined with compression moulding, and the effect of the composition of each seaweed species on the final performance of the films was also been investigated. The seaweed biomass was mainly composed of carbohydrates (35-50%), but significant amounts of proteins, lipids and ashes were also detected. The higher cellulose content of *G. sesquipedale* resulted in stronger films with good water vapour barrier capacity, while the higher agar content of *G. chilensis* improved its elongation capacity. *G. tenuistipitata* and *G. verrucosa*, despite their large compositional differences, produced very similar films in terms of mechanical performance. However, the films made from *G. verrucosa* showed a higher water barrier and water sorption capacity than the other samples also demonstrating a good potential for being used in biopolymer production.

Keywords: biopolymers, agar, cellulose, films, macroalgae

INFLUENCE OF GREEN HIGH HYDROSTATIC PRESSURE PRETREATMENTS ON THE STRUCTURE AND FUNCTIONAL PROPERTIES OF ALGINATE EXTRACTS

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Abstract

This work reports the effects of a novel green approach consisting on applying high hydrostatic pressure (HPP) as a pre-treatment for boosting alginate extraction from *Ascophyllum nodosum* and *Saccharina latissima*. The extracted alginates were characterized in terms of composition (NMR, PAEC-PAD, SEC-MALS, SAXS), functional (antioxidant properties and polyphenol content), and technological properties (rheology, gelling properties, texture, cryo-SEM). The HPP pre-treatment was differently affected depending on the recalcitrant nature of the two algae species used. The HPP pre-treatment was able to effectively increase alginate yields, especially in *A. nodosum*. The alginate extracts from *A. nodosum* presented lower molecular weight, producing softer gels, but neither the M/G ratio nor the M and G sequences were modified. In contrast, the HPP pretreatment increased both the G blocks and the molecular weight of alginate extracts obtained from *S. latissima*. This explained the higher viscosity of the corresponding solutions and the stronger hydrogels formed in this case. These results show the efficiency of the HPP pre-treatment method to produce cost-effective alginate-based extracts with potential applications within the food industry. These results also reveal differences in the cell wall architecture of the two algae families which directly affect the structural properties of the obtained alginates and the corresponding antioxidant and rheological properties (gelling or/and thickening).

Keywords: Alginate, nanostructure, molecular weight, brown seaweed, high hydrostatic pressure (HPP)

Acknowledgments: Grants CEX2021-001189-S, RTI-2018-094268-B-C22 and PID2020-117744RJ-I00 funded by MCIN/AEI/10.13039/501100011033 and, by "ERDF A way of making Europe". H. Bojorges acknowledges financial support from the Generalitat Valenciana for the award of a Santiago Grisolía grant (GRISOLIAP/2019/007).

TOPIC 6

APPLICATIONS IN CARE AND HEALTH PRODUCTS, FOOD AND AGRICULTURE TECHNOLOGY

STERILIZACION OF PERSONAL PROTECTIVE EQUIPMENT WITH SUPERCRITICAL CO_2

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Abstract

The current sanitary situation derived from COVID-19 has caused an increased demand for personal protective equipment (PPE) worldwide, with the economic impact that this is representing as most of these materials are single-use. The use of supercritical CO_2 is emerging as an alternative to sterilize and reuse these materials or their components as raw material (Fig. 1).

In this research, PPE biological components were subjected to sterilization using supercritical CO_2 at 40 ˚C and 100 bar pressure, using as additives mixtures of chemical compounds, such as hydrogen peroxide, peracetic acid and essential oils, among others, in a NovaSterilis equipment with 1 L capacity. Bioindicator strips with spores of *Geobacillus stearothermophilus* ATCC 7953 and *Bacillus atrophaeus* ATCC 9372 were used. To evaluate if the materials were affected in their physical properties, characterization techniques such as DSC and SEM, applied before and after treatment, were used.

Masks, gowns, overalls, caps, and shoe covers were not affected at all, but nitrile gloves and protective goggles suffered alterations. In the biosafety level 3 laboratory of the VISAVET center of the UCM, we are testing the inactivation of the SARS-CoV-2 coronavirus. The $scCO_2$ sterilization is effective for the inactivation of other types of viruses and pathogens, and it is applicable to many types of sensitive materials. It could be established as a new low temperature sterilization technique. Market studies give a very good growth prediction for this type of technology worldwide, especially in the hospital sector. There is technological maturity in the construction of high-pressure equipment, so it would be easily transferable to the industry.

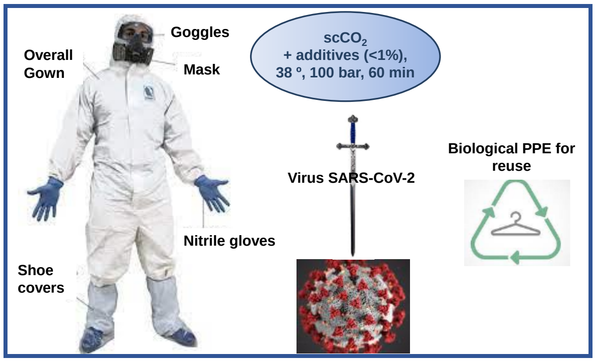

Figure 1. Objective of the ANTICIPA-UCM project. To sterilize all the elements of the biological PPE so that they can be reused or recycled as raw material.

Keywords: sterilization, supercritical CO_2, personal protective equipment, SARS-Co-V-2

Acknowledgements: This study was funded by a REACT-EU grant from the Comunidad de Madrid to the ANTICIPA project of Complutense University of Madrid. ***Figure 1*** *shows the objective.*

GREEN INHALERS CONTAINING BECLOMETHASONE DIPROPIONATE-LOADED AEROGELS

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Abstract

Drug delivery via pulmonary pathways has a variety of advantages for local and systemic treatments[1]. The use of inhalers without propellants (dry powder inhalers DPIs) as devices for this administration route would reduce greenhouse gas emissions. Many factors influence the inhaled particle performance, including lung deposition, flowability, and the percentage of remaining powder after administration. DPIs face additional challenges when delivering poorly water-soluble compounds [1]. Aerogels, known as the lightest solid materials in the world, are capable of producing inhaled porous microparticles with excellent aerodynamic behavior [2]. This work aims to develop green-free propellant inhalers that contained beclomethasone dipropionate (BDP)-loaded alginate aerogel microspheres. Supercritical fluid technology (SCF) was used to obtain alginate aerogels and to incorporate BDP in alginate aerogels by SCF- impregnation with contact times from 1 to 9 h. Textural and physical properties and *in-vitro* aerodynamic performance of obtained aerogel formulations were assessed.

Results: Aerogel particles exhibited a high porosities and specific surface area. Contact time had a significant effect on the loading yield of BDP into carriers (2.4-6.7%wt). BDP loaded in the aerogel microspheres remained in an amorphous state. The obtained powder displayed very good *in vitro* aerodynamic properties (in the range of 1-5 µm), a high Fine Particle Fraction FPF (above 68%), and low drug retention (Emitted Fraction EF>98%).

Conclusion: Green inhalers containing BDP produced from SCF CO_2 are promising for pulmonary drug delivery. Aerogel particles had a low particle cohesion force, good flowability, good aerodynamic performance and relevant BDP doses, which makes them useful for localized drug delivery.

Keywords: Green inhalers, supercritical fluid, alginate aerogels

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Acknowledgements: Th.Duong acknowledges to Fundación José Otero – Carmela Martínez for PhD student at Universidad de Santiago de Compostela, 2022-2023. Work supported by MICINN [PID2020-120010RB-I00], Xunta de Galicia [ED431C 2020/17], Agencia Estatal de Investigación [AEI] and FEDER funds. Work carried out in the frame of COST Action CA18224 (GREENERING) supported by COST (European Cooperation in Science and Technology).

SUPERCRITICAL CO_2 APPLIED ON THE PRODUCTION OF QUERCETIN-LOADED LIPOSOMAL DRY POWDER FORMULATIONS FOR THE TREATMENT OF INFLAMMATORY LUNG DISEASES

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Chronic obstructive pulmonary disease (COPD) is considered by WHO as the third leading cause of death worldwide. In a long-term therapy, COPD treatment based in inhaled corticosteroids (ICS) might cause adverse side ophthalmological and rheumatological. In the last years, the application of natural compounds on medicines has been increased to minimize such ICS's side effects[1]. Quercetin (Querc) is a natural polyphenolic flavonoid, which is present in vegetables and fruits. Querc has remarkable anti-inflammatory properties[2] and when incorporated in liposomes, quercetin's water solubility and permeability are improved, being a candidate for the treatment of inflammatory diseases. However, for a local treatment, particles should be inhaled, comprising a diameter between 1 and 5 µm to reach the deep respiratory region. In this work, we introduce quercetin-loaded liposomal dry powder formulations, obtained through the sustainable and green process – supercritical CO_2- assisted spray-drying (SASD)[3]. To maximize the incorporation efficiency of quercetin after drying process, different compositions of liposome's membrane were studied, as well as the percentage of leucine and ethanol. The resultant powders presented a mass median aerodynamic diameter of 1.7 µm and a fine particle fraction of 63 %, being suitable for inhalation. Resuspended liposomes showed quercetin's incorporation efficiency of 58 %. Cytotoxicity assays were performed for resuspended liposomes and dry powder formulations.

Keywords: Supercritical carbon dioxide, Inflammatory lung diseases, Pulmonary delivery, Flavonoids

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Acknowledgements: C. Costa and A. Aguiar-Ricardo are grateful for the financial support of the Associate Laboratory for Green Chemistry-LAQV, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal, which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020). C. Costa thanks FCT (Fundação para a Ciência e Tecnologia) and ESF (European Social Fund) through POCH (Programa Operacional Capital Humano) for her PhD grant ref. PD/BD/142880/2018 and Project PD/00184/2012-PDQS. M.L. Corvo is grateful for the financial support of the Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Lisbon, Portugal, which is supported in part by UID/DTP/04138/2020 and UIDP/04138/2020 from FCT/MCTES, Portugal.

A GREEN APPROACH FOR THE DEVELOPMENT OF CHITOSAN HYDROGELS USING OLIVE LEAF EXTRACT AS DISSOLUTION AND GELATING AGENT

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Hydrogels are 3D hydrophilic polymeric networks that do not dissolve but can swell, in water. In the last few years, there is increasing interest in these materials thanks to their solid and liquid-like properties, high biocompatibility, easy preparation, and versatile applications. Chitosan is a unique cationic polysaccharide, with well-known antioxidant, lipid-lowering and antimicrobial activities. The cationic nature of chitosan leads, under acidic conditions, to the development of various forms, such as nano/micro-particles, emulsions, fibers, hydrogels, films and membranes. Deep Eutectic Solvents (DES) are mixtures of two or more components, a hydrogen bond acceptor and a hydrogen bond donor, with a low-temperature eutectic point. When the components of the DES are naturally occurring compounds, the solvents are characterized as Natural Deep Eutectic Solvents (NADES).

In the present work, a greener approach towards the formation of chitosan hydrogels is presented. To this end, the ability of olive leaf extract (OLE), obtained using NADES as the extraction and storage medium, to act as dissolution agent for chitosan as well as a gelating agent was investigated. The components of the NADES were selected on the basis of their safety regarding pharmaceutic and food applications as well as on their acidic character which is an indispensable requirement for chitosan dissolution. The formation of chitosan hydrogels is usually a two-step process involving polymer dissolution and physical cross-linking.

Swelling ratio and water retention ratio were measured in the obtained hydrogel based on different molecular weights of chitosan in a hydrochloric acid solution at pH=1.2. The water retention ratio remained over 90%, after keeping the swollen sample in the HCl solution for 2 hours, showing the maximum value at 5 minutes. Furthermore, the ultra-low molecular-weight and low molecular-weight chitosan-based hydrogels-NADES-OLE achieved a water swelling ratio of 136% and 226% after 5 minutes, respectively.

Keywords: Hydrogels, Natural Deep Eutectic Solvents, Olive leaf extract

Acknowledgement: I.P. gratefully acknowledges State Scholarships Foundation (IKY). This research is co-financed by Greece and the European Union (ESF) through the Operational Programme (Human Resources Development, Education and Lifelong Learning) in the context of the project "Strengthening Human Resources Research Potential via Doctorate Research" (MIS-5113934), implemented by the State Scholarships Foundation (IKY).

EXTRACTION AND UTILIZATION OF BIOACTIVES FROM AGRO- AND FOOD INDUSTRIAL WASTES BY GREEN TECHNOLOGIES

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Abstract

In order to meet the EU's environmental goals (EU Green Deal) not only clean technologies are required to be applied but it is necessary to consider the choice of raw materials. An important task is to reduce agricultural and food waste, so that by further extraction, high-quality extracts with bioactivities can be produced before the waste ends up in landfill or as animal feed.

In our work, the successful applications of green technologies for the production of bioactive extracts using various agro-food wastes are summarized. Extracts with as strong antioxidant activity as those of synthetic counterparts (BHT, BHA) were obtained from lavender distillation residue, grape pomace and pomegranate peel. Natural pigments (lycopene and carotenoids) can be obtained from tomato pomace, while grape pomace is an excellent raw material for the production of resveratrol phenolic antioxidant obtained by alcoholic extraction. Applying supercritical carbon dioxide extraction at pressure of 30-45 MPa and temperature of 40-80°C green waxy cream (8.5%) can be obtained from grape pomace, while large amount fragrant oil (12.9-15.2%) can be extracted from pomegranate seed. The main component of this oil is punicic acid (48.1 mg/g oil), which is a unique polyunsaturated fatty acid (C18:3) found only in the seed of pomegranate. Furthermore, extracts obtained from pomegranate peel also inhibited the growth of Gram + *Bacillus subtilis* bacteria by 60-70%. Further the extraction of elderberry pomace was optimized using green solvents (ethanol, ethanol-water and $scCO_2$) and technologies (SFE and UAE). Extracts from late-autumn swept walnut leaves can be also utilized as they possess strong antioxidant properties with high polyphenol contents and strong antimicrobial activities against *B. subtilis* and *E.coli*. Furthermore, the extracts from grape pomace and pomegranate peel rich in polyphenols were successfully applied as plastic stabilizers. Also the environmental impacts of these extracts were studied by microbial and pot studies.

For conclusion, environmentally friendly technologies can be successfully applied to obtain fatty oils, pigments, natural antioxidants and antimicrobial extracts from agro-food wastes, which extracts show applicability in cosmetic-, food- feed and plastic industries.

Keywords: agro- food wastes, green solvents, supercritical CO_2, ultrasound assisted extraction, stabilizers

The separation of biologically active extracts from chamomile seeds

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Abstract

The main aim of this study was to evaluate chamomile seeds as a new source of valuable bioactive compounds. For this purpose, a green extraction technique was employed with supercritical carbon dioxide (sc-CO_2) as a solvent and ethanol as a co-solvent. The extracts from chamomile seeds with an average particle size of 0.20 mm were extracted at pressures of 30 and 45 MPa and temperatures of 40 and 60 °C. The composition of extracts was investigated by a gas chromatography-mass spectrometry analytical method as well as Folin–Ciocalteu assay (for total phenolic content) and total flavonoid content test. The antioxidant activity of obtained chamomile extracts was evaluated using DPPH radical. The antimicrobial effect of extracts was tested on yeasts, Gram-positive, and Gram-negative bacteria while the cytotoxic effect was evaluated on normal and cancer cells. The extraction process parameters were evaluated and results showed a significant effect of operating pressure, temperature, and the addition of co-solvent on the amount of separated chamomile extract and its composition. The extraction yield ranged from 2.1 to 5.4% and extracts contained high amounts of unsaturated fatty acids. The addition of ethanol as a co-solvent (40 w/w%) had a slight influence on total phenolic and flavonoid contents increasing their values from 29.1 to 31.5 mg GAE/g and from 2.1 to 4.2 mg QE/g, respectively. The obtained supercritical chamomile extracts showed antioxidant activity achieving values of IC_{50} around 10 mg/mL. The antimicrobial activity of extracts was most pronounced against *Bacillus subtilis*. Extracts did not show cytotoxic activity against normal cells. Overall, results indicated a significant potential of extracts from chamomile seeds, produced in an environmentally friendly manner, to be used as a functional food or phytopharmaceuticals.

Keywords: Antimicrobial activity, Antioxidant activity; Chamaemelum nobile, Supercritical carbon dioxide extraction, Cytotoxic activity.

Acknowledgements: Stoja Milovanovic acknowledges the scholarship from the Polish National Agency for Academic Exchange (NAWA) from Poland (ULAM PROGRAMME 2020, the agreement number PPN/ULM/2020/1/00023/U/00001). This work was in the frame of the COST Action CA18224 "Green Chemical Engineering Network towards upscaling sustainable processes" (GREENERING) supported by COST (European Cooperation in Science and Technology), Funded by the European Union The Ministry of Education, Science and Technological Development of the Republic of Serbia supported this work (Contract No. 451-03-68/2022-14/200135).

A new and green media for ocular drugs based on Natural Deep Eutectic Systems

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Abstract

More than 2 billion people in the world suffer from some type of vision impairment or blindness, and at least half of them have a treatable or preventable condition using proper treatment. Topical eye drops remain the most convenient route for ocular drug administration; but, the physiology of the eye limits their use, especially because most drug is lost to precorneal drainage and only a small portion is absorbed at the nasolacrimal duct, becoming systemically available. Therefore, during the design of an ocular formulation it is important to increase the retention time of the drug in the ocular surface. There are several strategies for this, but in this work, we explore for the first time the use of Natural Deep Eutectic Systems (NADES) as a new media for ocular drugs, mainly due to their intrinsic viscosity. NADES are composed of natural metabolites hence, greener alternatives for common solvents. Using NADES, it is possible to decrease or even avoid toxic and undesired additives present in ocular applications. Hence, several systems composed of different combinations of sugars, polyols, amino acids, and choline derivatives were prepared. Then, NADES aqueous solutions were characterized in terms of rheological and physicochemical properties. The results obtained showed that NADES solutions have an optimal viscosity profile (0.8 to 1.2 mPa.s). Moreover, other parameters were also within the standard values including osmolarity (412 to 1883 mOsmol), and pH (7.4). Additionally, contact angle and refractive index were determined. Furthermore, the selected systems showed low cytotoxicity towards retinal epithelium cells (ARPE-19 cells).

In summary, NADES have promising physical and chemical properties to be used during the design of ocular formulations.

Keywords: ocular drugs, natural deep eutectic systems, drug delivery, ocular diseases.

Acknowledgements: This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Programme, under grant agreement No ERC-2016-CoG 725034 and ERC Proof of Concept Grant, CryoDES. This work was also supported by the Associate Laboratory for Green Chemistry – LAQV, financed by national funds from FCT/MCTES (UID/QUI/50006/2019), by FCT/MCTES through the project CryoDES (PTDC/EQU-EQU/29851/2017) and FCT for the PhD grant 2021.07457.BD.

IMPREGNATION OF THYMOL IN BIOFILMS FOR ACTIVE FOOD PACKAGING USING SUPERCRITICAL CARBON DIOXIDE

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Active food packaging offers the shelf-life extension and kill or inhibit microorganism growth of the product, enhanced quality, and safety of food products. This can be accomplished by the incorporation of volatile antimicrobial and antioxidant compounds (active agents) into the food packaging material and their subsequent release from the packaging material. Extrusion, the traditional process for incorporating active agents into plastic films, cannot be applied for the incorporation of such compounds due to the high processing temperatures that can lead to the volatilization or degradation of the active agents. As an alternative, the supercritical impregnation using carbon dioxide (CO_2) as solvent can be applied. The organic compounds dissolved in supercritical CO_2 ($scCO_2$) are not susceptible to thermal degradation, because the critical point of CO_2 is relatively low (31ºC) and its high diffusivity can provide high active agent loading. As active agents are preferred molecules of natural origin are instead of synthetic ones. Essential oils or terpenes are typically volatile natural extracts with strong antimicrobial and antioxidant capacities. Waste from petroleum-based plastic packaging causes pollution and environmental problems, therefore they need to be substituted by biodegradable plastics.

In this work, the supercritical impregnation using CO_2 was studied as a promising technique for the incorporation of terpene thymol into thermoplastic starch (TPS), poly(butylene adipate terephthalate) (PBAT) and polybutylene succinate (PBS) films as a potential biodegradable active packaging materials and plastic polyethylene (PE) for comparison with conventional thermoplastic films. The films were made by a thermoforming process. Impregnation experiments were carried out with $scCO_2$ at 10 and 14 MPa and 40 °C. The time of impregnation was 1-8 h. High impregnation yields of PBAT and PBS films ~15 %w/w were achieved already in 1 hour of supercritical impregnation at 40 °C and 10 MPa, whereas PE films reached only ~0.5 %w/w. Mechanical properties were tested for all materials. It was shown that tensile strength (%) for PBS was doubled respect raw material. Finally, DSC and FTIR analysis were performed to determine thermal properties as well as the nature of the interactions between thymol and the polymers.

Keywords: active packaging, supercritical impregnation, biofilms

Acknowledgements: This work was supported by the Regional Government of Castilla y León (Spain) and the EU-FEDER program (CLU-2019-04).

NADES GOODNESS liquid food supplements

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Abstract

Petroleum-based solvents are currently used in all areas of industry, and these solvents are toxic, flammable, and volatile. Also, these solvents are the cause of 60% of all industrial emissions and 30% of emissions of volatile organic compounds. Despite all of the above, the fact is that in the 21st century according to the directive 2009/32/EC (Food) it is still allowed to consume 2.9 mg/kg of hexane or 6 mg/kg of dichloromethane per day. The goal of green deal is to replace such solvents in an ecological way acceptable alternatives. NADES solvents are mixtures of at least two metabolites from nature and are liquids at room temperature. These solvents are non-toxic, biodegradable, and non-volatile, which ensures safety for workers in industries and is favorable for the environment.

Our products are plant extracts in 100% green bio-solvents named natural deep eutectic solvents (NADES) - that can fully replace used toxic solvents in industry. NADES can be found throughout nature, even in the human body. Using those solvents, 3 novel food supplements were developed - plant-based extracts for application in food industry. First, food supplements were designed using COSMOtherm software in agreement with regulatory aspects and market research studies. Secondly, lab-scale studies were performed. Solubility of active molecules – polyphenols from plants were enhanced 100 x compared to the conventional extraction solvent. The NADES-based extracts are 100% non-toxic and biodegradable. The shelf life at room temperature is prolonged for 3 months. Finally, products will be produced in outsourced laboratory and registered.

Keywords: food supplements, natural deep eutectic solvents, plant extracts

IN VITRO ASSESSEMENT OF THE PERFORMANCE OF POLYMERIC MEMBRANES ENCAPSULATED WITH LAVENDER ESSENTIAL OIL FOR WOUND HEALING

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Abstract

Wounds are a common medical problem associated with discomfort and pain that result from any skin trauma[1]. Although this is an omnipresence problem, there are very few treatments capable of increase wound healing. Therefore, there is the need to find alternative solutions to hasten wound healing combined with antimicrobial and anti-inflammatory properties. Lavender essential oil (LEO) as already been described as a wound healing enhancer though its capacity to accelerate wound contraction and its antimicrobial, analgesic and anti-inflammatory properties[1,2]. Therefore, four membranes were developed (Chitosan (CHT), Alginate (ALG), ALG+LEO and CHT/ALG+LEO), using $CaCl_2$ 2% (w/v) as crosslinker. The membranes were tested on HaCaT cell line to evaluate their behaviour when in contact with skin cells. For that, viability and biocompatibility tests were performed as a combined result of the effect of membrane leachable on cell viability, cell adhesion to the membranes (DAPI-Phalloidin staining) and consequent DNA quantification. The LEO release profile shows that after 48h at least 35 mg/L of LEO is released, which is a concentration non-toxic for HaCaT cells like it is supported by the leachable results. In fact, the membrane ALG/CHT +LEO significantly increases cell proliferation in around 10%. In terms of direct contact assessment towards HaCaT cells, it was observed that there is an impact on HaCaT cells proliferation capability, reflecting that the surface of the synthesized membranes is not ideal for cell proliferation. These results suggest suitability of CHT/ALG+LEO-based membranes to be used as patches for wounds.

Keywords: Wound Healing, Lavender Essential Oil, Chitosan, Alginate

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VOC ADSORPTION BY MEANS OF ACTIVATED CARBONS DERIVED FROM WASTED COFFEE GROUNDS AND OLIVE STONES

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Abstract

Typical everyday waste materials such as agricultural by-products, food waste, and industrial by-products, are potential precursors of activated carbon. Furthermore, these materials need an environmentally friendly way of reducing the problems related to their disposal. In this work, as bio-precursors of porous carbons, we have chosen coffee grounds and olive stones and we studied physical and chemicals properties within the adsorption capacity of Volatile Organic Compounds (VOC) as typical indoor pollutants. Firstly, the biomasses were pyrolyzed at 500°C and biochars were obtained, and then microporous activated carbons were produced by means of chemical (K_2CO_3) and physical (CO_2) activation. The influence of the activation process, type, and time of activation have been also investigated. The physico-chemical properties were characterized by N_2 and CO_2 isotherms, SEM, TGA and FTIR. Measurements of VOC adsorption were performed in a 17L chamber, at room temperature for 120min and Methyl Ethyl Ketone (MEK) was chosen as a model of VOC. The concentration was monitored using a photoionization detector (PID). As expected, carbon without activation (biochars) showed the lowest surface area equal $330 m^2 g^{-1}$ and hence the lowest adsorption capacity. The surface for chemically activated carbons area was respectively $1487 m^2 g^{-1}$, and $870 m^2 g^{-1}$, from coffee grounds and olive stones, whereas physically activated carbons yielded values of $716 m^2 g^{-1}$, and $778 cm^2 g^{-1}$, respectively. The highest adsorption capacity value (80% after 120min of exposure) for MEK was detected for the coffee grounds chemically activated carbons, the one with the highest surface area.

Keywords: Agriculture waste valorization, biomass, adsorption, depollution, VOC

Acknowledgements:
Production of biomass derived activated carbons was carried out during STSM (Short-Term Scientific Mission) at the Nova University in Lisbon, Portugal, under the supervision of Dr. Maria Bernardo and Dr. Ines Matos, thanks to financial support from Greenering Cost Action CA18224 (www.cost.eu)

CHEMICAL COMPOSITION, ANTIOXIDANT AND ANTIBACTERIAL POTENTIAL OF *Diplolepsis rosea* GALLS

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Abstract

Rosa canina is a medicinal plant that belongs to the *Rosaceae* family and it is largely used in traditional folk medicine due to many beneficial health effects. Unfortunately, this plant is often attacked by insects, such as *Diplolepis rosae*, which can induce the formation of galls on the plant's leaves. Galls can be found in sizes from 5 mm to 8 cm, and they look like bulges covered with thick yellow-green shades of hair. Interestingly, interactions of plants and insects resulting in gall formation are considered to have stimulating effect on plant chemical defence mechanism. Therefore, in this study gall of *D. rosae* formed on *Rosa canina*, which is collected from Eastern part of Serbia, was analysed. In sample was determed content of bioactive compounds (polyphenolics, carotenoids and vitamin C) and antioxidant activity (DPPH, ABTS and reducing power assay). The results show that content of bioactive compounds were: polyphenolics 186.37 mg/g dw, carotenoids 44.1 μg/g dw and vitamin C 64.43 mg/g dw, while antioxidant assays have shown the scavenging activity against DPPH• and ABTS•+ to be 1520.71 mM TE/g dw and 6366.70 mM TE/g dw, respectively, and reducing power to be 1078.42 mM TE/g dw. Furthermore, samples are evaluated for antibacterial activity against two Gram-positive and two Gram-negative cultures of microorganisms. The extracts have shown to have antibacterial effect against *Staphylcoccus aureus*, *Enterococcus faecalis* and *Pseudomonas aeruginosa*. Therefore, this study shows that galls of *D. rosae* formed on *Rosa canina* are rich in bioactive compounds and due to expressed antioxidant and antimicrobial activity have potential to be used as a new antibacterial agent.

Keywords: Rosa canina, Diplolepis rosae, bioactive compounds, antioxidant activity, antimicrobial activity

Acknowledgements: This research study was funded by the Ministry of Education, Science, and Technological Development of the Republic of Serbia (Grant No. 451-03-9/2022-14/200134).

EFFECTS OF SUPERCRITICAL CO_2 STERILIZATION ON THE PHYSICOCHEMICAL PROPERTIES OF BIOAEROGELS

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Abstract

Aerogels are lightweight materials with high specific surface area and open porosity. Aerogels can be produced from many sources and customized morphologies finding applications ranging from aerospace engineering to biomedicine. For the latter purpose, the use of aerogels made from natural polymers (bio-aerogels) as grafts is of great interest due to their bioactivity, biocompatibility and biodegradability. The main limitation of these implantable materials is ensuring the sterility to avoid life-threatening infections while maintaining their future functionality. Current hospital sterilization techniques (steam, gamma radiation, ethylene oxide) cause changes in the structure and physicochemical properties of the material or results in the presence of toxic residues after the process. Supercritical carbon dioxide ($scCO_2$) is proposed as a green and efficient sterilization technique, operating under mild working conditions and leaving no residues in the final product [1]. In this work, $scCO_2$ sterilization process was used for the treatment of aerogels made of alginate and starch in two different morphologies, beads and monoliths, respectively. Three types of $scCO_2$ exposure regimes were used: static, dynamic and combined. Commercial *Bacillus pumilus* spore strips contatining 10^6 spores were used as a biological indicator to evaluate the sterilization efficacy. Moreover, physicochemical properties of the aerogels were characterized before and after the sterilization treatment by scanning electron microscopy (SEM), N_2 adsorption-desorption tests and gas pycnometry to evaluate any relevant changes in the nanostructure. Preliminary results show effective sterilization of the material after being subjected to sterilization with scCO2 and showing varying physicochemical changes depending on the polysaccharide source.

Keywords: Supercritical CO2, Sterilization, Biopolymers, Aerogels.

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ENANTIOSELECTIVE SUPERCRITICAL FLUID CHROMATOGRAPHY SEPARATION OF CHIRAL ANTICOAGULANT RODENTICIDES

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Abstract

Supercritical fluid chromatography (SFC) is a separation technique which has increased in popularity due to its similarity to liquid chromatography but with the advantage of being considered as *"green"* technique, due to the main component of the mobile phase is CO_2. The application of SFC has showed excellent results in many different scientific fields because it allows obtaining good results in terms of efficient, robust and fast separations [1].

Anticoagulant rodenticides (SGARs) have been used to control wild rodent infestation and to reduce the associated crop damage [2]. This fact explains the possible appearance of rodenticide residues in urban and agricultural environments as well as the importance of analytical methods to monitor them in different samples. Second generation of SGARs are chiral pesticides, while pure enantiomers of chiral compounds have identical physical-chemical properties, their toxicity, and their environmental impact may be different. Due to these facts, the role of chirality in environmental chemical pollution cannot be underestimated making necessary a novel suitable analytical methodology able to distinguish between the enantiomers of a chiral compound and to determine them individually.

The aim of this work was optimization of the separation of seven different SGARs chiral centers: one achiral, three with two chiral centers and four with only a chiral center that means a total of nineteen compounds perfectly resolved with SFC coupled to ultraviolet (UV)-mass spectrometer (MS) detector. Hence, a screening of eight different chiral stationary phases, different mobile phase and several conditions of pressure/temperature were tested in order to achieve the enantiomeric separation of all rodenticides. Finally, the proposed method was applied to the determination of the persistence of these residues in agricultural samples.

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Keywords: Supercritical Fluid Chromatography, Rodenticides, Chiral, Enantiomers;Pollution

RHEOLOGICAL PROPERTIES AND INHIBITORY EFFECT ON DIGESTIVE ENZYMES OF MODEL BEVERAGES WITH SAFFRON FLORAL BY-PRODUCTS

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Abstract

Despite the rapid and dynamic evolvement of research into dietary polyphenols, there is still a knowledge gap regarding their bioaccessibility, since chemical and nutritional compositions of the food matrix are critical factors that could influence their interactions, digestibility, bioaccessibility and bioavailability. The main objective of this research was to develop functional model beverages incorporating saffron floral by-products, a promising phenolic-rich biomass that is currently unexploited, to understand the impact of the food matrix in achieving the positive health effects. The development of model beverages was carried out incorporating saffron floral waste as a minimally processed sustainable ingredient, with the addition of different thickeners (xanthan gum, guar gum, beta-glucan, pectin). The inhibition of digestive enzymes of the beverages before and after the heat treatment as well as their rheological properties were monitored using a Discovery series Hybrid Rheometer (HR-2) from TA Instruments by measuring concentric cylinder geometry. For each test solution, shear stress (τ in Pa) vs. shear rate ($\dot{\gamma}$ in s^{-1}) profiles were measured for shear rate ranging 10^{-1} to 10^{3} s^{-1}. Regarding the inhibitory activity of phenolic compounds on digestive enzymes, alpha-amylase inhibitory activity was only present in some heat-treated samples. This fact may be related to the thermal processing that would enhance the release of phenolic content from the plant material due to the hydrolysis of polysaccharides. However, in the presence of fibers, as pectin and beta-glucan, enzymatic inhibitory activity was not detected since fibers tend to retain the bioactive compounds, so that the bioavailability of several polyphenols might be reduced. Furthermore, the rheological properties of beverages could influence the bioaccessibility of polyphenols providing in-depth information on the structural changes associated with food processing treatments such as thermal heating. All the samples studied exhibited non-Newtonian behavior: model beverages without thickener, with pectin and with beta-glucan showed a dilatant flow behavior, but model beverages with xanthan gum and guar gum exhibited a pseudoplastic flow behavior. Therefore, this study provides new information on the functional activity of saffron flower model beverages to ensure that they exert the beneficial effects, without applying extraction and purification techniques of saffron bioactives. The minimal processing of the raw material could be an important issue for the food industry, involving minimal transformation and implementing sustainable production processes reducing the generation of waste and the environmental impact.

Keywords: sustainability, saffron floral bio-residues, valorization, environmental impact, model drinks

Acknowledgements: Thanks to Green Chemical Engineering Network towards upscaling sustainable processes (CA18224)—GREENERING funded by COST (European Cooperation in Science and Technology) for the STSM grant. Funding: This article is supported by the Partnership for Research and Innovation in the Mediterranean Area (PRIMA) program, project SAFFROMFOOD.

THERMAL STABILITY OF CHITOSAN COATED PACKAGING PAPERS

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Abstract

Paper as a nonhomogeneous sheet material that is made essentially from fibers of plant origin is suitable for a weight variety of packaging applications. Based on the type of coating or finishing processes it could be a key material with an extremely wide range of properties, optimal for printing and wrapping; care and health products; food or agriculture and others. Paper aging depends not only on the depository conditions of the paper (temperature and relative humidity), the degree of light and temperature exposition, and some microbiological factors but also on the chemical composition of the fiber raw material and chemical additives used. Chitosan has been stated to be used as wet-end additive and as a coating in paper-manufacturing process, to improve barrier, mechanical and optical properties of variety of paper grades. On the other hand, it could be used as crosslinking agent. In this sense and in line with the increased chitosan treated or coated paper consumption as printing and wrapping papers, the aging stability of these papers is of a vast scientific and applied interest. In accordance with the above written, in developing this experiment, the aim was to prepare and study the thermal stability of chitosan-coated wood-free wrapping paper. Pulp sample and four paper samples (three of them coated with different chitosan quantity) have been examined for their structural-dimensional and strength properties together with the focus of the experiment – accelerated thermal aging at temperature of 105 °C and duration of 72 h and dynamic thermogravimetric analysis (TGA). The degree of color changes in the CIE Lab color space have been studied, bearing in mind that the changes in color characteristics define the stability over time and even more – the influence of chitosan coating. As a result, of the studies carried out it was found out that with increasing the chitosan coating, the ageing stability also increase, due to the improved crosslinking proses between chitosan and paper. During 72 h of accelerated thermal ageing, the color of the coated paper becomes yellowish corresponded to the amount of chitosan. The change of the weight of the paper samples as a function of temperature was monitored by TGA. When comparing the weight losses, it was found out that with increasing the chitosan coating the temperature of complete burning of the sample increased to 2.6 °C. In addition, the surface of the coated paper samples is more even and with increased barrier properties.

Keywords: Chitosan, Coating, Papermaking, Ageing, Thermal stability

Acknowledgements: Authors gratefully acknowledge the financial support of Scientific Research Fund, Bulgaria under project № 920 (КП-06-Н49/1).

TO CHOOSE OR NOT TO CHOOSE HYDROPHOBIC DEEP EUTECTIC SOLVENTS FOR PHARMACEUTICAL APPLICATION

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Abstract

Recently, a new window is opened with subclass of DESs, a hydrophobic DESs (hDESs), which application could be of great value for the pharmaceutical and cosmetic industry. It could be expected that hDESs can overpass the problems that occur with substances poorly soluble in water by increasing their solubility, permeability and stability. To be safely used in aforementioned industries it is of great importance to test hDESs cytotoxicity, solubility and permeability potential. Therefore, in the presented work we have prepared eight hDESs which are physico-chemically characterized and their cytotoxic profile was assessed on two human cell lines. The Parallel Artificial Membrane Permeability Assay (PAMPA) was applied as an *in vitro* model of passive permeation to determine potential of hDESs to be used as a solvent or a carrier for different compounds of interest. Furthermore, properties important for stability of formulation are also assessed i.e. antioxidant and antimicrobial potential of eight synthetized hDESs were evaluated based on ORAC method and disc diffusion assay.

Keywords: antioxidant activity, antimicrobial activity, hydrophobic deep eutectic solvents, physico-chemical characterization

Acknowledgements: This work was financed by HRZZ (Croatian science foundation) IPP-2019-04-7712

VALORISATION OF ORANGE PEELS USING DEEP EUTECTIC SYSTEMS

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Abstract

Nowadays, one of the main concerns in the agricultural and food industries is their waste production and how it can be reduced. For instance, in the production of juices, large quantities of oranges are processed which generates large quantities of by-products. The by-products, such as peels, seeds and pulp account for more than half of the fresh fruit weight. Although the primary valorisation process for orange peels (OP) focuses on the recovery of essential oils or pectin, there are other compounds of interest, such as, naringin, hesperidin, narirutin, and neohesperidin, that could also be recovered. These natural antioxidants have a huge importance since they can replace synthetic additives such as BHA and BHT, which might be toxic or even carcinogenic. One way to valorise these by-products is by extracting its bioactive compounds using a new class of green solvents called deep eutectic systems (DES). The main objective of this work was to assess different hydrophilic DES for the extraction of bioactive compounds from orange peels and to optimize the extraction conditions such as ratio DES/raw material, extraction time, and temperature. Taking this into account, total phenolic content and antioxidant activity were determined in the final DES extract. DES extracts were compared with a conventional extraction method, using an hydroalcoholic mixture as extraction solvent. The latter obtained a total phenolic content of 14 mg GAE/g_{OP}, while DES extracts presented contents of total phenolics between 12 and 38 mg GAE/g_{OP}, representing significant improvements in the yield of the extraction. In this work, the antioxidant activity was also assessed *in vitro* through the reactive oxygen species assay in HaCat and Caco-2 cell lines and finally the cytotoxicity of the extracts was also evaluated.

Keywords: Orange peels, Deep eutectic systems, Extraction, Bioactive compounds, Antioxidants.

Acknowledgements: This work was supported by the Associate Laboratory for Green Chemistry- LAQV which is financed by national funds from FCT/MCTES (UID/QUI/50006/2019) by Fundação para a Ciência e a Tecnologia through PhD grant 2022.12770.BDANA and by DES Solutio - Scientific Consulting Solutions Lda,.

CHLORELLA VULGARIS AND *TETRADESMUS OBLIQUUS:* IMPACT OF PRETREATMENTS ON SUPERCRITICAL CO_2 EXTRACTION YIELD AND CYTOTOXIC ACTIVITY OF EXTRACTS

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Abstract

In this work different pretreatments were applied to enhance the supercritical carbon dioxide ($scCO_2$) extraction yield of microalgae *Chlorella vulgaris* and *Tetradesmus obliquus*. Furthermore, the obtained extracts were investigated with regard to the activity towards cancers (HeLa and MDA-MB-453) and normal cells (MRC-5). $ScCO_2$ extraction was conducted at conditions 300 bar and 40°C, while the pretreatments were conducted under the following conditions: microwave - irradiation power 800 W and time 3 min; ultrasound - temperature 60°C and time 5 min, and enzymatic - incubation temperature 45°C and time 60 min, conducted with Viscozyme enzymatic solution.

It was determined that the application of the pretreatments resulted in a significant increase in the extraction yield of *C. vulgaris* and *T. obliquus* compared to the control extraction (without the pretreatment). For both microalgae, the most prominent increase was recorded after the microwave pretreatment, where the extraction yield of *C. vulgaris* (1.06%) was increased by 2.5 times compared to control (0.41%). Moreover, the application of the microwave pretreatment of *T. obliquus* resulted in a 3.37% extraction yield compared to the control (0.06%). In addition, the pretreatments impacted the activity of the extracts against cancer cells. *C. vulgaris* extracts were more active against the cancer cells than *T. obliquus* extracts. IC_{50} values of *C. vulgaris* extracts against HeLa cells were 208-232 µg/mL, while towards MDA-MB-453 the were 178-190 µg/mL. The most potent extract was the *C. vulgaris* extract obtained after the enzymatic pretreatment. The lowest IC_{50} value (332±30 µg/mL) of *T. obliquus* extracts was determined for the extract with the ultrasound pretreatment. The results of the study demonstrated that the application of pretreatments can significantly improve the exploitation of the microalgae biomass and the biological activity of the obtained extracts.

Keywords: microalga; Chlorella vulgaris; Tetradesmus obliquus; supercritical carbon dioxide; pretreatment

Acknowledgements: This work was supported by the Bilateral project Portugal-Serbia 5554/2020 (FCT) and 337-00-00227/2019-09/72 (Serbia) and Serbian Ministry of Education, Science and Technological Development (451-03-9/2021-14/200134).

Morphological control of Ciprofloxacin micronized by the Supercritical Antisolvent Technique (SAS).

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Abstract

Ciprofloxacin (CIP) is a broad antibiotic spectrum which is currently used to treat different infections[1]. Here we propose the use of supercritical CO_2 ($scCO_2$) as a green solvent for the preparation of a CIP inhalation device. The recommended particle size for inhalation is ≤ 5 µm, to allow a deeper distribution in the airways, so micronization of the drug is required. Reduction of the drug particle size improves its bioavailability, reducing the adverse effects. The addition of excipients (PVP K30, PVP K10 and lactose) changed the particle shape and size.

Micronization was performed using the Supercritical Anti-Solvent (SAS) technique. The apparatus and experimental procedure have been previously described[2]. Ciprofloxacin hydrochloride hydrate alone or mixed with different excipients (25% mass) was dissolved in methanol and sprayed into the precipitation chamber filled with $scCO_2$ through a 100 µm nozzle at a flow rate of 1.5 mL/min forming droplets. $scCO_2$ was also pumped into the chamber at 20 g/min. $scCO_2$ mixed with the methanol, leading to the expansion of the methanol solution, its supersaturation and the precipitation of the drug. Particles were collected in the chamber whilst CO_2 and methanol flew through the BPR to a cyclone separator. The precipitate was extensively washed with $scCO_2$ to completely remove the solvent. Experiments were performed at 40-50 ºC and 12.0-15.0 MPa.

The precipitates were characterized using SEM, XRD, FTIR and DSC. SEM micrographs of the precipitate showed elongated particles of submicron width and up to 5 µm long, demonstrating the successful micronization of the drug. Morphology and size were similar to those found for the precipitation of Ciprofloxacin base from ethanol[3]. The addition of excipients led to greater changes in morphology and particle size. Particles coprecipitated with PVP K-10 were submicron in size and exhibited a regular polyhedral morphology. This nanocomposite could be used as a good oral delivery system.

Keywords: Supercritical CO_2, micronization, drug delivery.

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Acknowledgements: We acknowledge financial support from the Spanish Ministry of Economy and Competitiveness (MICINN), research project RTI2018-097230-B-100. F.Z. thanks the Ministry of Higher Education of Egypt for funding his research stay at UCM.

MICROBIAL INACTIVATION OF SANITARY MATERIAL WITH SUPERCRITICAL CO_2

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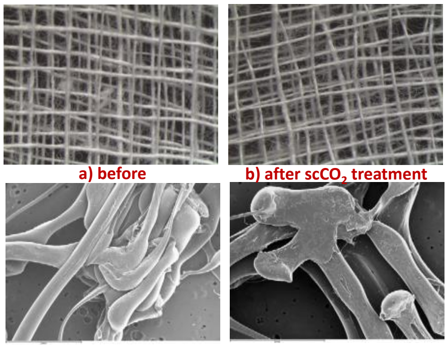
Abstract

The bacterium *Staphylococcus epidermidis* is the main cause of most infections related to sanitary material and to prosthesis insertion. In this work, experiments were carried out evaluating its inactivation in a sterile gauze and a polymer used in 3D printing (PVA), using supercritical CO_2 ($scCO_2$) alone and in combination with essential oils (EOs) such as lemon, cinnamon, oregano, clove and mint, and their bioactive components as thymol. The operating conditions were 10 MPa and 40°C for 30 min, and concentrations of 200 to 1000 ppm were used.

The $scCO_2$ treatment by itself achieved a two orders of magnitude reduction in *S. epidermidis* contamination. The EOs, which have antimicrobial power by themselves, improved the efficacy of $scCO_2$, being mint essential oil, the best. With a low concentration of 200 ppm, it was possible to achieve four log reductions, and with 500 ppm, the total inactivation. The same quantities of water alone were tested to evaluate the possible moisture in the materials used in practice. At 200 ppm 3.6 log reductions were achieved, at 1000 ppm 4.5. This result indicates that under humid atmosphere, microbial inactivation by $scCO_2$ is easier. However, adding water would not be an option for hydrolysable materials, such as the 3D polymeric implants used in this work. For them, the solution would be the use of essential oils.

The integrity of the materials after treatment with $scCO_2$ was evaluated using DSC and SEM. In the gauze, no appreciable changes were observed, but some voids and delaminations appeared in the polymer (Figure 1). In addition, there was a significant reduction in its *Tg* after CO_2 absorption and subsequent release in gaseous form during depressurization.


a) before

b) after $scCO_2$ treatment

Figure 1. Above magnifying glass images of the fibers of the gauze and below SEM images of the fibers of a PVA 3D print, before and after treatment with $scCO_2$.

Keywords: sterilization, supercritical CO_2, essential oil, medical materials

Acknowledgements: This study was funded by a REACT-EU grant from the Comunidad de Madrid to the ANTICIPA project of Complutense University of Madrid

(RE)VALUATION OF WINE INDUSTRY BY-PRODUCTS USING OHMIC HEATING AS AN EMERGING TECHNOLOGY

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Abstract

Grape Pomace (GP) resulting from wine industries can cause serious environmental and economic impacts. However, these by-products are often undervalued but constitute a potential source of bioactive and functional compounds that can be applied in several food and pharmacological industries. This work aimed to study the chemical and bioactive value of GP extracts. Ohmic heating (OH) was compared to conventional heating extraction, using water and 50% ethanol for phenolics recovery. Extracts were evaluated for their content in total phenolics (TPC), total flavonoids (TFC), and total anthocyanin's (TA). Their potential antioxidant capacity was assessed by chemical assays (DPPH, FRAP) and cellular ROS assay (DCFDA/H2DCFDA), and its toxicity was assessed in normal (L929, HEK293t) and cancer (Caco-2, HeLa) cells. Moreover, individual phenolic compounds were identified and quantified by HPLC, and GP structure was assessed by Scanning Electron Microscopy (SEM). The use of the OH method increased the extraction of phenolics, especially when using 50% ethanol as solvent. In addition, UHPLC-DAD analysis allowed the tentative identification of 15 phenolic compounds. All the GP extracts presented high *in vitro* antioxidant activity, preventing oxidative stress (ROS) in normal and cancer cells. Moreover, selected ethanolic extracts showed low cytotoxicity and selective activity against cancer cells as these were negatively affected. These features indicate that the extracts may be appropriate as bioactive ingredients and food preservatives, but they also show potential application on the pharmaceutical or nutraceutical sectors. Furthermore, OH proved to increase the extraction yield of bioactive phenolic compounds from the wine industry by-products.

Keywords: Electric fields, Phenolic compounds, Grape pomace, Waste valorization, Bioactivity.

Acknowledgments: This work was supported by the Portuguese Foundation for Science and Technology under the scope of the strategic funding of UIDB/04469/2020 unit and by LABBELS – Associate Laboratory in Biotechnology, Bioengineering and Microelectromechanical Systems, LA/P/0029/2020. Also by the European Regional Development Fund (ERDF) through the Competitiveness factors Operational program – Norte 2020, COMPETE and by National Funds through the FCT - under the project AgriFood XXI (NORTE- 01-0145-FEDER-000041). Pedro Ferreira-Santos would like to express gratitude to the Spanish Ministry of Science, Innovation and Universities for financial support (FJC2021-046978-I).

BIODEGRADABILITY ASSESSMENT OF CHOLINE-BASED PROTIC IONIC LIQUIDS AND DEEP EUTECTIC SOLVENTS

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Abstract

Protic Ionic Liquids (PILs) as well as Deep Eutectic Solvents (DES) are considered as promising solvents with desirable physicochemical properties for a variety of applications. They are considered as greener alternatives to common organic solvents but in order to efficiently be characterized as green their environmental impact has to be assessed . The use of biodegradable and non-toxic or of low toxicity compounds, are in accordance with the principles of green chemistry. Taking advantage of the task-specific design and the structure-properties relationship of both PILs and DES, the design of biodegradable green solvents becomes a feasible objective [1-3].

In the present study, the design, synthesis and an initial potential hazard assessment in aquatic system of 9 choline-based PILs and 7 choline-based DES is presented. The biodegradability was assessed according to a standard method by measuring the biological oxygen demand closed bottle test in five days (BOD_5).

Most of the studied choline-based green solvents could be characterized as "readily biodegradable" since, in some cases, the biodegradability of the PILs reached up to 81.3% while regarding the DES the & biodegradability reached up to 95.5%. Finally, the effect of modifications on the ILs' anions and the hydrogen bond donor of the DES on their environmental impact and some of their most important physicochemical (such as polarity and viscosity) properties has been investigated.

Keywords Biodegradability, BOD_5, Green Solvents, Natural Deep Eutectic Solvents, Ionic Liquids

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Acknowledgements: Funding by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH-CREATE-INNOVATE, grant number T2EDK-0233, "Green_Wild_ ROSE.gr" is gratefully acknowledged.

PREPARATION OF DRUG PARENTERAL FORMULATIONS FOR THE TREATMENT OF VISCERAL LEISHMANIASIS

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Abstract

Visceral Leishmaniasis is a parasite-transmitted disease that causes more than 60.000 deaths every year. The most common treatment is a liposomal formulation of Amphotericin B (AmB) of 70 nm diameter, called Ambisome®. The aim of this project was to obtain an alternative formulation through Supercritical Fluid Extraction of Emulsions (SFEE). AmB was coupled with a hyperthermia agent Superparamagnetic Iron Oxide Nanoparticles (SPIONs), and encapsulated in poly(D,L lactide-co-glycolide) (PLGA).

From a double emulsion in which the inner aqueous phase contained the SPIONs and the organic phase contained Amb and PLGA, the solvent was extracted with CO_2 at 9 MPa, 313 K and a flow rate of 2.2 g min^{-1}. The emulsion droplets acted as a stencil, resulting in particles with an average size of 600 ± 200 nm that were suspended in the outer aqueous phase and stabilized by the surfactant Tween 80. For comparison, particles were also produced with reverse phase evaporation (REV) leading to larger average size of 900 ± 100 nm. They could be used to address passive targeting, as particles larger than 400 nm are phagocytized preferentially by macrophages.

The spherical morphology of the particles was confirmed by TEM (see Figure 1), while the encapsulation efficiency was > 95%. The loading of the particle with AmB was about 33 %. Amphotericin release tests in the presence and absence of a magnetic field were compared with the release kinetics of the commercial formulation Ambisome®.

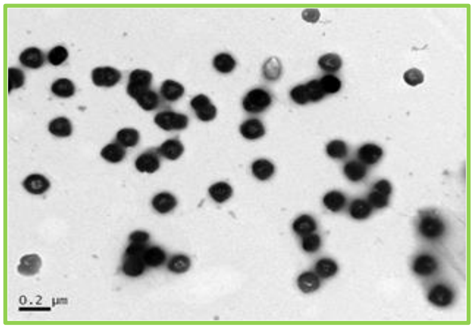

Figure 1. TEM images of the SFEE produced particles. The inner core contained the AmB and the SPIONs. The outer shell was made by the PLGA.

Keywords: Supercritical Fluid Extraction of Emulsions, nanoparticles, Amphotericin B, SPIONs,

Acknowledgements: Ministry of Science, Innovation and Universities, project RTI2018-097230-B-I00.

TOPIC 7

SCALE-UP AND INDUSTRIAL APPLICATIONS

SCALE-UP OF A NEW FLEXIBLE PROCESS FOR PHOSPHORUS AND PHA RECOVERY FROM SEWAGE SLUDGE AND ORGANIC WASTES TREATMENT

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Abstract

In the wastewater sector, Volatile Fatty Acids (VFAs) can be used to support and increase the removal of nutrients (nitrogen and phosphorus) both in conventional biological processes with activated sludge and in Enhanced Biological Phosphorus Removal processes (EBPR). Alternatively, a possible application for VFA, is to recover bio-polymers, including PHA (polyhydroxyalkanoates). These polymers, which can be used as bases to produce bio-plastics, are thermoplastic, biodegradable and biocompatible materials. In this context, a new flexible process for the building on the results of the H2020 SMART-Plant Innovation Action, the Short-Cut Enhanced Phosphorus and PHA-Recovery (SCEPPHAR) system was fully scaled-up within the CIRCULAR BIOCARBON BBI JU project to integrate the existing Sesto San Giovanni Anaerobic Digestion section (Italian wastewater treatment plant). The sidestream SCEPPHAR process was developed by the University of Verona and Politecnica delle Marche to treat sludge liquor, which is highly loaded with nutrients nitrogen (N) and phosphorus (P). It is composed by: (i)Sequential Batch Reactor dedicated to Nitritation (N-SBR) of the anaerobic sludge reject water; (ii)Sequential Batch Reactor dedicated to the selection of PHA storing biomass by the alternation of aerobic-feast and anoxic-famine conditions for denitritation driven by internally stored PHA as carbon source (S-SBR); (iii)Sequential Batch Reactor dedicated for the PHA production in a fed-batch reactor (A-SBR) to accumulate the intracellular PHA content in the selected biomass using VFA-rich liquid from sludge and organic fraction of municipal solid wastes (OFMSW) co-fermentation. (iv)Thickening and dewatering of PHA-enriched biomass. In Sesto San Giovanni Wastewater Treatment Plant, SCEPPHAR System will be implemented in demo scale, as the first Italian biorefinery. From the acidogenic co-fermentation of sewage sludge and OFMSW is expected to produce around 150 kgVFA/d, from the N-SBR it could be expected a nitritation efficiency of 80-90%, and from the accumulation stage an average PHA production yields of 0.36 kgPHA/kgVFA and an annual productivity of 12-ton PHA are expected. The final PHA-rich biomass will be further processed and PHA will be extracted and purified and used as component in biodegradable soil mulching films for agriculture purposes.

Keywords: biopolymers, polyhydroxyalkanoates, resource recovery, wastewater, organic wastes

Acknowledgements: The authors kindly acknowledge CIRCULAR BIOCARBON Project, funded from the Bio Based Industries Joint Undertaking (JU) under grant agreement No 101023280. The JU receives support from the European Union's Horizon 2020 research and innovation programme and the Bio Based Industries Consortium.

STIRRED EXTRACTION COLUMNS FOR INDUSTRIAL REACTION PROCESSES

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Industrial scale stirred liquid-liquid extraction columns are designed to provide perfect mixing of two immiscible liquid phases. Industrial scale reactors can't be scaled up linearly from lab experiments. They often suffer from insufficient mixing caused by scale up errors. In recent time, high performance CFD simulations does help to understand the mixing in large size reaction vessels and multiphase contactors. In liquid-liquid extraction, high effort was spent on providing adequate rules for mixing from batch to industrial scale size. Scale up algorithms are available and proven. This knowledge has been applied in the design of perfectly mixed "multiphase reaction vessels" based on the design principle of extraction columns. Mixing units in extraction columns are divided in individual compartments. This compartments can be seen as multiple continuously stirred tanks, arranged vertically to obtain space and equipment savings for a cascade of reaction vessels.

The Taylor Couette reactor makes use of toroidal Taylor vortices between two rotating cylinders to provide the mixing energy. Application of the Taylor Couette reactor in biosynthesis or crystallization has been reported in literature [1]. This reactor type comes with the disadvantage of instable flow regimes and small reaction volume. To overcome this obstacle, the flow regime can be stabilized by equipping the rotor with discs. The reaction volume can be increased by decreasing the rotor diameter. This design approaches are used to build a simple and effective multiphase reactor for handling up to four phases (gas, liquid, solid, liquid) at the same time. This column type apparatus is called Taylor-Couette Disc Contactor (TCDC). It combines the benefits of stable Taylor-Couette flow with high hydraulic load in continuous processes [2].

In this study two different reactive systems in a lab scale DN 50 TCDC are presented. First the continues synthesis of 2-Methoxyhydroquinone (MHQ) in a two phase reaction system was demonstrated in a pilot scale TCDC reaction column. This organic molecule is a high potential candidate as electroactive molecule that can be used in organic redox flow batteries for large scale energy storage. A production capacity of 0.5 kg/h MHQ was reached. Second the continuous heterogeneous precipitation of lithium carbonate with CO_2 was performed in a TCDC column. The, dispersed gas phase holdup, axial backmixing and flowregime were investigated is an air-water testsystem. The neutralization of 0.1 molar sodium hydroxide solution with CO_2 was investigated under variation of gas federate, rotational speed and temperature. The experimental results were used for modeling the concentration trajectories of the ion species over the column height. Having this continuous neutralization process under control allows to control the precipitation reaction, ending in a continuous counter current gas-liquid precipitation process. This process demonstrates a process route for economic lithium recovery from battery scrap.

Keywords: extraction columns, multiphase flow, gas-liquid reactions, multiphase reactors, Taylor-Couette

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DETERMINATION OF SCALE-UP PARAMETERS TO DESIGN AN INDUSTRIAL MICROWAVE TO EXTRACT PECTIN FROM SUGAR BEET PULP

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Abstract

The scaling up of microwave operations is a considerable challenge because of various issues, like increased heat loss, changes in absorption, or limited depth of radiation penetration into the reaction media. Due to these restrictions, scaling must be exact to provide the desired outcomes. To execute microwave scaling, operating conditions must be precisely measured, and scaling parameters must be kept constant. For instance, the power and energy needed can be adjusted depending on variables like absorbed power density (APD) and absorbed energy density (AED)[1] or by theoretical power calculations[2].

For this case of study, the microwave reactor proposed to perform the scale-up is used for the pretreatment with water of sugar beet pulp (SBP) for pectin extraction. The microwave equipment is a Multiwave PRO SOLV reactor 50 Hz with Rotor type 16HF100 (Anton Paar GmbH, Austria, Europe). The operating conditions are based on del Amo-Mateos et al.[3]: SBP and water with an S/L ratio of 10% w/v, the operation temperature of 165 ºC, the heating time of 25 min, and the operation time of 12 min.

To scale the microwave reactor, first, it's necessary to check the calculus at the lab scale. The C_p of the mixture had been estimated at 6.2 kJ kg^{-1} $ºC^{-1}$. With this data, the theoretical power was 300 W. The error margin concerning the real one is less than 10%, so it is within what is expected. On the other hand, the solvent's necessary heat was 35 kJ, and APD and AED could be calculated, being 480 W L^{-1} and 144 kJ L^{-1}, respectively. These fundamental calculations provide an excellent indication of the initial MW heating parameters when a scale-up is started.

Keywords: microwave, scale-up, APD, AED, parameters

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Acknowledgements:
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MASS TRANSFER PHENOMENA IN LIQUID-LIQUID EXTRACTION OF BIOBASED CARBOXYLIC ACIDS WITH TiOA

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Abstract

Apart from physical extraction of polar non dissociating constituents, liquid-liquid extraction of biobased products such as acetic acid or hydroxypropionic acid with tertiary amines is seemingly on a rise again. Formation of stable amine salts and amides, solvent disintegration and the problematic mixing properties have mothballed this solvent class. Amine based solvents need admixture of modifiers and diluents to correct the physical properties of the laden solvent by adjusting density, interfacial tension and viscosity, and to avoid third phase formation. Single droplet liquid-liquid extraction of acetic acid (HOAc) was investigated with solvent mixtures comprising triisooctylamine TiOA dissolved in Shellsol T (SST) and the modifiers isodecanol (ISO) and tributyl phosphate (TBP). The equilibrium data were obtained from temperature controlled shaking funnel experiments. Different solvent mixtures as well as different acid concentration of the aqueous phase were investigated. Systematic analysis of single droplet mass transfer in quiescent carrier phase recommends the determination of the overall mass transfer coefficient k_{od} from single droplet mass balance according to Eq. 1 and 2, with the droplet volume V, the droplet surface area A, droplet diameter d, overall mass transfer coefficient k_{od}, droplet rise time t, local solute concentration c and apparent equilibrium concentration c*.

$$V * \frac{d_c}{dt} = A * k_{od} * (c^* - c) \qquad (1)$$

$$k_{od} = \frac{d}{6 * t} * \ln\left(\frac{(c - c_0)}{(c^* - c_0)}\right) \qquad (2)$$

Modeling starts with the specification of mass transfer resistances in the carrier phase and in the droplet. Analysis of the overall mass transfer coefficient kod according to Eq. 1 shows a distinct dependency of the droplet residence time t, except when the apparent equilibrium concentration c* is varied. The discrepancy can be explained by mass transfer limitation of the solute transfer from the interface into the droplet bulk. The modifier does not play a distinct role.

The results of this study confirm that mass transfer with chemical reaction is limited by the transfer of the laden solvent from the interface into the solvent phase, because mass transfer of the laden amine into the solvent bulk of the droplet is rate controlling by fixing triisooctylammonium acetate at the interface. This constraint has to be considered in process design and in equipment choice.

Keywords: Solvent Extraction, Amines, Mass Transfer

PHASE SEPARATION AND SETTLER DESIGN

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Abstract

Phase separation of liquid-liquid dispersions is a crucial step in liquid-liquid extraction of constituents from broths with unfavorable physical properties. We are faced with these problems in liquid-liquid extraction of valuables from biobased feed. Based on the balance of settling processes the design of batch settlers according to equation 1,

$$dh = w * dt \qquad \text{Equation 1}$$

and the design of continuous settlers according to equation 2, with the settler height h, settling time t, rate of settling w and the horizontal flow velocity v_0

$$\frac{dL}{v_0} = \frac{dh}{w} \qquad \text{Equation 2}$$

should be a simple task. Actually the rate of settling w is not constant but changes with height ($w = w(h)$). Several investigations have focused on the development of design algorithms, addressing the phenomena which affect the rate of hindered settling of the dispersed phase. In this study the monitoring of phase separation of liquid-liquid dispersions in an optical cell and in an ultrasonic scanner was investigated. The system properties density, viscosity and surface tension were adjusted by adding PEG 4000 and sodium chloride to the aqueous carrier phase. From a kinetics point of view droplet sedimentation from aqueous dispersions may follow a mixed order rate model, combining zero order and first order rate of sedimentation, and combinations of first order rate approaches. Initial turbulences may induce pronounced retardation of droplet sedimentation from dispersions, best modeled by a first order consecutive step model. The rate models were investigated, resulting in easy to apply algorithms for accurate specification of the sedimentation rate. Application of the mixed order rate approach results in a two parameter function of the dispersion height h and the maximum height of the clear liquid aqueous phase h_{max}. The advantage of this mixed order rate model is the simple correlation of the height dependent settling rate $w(h)$. When applying the consecutive step model the correlation of the height dependent rate of settling also follows a two parameter algorithm for the rate of sedimentation $w(h)$. The fit parameters compare well with the physical properties of the systems. From the mixed order rate model the initial rate of settling can easily be determined, giving quick access to the initial mean drop size. From comparison of the actual rate of sedimentation with the initial rate, the height dependent volumetric amount of dispersed phase in the dense packed zone is accessible.

Rate based algorithms provide simple strategies in quantifying the sedimentation of droplets from aqueous dispersed systems with simple and quick determination of the system properties needed for successful industrial settler design.

Keywords: Solvent Extraction, Phase Separation

NATURAL DEEP EUTECTIC SOLVENTS (NADES) AS ALTERNATIVE MEDIA FOR THE DEVELOPMENT OF A GREENER LEATHER DYEING PROCESS

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Abstract

The leather processing is an industrial process that dates back over 7000 years. However, the chemicals and the water consumption in such processes have not changed much the past 100 years. The aqueous waste produced by the leather manufacturing process is the most well-known problem that needs to be addressed. In the current approach, transformative dyeing stages for leather manufacture are proposed using natural deep eutectic solvents (NADES) as a novel type of solvent. NADES demonstrate several advantages, more specifically regarding the studied processing, they show high solubility for polar and non-polar compounds (e.g. tanning agents and dyes) thus they can be used as alternative solvents in order to reduce the large amount of water used in several stages of the process. Furthermore, it is important that they can be task-specifically designed to possess specific and desirable physicochemical characteristics such as pH, polarity, viscosity etc.

In this study, five NADES have been prepared using the heating and stirring method. All the NADES have been structurally characterized and some of their most important properties have been measured (e.g. polarity and pH) and they were studied for their solvation ability over five different dyeing agents such as solvent green 7, acid orange 7, solvent black 5 and direct orange 39. The selected NADES were studied for their ability to act as dyeing media of wet blue leather samples in laboratory scale. Dyeing conditions such as dye and solvent concentration, mass of the leather sample and process duration were investigated. The optimum NADES for the process was determined and its' scalability was further examined by implementing experiments in a pilot scale.

Finally, dyed leather samples were characterized using methodologies such as FTIR, XRD and some of their most important characteristics such as the colour durability to light exposure and possible colour migration in PVC have been measured. The obtained results were very satisfactory since they were comparable or better to those derived for the conventionally used dyeing methodologies. Thus, according to the findings of this study, NADES could be considered as emerging alternative media in leather dyeing processes.

Keywords: Dyeing process, Leather, Natural Deep Eutectic Solvents.

CONSTRUCTION OF A PILOT PLANT FOR THE REDUCTION OF CO_2 CAPTURED BY AMINES

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Abstract

The accumulation of CO_2 in atmosphere is a growing concern. To avoid it, focus is made in reduction of CO_2 emissions as well as in its capture. The last years, in the PressTech research group of Universidad Valladolid has developed several solutions for converting CO_2 captured in basic aqueous solutions [1]. Recently, it was proved that the CO_2 captured by amines can be directly transformed to formic acid in aqueous media without intermediate separation or purification steps using gaseous hydrogen as reductant. This reaction can successfully proceed using the amines 2-amino-2-methyl-1-propanol and 3-amino-1-propanol in residence times from 60 to 120 min at temperatures in the range from 70 to 125ºC. Formic acid yields between 30 and 67% are obtained observing that reaction time, temperature and hydrogen pressure has a positive influence.

Several factors such as the prospect of the high reliability of the process of CO_2 capture by amines or the prospects of the availability of huge amounts of green hydrogen in the near future make this process very promising.

In the Presstech group we are working in the scaling up of the process. To do so, we are designing a pilot plant that can integrate the different steps of the process: absorption, reaction and separation of the produced formic acid and recovery and recirculation of the amine.

The experimental results as well as the design of the facility will be presented.

Keywords: CCU, Hydrogen, Formic acid

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Acknowledgements: This project has been funded by the Ministry of Science and Universities through project RTI2018-097456-B-I00 and by the Junta de Castilla y León through project by FEDER FUNDS under the BioEcoUVa Strategic Program (CLU-2019-04).

THANKS FOR SHARING YOUR GREEN IDEAS