# BOOK OF ABSTRACTS

**February 2021**
**15th - 16th**

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**COST Action GREENERING**
**CA 18224**
Green Chemical Engineering Network
towards upscaling sustainable processes

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ABOUT

Green Chemical Engineering Network towards upscaling sustainable processes (CA18224) – GREENERING, is project (Action) funded by COST (European Cooperation in Science and Technology).

The objective of GREENERING COST action is to promote and boost the industrial application of green chemistry and sustainable technologies, developing the tools for the scale-up and implementation of emerging processes into industry.

ACTION DETAILS

- MoU - 041/19
- CSO Approval date - 04/06/2019
- Start of Action - 14/10/2019
- End of Action - 13/10/2023

1ST GREENERING INTERNATION CONFERENCE
15th - 16th February 2021

SCIENTIFIC AREAS/TOPICS AND PROGRAMME

- Keynote lectures
- Alternative solvents
- Biofuels and Bioenergy
- Cosmetics
- Food technology
- Pharmaceuticals
- Raw materials
- Waste treatment/valorization
- Green policies and innovation

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# GREENERING – GREEN CHEMICAL ENGINEERING NETWORK TOWARDS UPSCALING SUSTAINABLE PROCESSES

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COST (European Cooperation in Science and Technology) is a funding agency for research and innovation networks, the so-called Actions. COST Actions help connect research initiatives across Europe and beyond as well as to enable scientists to grow their ideas by sharing them with their peers and take new initiatives across all fields of science and technology, while promoting multi- and interdisciplinary approaches. COST Actions involves more than 45,000 researchers and innovators and are described as Open and Inclusive, Multi and interdisciplinary, Pan-European and Career enhancing.

GREENERING COST action intends to promote Europe industrial leadership in which concerns the use of green technologies for the development of sustainable processes. To achieve this, the GREENERING consortium gathers experts from academia, industry and technology transfer institutions with the aim to: i) create a network with common interests; ii) create working groups to influence decision makers and stakeholders in adopting sustainable processes; iii) create competitive consortiums able to apply to H2020 competitive calls and iv) increase the entrepreneurial mindset of researchers and particularly young students who with their youth and willful energy will be able to transpose technology into products.

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# A UTILITY FOR GREENESS AND EFFICIENCY METRICS: HOW TO EVALUATE THE GREENNESS OF YOUR MULTI-STEP SYNTHESIS

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Green chemistry and engineering has become an increasingly important topic in the development of pharmaceuticals and fine chemicals to ensure manufacturing processes are sustainable and efficient. In the multi-step synthesis of pharmaceuticals and fine chemicals, the assessment of the environmental footprint or 'greenness' of a process can be complicated by the large number of synthetic steps, convergent chemistries, and environmental impact of different chemicals. Scale-up Systems has developed a utility to aid the calculation of green chemistry metrics, such as process-mass-intensity (PMI), atom economy, and reaction mass efficiency, from the basic synthesis, yields, and material quantities. This utility allows the user to take a holistic view of synthesis and provide insights into the steps and materials that have the highest impact on the process greenness and the opportunities for process improvements. In addition, the utility may be used to evaluate different synthetic routes and evaluate the synthesis throughout the development life cycle. This presentation will show how this utility may be used to quickly assess the greenness based a case-study of multi-step synthesis with known yields and material quantities, information that is typically available from the onset of development.

*Keywords: Greenness, Metrics, Synthesis*

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# HOW AI COULD HELP DESIGNING MOLECULES FASTER; CHEAPER; GREENER

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Drug design is a challenging task. From hit identification to hit-to-lead and lead optimization, the quest to discover a new chemical entity (NCE) with desired properties is burdensome. Exploration of a nearly infinite chemical space ($10^{60}$ drug-like molecules is a low range figure) is required in order to solve a multi-parametric optimization (MPO) challenge: identifying the rare compounds which satisfy a blueprint encompassing criteria such as biological activity, selectivity, (lack of) toxicity, pharmacokinetics (i.e. DMPK), synthetic accessibility and finally novelty. Around 1,500 molecules are needed to develop a preclinically validated drug candidate, which corresponds to around 9,000 organic reactions, associated analysis experiments and also associated wastes (solvent, consumables, glass…). In this presentation we will show how AI could reduce this huge number. First by using generative AI for *de novo* design to find the clinical candidate faster, reducing the number of Design Make Test cycles, and second by using AI-driven retrosynthesis to find easy to make molecules, thereby reducing the number of reaction steps.

*Keywords: Artificial intelligence, Medicinal chemistry, Retrosynthesis, Drug design*

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# INTEGRATED THERMOCHEMICAL PROCESSING OF MIXED WASTES

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Various complex wastes are still deposited in landfills or incinerated due to properties that hinder alternative valorization pathways. High concentrations of water, ashes and chorine preclude their energetic valorization, but these limitations may be overcome by mixing with other residual materials followed by thermal upgrading. Lipid wastes with high levels of water, free fatty acids and solid contaminations were combined with pine wastes and subject to low temperature pyrolysis yielding bio-oils and biochars with heating values of 37.8-43.4 MJ/kg and 32.8-36.9 MJ/kg respectively. The presence of biomass wastes improved the yield of biochar and the heating values of both bio-oils and biochars leading to process energy efficiencies of 59.1-71.1%. Another complex and hazardous waste is the hydrocarbon sludge formed during cleaning of oil storage tanks and usually eliminated by mixing with refuse derived fuel and co-incineration. This sludge was combined with biomass wastes and diesel (entraining liquid) and heated at atmospheric pressure until all liquid components were recovered. This process designated as simultaneous distillation and hydrothermal carbonization (SD-HTC) produced gas, liquid and solid products and involved fractionation of the sludge components between these three phases. The liquid organic products contained diesel and volatile components from the hydrocarbon sludge while the non-distillable components are concentrated in the biochar. Finally, many polymeric wastes cannot be valorized for energy production because of their high chlorine content that leads to the production of corrosive gases during combustion or gasification. These polymeric wastes can be upgraded by hydrothermal carbonization to yield biochars with higher carbon contents and lower chlorine contents than the original wastes. Adding 20% of lipid wastes to those polymeric wastes increased hydrochar yield and its heating value by 0.8% and 4.3 MJ/kg, respectively. Combining lipid or hydrocarbon wastes with biomass or polymeric wastes allows for their integrated upgrading and may contribute to improve the properties of the conversion products.

*Keywords: Polymeric wastes, Lipid wastes, Hydrocarbon wastes, Lignocellulosic biomass, Thermochemical processing*

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# DEVELOPING RESOURCES IN SUSTAINABLE WAY

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Symrise has a long history of employing ambitious measures for the conservation of natural resources like water, Biodiversity, forests and for empowering people. Very soon we have established a comprehensive strategy which addresses all the dimensions of sustainability, consisting in 4 pillars which are Footprint, Innovation, Sourcing and Care.

The contributions toward the United Nations' Sustainable Development Goals (SDG) play a decisive role in this context. Symrise makes effective contributions to the implementation of the SDGs in its key areas of activity. As a signatory of the United Nations Global Compact, we actively support the principles of responsible business outlined therein.

Several commitments illustrate how these goals are embedded in our operations and businesses.

In concert with the content of SDG 6, Symrise considers the availability of fresh, high-quality water to be absolutely essential for its activities. The company is dedicated to using water efficiently and reducing wastewater volumes and emissions at all its sites worldwide. We aim to reduce both chemical oxygen demand in water and sensitive waste by 60 % as compared with 2010 levels.

When it comes to climate protection, Symrise has committed to completely obtaining its energy from renewable sources in 2025 by joining the R100 Initiative.

And last but not least, as one of the founding of the OP2B initiative, Symrise reinforce on its strong commitment to Biodiversity. The goal of this cross-industry coalition is to develop jointly more environmentally friendly agricultural methods.

For us, the goal 17on Partnerships, is centric and we rely on the collaboration with our stakeholders who are non-profit organizations like UEBT or with governmental agencies like GIZ to support our ingredients transparency.

These commitments and achievements have been recognized by third-parties, among them, by the non-profit organization CDP achieving the highest rating A-list and by Ecovadis, achieving the Gold status.

*Keywords: Biodiversity, Sustainability, Natural resources*

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# SCALING-UP MECHANOCHEMISTRY IN COST ACTION CA18112

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COST Action CA18112 – Mechanochemistry for Sustainable Industry (MechSustInd) [1,2] is a European Union networking initiative to nurture and catalyse interactions between European and overseas researchers in Mechanochemistry. Mechanochemistry is a rapidly emerging multidisciplinary field of science, deeply rooted in and intertwined with chemical, material and environmental sciences. This field studies chemical transformations induced by mechanical forces (*e.g.*, compression, shearing, *etc.*). Unlike conventional solution-based chemistry, mechanochemical reactions can be performed in the absence (or involving only a nominal amount) of solvents, reducing the environmental footprint of a chemical process significantly.

This presentation will discuss several examples of scale-up mechanochemical syntheses in both batch and continuous processes within the COST Action CA18112 [1,2]. These examples demonstrate the exploitation of mechanical activation in the production of chemicals, including Active Pharmaceutical Ingredients, through sustainable and economically convenient practices on the medium and large scales.

*References: [1] Hernández et al., Eur. J. Org. Chem, 8-9, 2020.; [2] COST Action CA18112 'Mechanochemistry for Sustainable Industry' (www.mechsustind.eu and www.cost.eu).*

*Keywords: Mechanochemistry, Scale-up, Batch Synthesis, Continuous Manufacturing*

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# Alternative solvents

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# ENHANCED ANTIBIOFOULING PAINTS USING DEEP EUTECTIC SOLVENTS BASED ON NATURAL COMPOUNDS

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Marine biofouling is one of the most challenging problems currently faced by marine technology. This phenomenon is defined as the undesirable colonization of submerged surfaces by fouling organisms, including micro-organisms (bacteria, algae and protozoa) and macro-organisms (barnacles, bryozoans and tubeworms). Presently, this represents a great material and economic loss in marine operations, while rising a series of environmental concerns.

It is estimated that antifouling coatings provide the shipping industry with annual fuel savings of $60 billion, and reduced emissions of 384 million and 3.6 million tonnes per annum, for carbon dioxide and sulphur dioxide, respectively. However, there is still absent an universal and green antifouling system.

Natural marine products are a potential source for the discovery of antifouling compounds, representing an excellent sustainable alternative. In this study, the ability of napiradiomycins, to inhibit micro and macrofouling species was explored, with particular emphasis on developing sustainable antifouling products, namely paints and coatings. Deep eutectic systems (DES) fully represent the green chemistry metrics, which makes them highly desirable and a promising alternative to organic solvents commonly used in conventional antifouling products. DES are commonly defined as systems composed of a mixture of at least two components, which when when combined at a particular composition become liquid at room temperature. Among the remarkable properties of DES are their low preparation and production costs, straightforward and green synthesis, no need of post synthesis purification, low volatility and biodegradability. The DES prepared were based on natural occurring molecules with antifouling activity, such as fatty acids (oleic acid and 3-hydroxybutyric acid) and terpenes (menthol), which prove to be good candidates for preparing sustainable, effective and cheap antifouling painting supplements.

*Keywords: Marine biofouling, Napyradiomycins, Deep eutectic system, Antifouling paints*

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# BIOMASS FRACTIONATION BY ULTRAST SUPERCRITICA WATER HYDROLYSIS (SCWH): SUSTAINABILITY ANALYSIS

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Conventional biomass fractionation processes require long reaction time, strong and hazard reagents, in addition to collection of large volume of eluent that require expensive treatment. As an alternative to conventional methods we will discuss the use of supercritical water as solvent and reaction media for fractionation and valorisation of lignocellulose biomass. This process is based in the SCW properties and the use of extremely low residence times (below 1s) to avoid the hydrolysis products degradation. Pervious work in our group has already proved practicability of sugar production from several lignocellulose biomass, in our continues ultrafast supercritical hydrolysis pilot plant by so called FASTSUGAR process, demonstrating the challenges and in the main time versatility and potential of the process [1].

Although the extremely low reaction time leads to a reduction in energy consumption, the operation at high temperature and pressures mains a high energy consumes. The heat integration allows to recovery the effluent work and heat. Authors have demonstrated as the energy consume can go until zero by SCWH process integration with a gas turbine [2].

In this contribution the ultrafast SCWH process is analyzed against the 12 principles of green engineering to demonstrate that is a sustainable process [3]. SCW improve the mass transfer, that it is the limit step in the biomass fractionation process. Also, it produces an extremely high process intensification, with operation times below 1s, so it reduces dramatically the reaction volume. The concentration of the liquid effluent is done by a flash step with no extra energy. The high selectivity allows to get final products that can be commercialized or used in other valorization processes. SCWH process is a continuous process easy to scale up. The extremely high process versatility allows operation with different biomass to get different final products, nature based, so they can be durable but also biodegradable.

*References: [1] Cocero et al., J. Supercrit. Fluids 133, 550-565, 2018.; [2] Cantero et al., Bioresour. Technol., 179, 136-143, 2015.; [3] Zimmerman et al., Science 367, 397–400, 2020.*

*Keywords: Biorefinery, Green process, Engineering vision*

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# SUPERCRITICAL $CO_2$ APPLIED ON THE PRODUCTION OF LIPOSOMAL DRY POWDER FORMULATIONS

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Nowadays, up to 400 million people worldwide suffer from inflammatory lung diseases, like asthma and cystic fibrosis. Unfortunately, the long-term systemic therapy with high doses of anti-inflammatory drugs results in adverse effects such as osteoporosis, adrenal suppression, diabetes, and cardiovascular diseases. Liposomes are concentric lamellar vesicles that, due to their biocompatibility and similarity with cells, have a great interest on the targeted delivery of hydrophilic drugs and macromolecules with anti-inflammatory therapeutic action. However, upon storage in solution, liposomes can present limited stability, that might limit their use. Through a synergy between the green chemistry and the pharmaceutical technology, this drawback can be overcome. Using $scCO_2$-assisted spray drying (SASD), 5(6)- Carboxyfluorescein- loaded liposomes were encapsulated in excipients, forming liposomal dry powder formulations (CF_Lip@DPFs), with an increase of their stability. The hydrophilic dye (5(6)-Carboxyfluorescein) was loaded in the liposomes (CF_Lip) by the thin-film hydration method, followed by extrusion, in order to monitor the process. A quality-by-design (QbD) approach using the design of experiments (DoE) tool, followed by a statistical analysis, was implemented. The design was used to study the effects of the process parameters on the aerodynamic properties and the morphology of the liposomes. The $scCO_2$-assisted spray-dried formulations presented suitable aerodynamic properties for inhalation. Finally, the physical and chemical stability of CF_Lip@DPFs, upon storage at different relative humidities, was assessed after one week and one month.

*Keywords: Inflammatory lung diseases, Liposomes, Supercritical carbon dioxide, Liposomal dry powder formulations, Design of experiments*

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# SUBCRITICAL WATER EXTRACTION TO EXTRACT ANTIOXIDANT COMPOUNDS FROM THE RED SEAWEED *Chondrus crispus*

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Algae are marine species with biological properties associated with their composition. Red seaweeds represent a great source of active compounds with interest in different industries. Seaweeds are continuously under oxidative stress, then it would be expected that in their chemical composition there were antioxidant compounds. Different extraction technologies have been used to recover them, both conventional and green technologies such as ultrasounds, pressurized water extraction, microwave and others. In this context, the aim of this work was to study the antioxidant activity of the extracts obtained at different temperatures by subcritical water extraction using as raw material the red seaweed *Chondrus crispus*.

The red alga was gently provided by CEAMSA (Pontevedra, Spain). *Chondrus crispus* was processed in a stainless steel reactor at ratio 1:30 (seaweed:water; w/w). The reactor was heated until the selected temperature. For this purpose, five temperatures were studied: 120, 140, 160, 180 and 200 °C (non-isothermal process). After the solid and liquid phases were separated, the carrageenan of the liquid fractions was precipitated with an organic solvent (ethanol: liquid phase ratio 1.5:1, v/w). The carrageenan-free liquid fractions obtained at different temperatures were analysed for antioxidant activity, phenolic content and sulphate.

According to the results, this was a suitable extraction technology to obtain liquid phases with potential antioxidant activity from *Chondrus crispus*. The maximum temperature tested (200 °C) showed the highest content in phenolic compounds (1.7%), trolox equivalent antioxidant capacity (4.5%) and sulphate content (54.7%), whereas the protein content was maximum at 160 °C (0.3%). To conclude, it should be highlighted that the fraction with maximum antioxidant potential, using this green extraction technology and this red seaweed, was obtained during nonisothermal heating up to 200 °C.

*Keywords: Antioxidant activity, Phenolic content, Green extraction technology, Red macroalgae*

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# FUNDAMENTAL UNDERSTANDING OF DEEP EUTECTIC SOLVENTS FOR INDUSTRIAL APPLICATIONS

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Science, in the past century's, has applied empirical techniques and indirect techniques to understand the behavior and proprieties of molecules in solution. This kind of understanding, gave humanity, and mostly, industry, tools to evolve in different fields such as food, pharmaceutical, textile industry and others. After the introduction of computers in our life, scientists started using this tool for a better understanding of the microscopic world. Molecular Dynamics is a computational method with the capability of simulating proteins, enzymes, sugars and other molecules that can be used to understand the behavior of systems in natural conditions and predict how they will act in the presence of other molecules. The use of computational methods is a step forward in the comprehension of complex systems with a vast world of advantages, being the time consume for experimental work and profit as the major reasons.

Another major evolution in science in the past years is the substitution of toxic compounds to both the living beings and for the environment, herein with special focus on green solvents. Deep Eutectic Solvents (DES) are a class of green solvents with a vast field of applications such as replacing oils, drug delivery, enzyme extraction and others with advantages such as the use of natural compounds and the cheap production. The results obtained using DES have been showed that these kind of solvents are a path towards the future for a cleaner world, but due their intrinsical proprieties such as viscosity, it is difficult to have a major understanding of the systems. Molecular Dynamics comes up to open a new world of applications of these kind of systems as it will contribute to break the existing lack of information of these systems.

*Keywords: Molecular Dynamics, DES, NADES, Industry*

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# SUSTAINABLE SYSTEMS FOR THE EXTRACTION AND STABILIZATION OF BIOACTIVE COMPOUNDS FROM AROMATIC PLANTS

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This work reports an innovative and sustainable approach for the extraction of essential oils and individual bioactive products from aromatic plants, particularly from sage (*Salvia officinalis*), in line to the market needs. This plant is rich in unique and highly concentrated essential oils, with extremely attractive properties, being highly sought after for applications in cosmetic, pharmaceutical and food industries. The biological products present in sage are a promising source of bioactive compounds with high added value. Properties such as antioxidant, anti-inflammatory, antimicrobial, anti-cancer, antimutagenic and applications with health benefits are very interesting to develop, especially in the field of oncology and neurodegenerative treatments.

The extraction of essential oils from sage is usually done by hydrodistillation and steam distillation, but these methods present some drawbacks, being expensive, and having a high energy and solvent consumption. Towards a more sustainable extraction process, greener solvents such as deep eutectic systems (DES) can play an important role in the reduction of the use of toxic extraction solvents. In this work, we use natural deep eutectic systems (NADES). Combinations of compounds such as glucose, trehalose, lactic acid, glycerol, menthol or betaine, are used in adequate molar ratio to form our systems. The use of NADES can improve extract quality and at the same time, valorize the compounds found in this aromatic plant, once they can also act as antioxidant stabilizers. This method can easily produce bioactive extracts, maintaining all the desired properties and components, diminishing purification steps attracting, for example, the interest of cosmetic and nutraceutical industries.

*Keywords: Natural deep eutectic systems, Antioxidants, Extraction, Salvia officinalis*

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# NADES AS EMERGING SUSTAINABLE SYSTEMS FOR THE EXTRACTION AND STABILIZATION OF BIOACTIVE COMPOUNDS FROM ROSEMARY

***Vieira C.*[1], *Rebocho S.*[1], *Craveiro R.*[1], *Paiva A.*[1,2], *Duarte A.R.*[1,2]**

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Rosemary (*Rosmarinus officinalis*) is a natural source of bioactive compounds and essential oil, widely used in several areas, due to pharmacological properties and therapeutic potential. The development of new promising and sustainable techniques of extraction has received a lot of attention due to environmental restrictions. Recently, natural deep eutectic systems (NADES) came to offer a suitable solvent with high solvent power and low toxicity interesting for bioactive extractions. Moreover, these natural based solvents are biodegradable and help to lower the environmental impact by reducing solvent and energy consumption leading to a minor cost of the process. The present work aims to extract the principal biocomponents from rosemary, such as: rosmarinic acid, carnosol, carnosic acid and ursolic acid, using these alternative solvents. A NADES screening of ten combinations using the same conditions of temperature, solid liquid molar ratio, time, were perform under two different methods, heat and stirring (HS) and ultrasound assisted extraction (UAE), to test the solvent efficiency. To quantify the total phenolic compounds of the extracts, in the form of galic acid equivalents, the Folin method was used, reaching up to 2% mg GAE/mg rosemary with lactic acid:glucose (molar ratio 5:1). Furthermore, the compounds were identify and quantify by high performance liquid chromatography (HPLC), with the most promising results for rosmarinic acic 14.34 mg/L using lactic acid:glucose (molar ratio 5:1), carnosol 86.88 mg/L and carnosic acid 145.68 mg/L with menthol:lauric acid (molar ratio 2:1).

*Keywords: Natural deep eutectic systems, Extraction, Rosmarinus officinalis, Antioxidant activity*

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# INFLUENCE OF SUPERCRITICAL $CO_2$ IN THE THERMAL PROPERTIES OF POLYLACTIC ACID AND POLYAMID 12

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The increase of concentration of greenhouse gases in geosphere is reported as the main cause of climate change. Air concentration of carbon dioxide ($CO_2$), one of the substances known to show greenhouse gas potential, reached 409 ppm in 2019, equal to an increase of 31.5 % since the beginning of industrialization. However, $CO_2$ is an inert and non-toxic gas, with a critical point of $p_c$=73,75 bar and $T_c$=30,98 °C. Called a green solvent, it has found a wide range of applications in industry as extracting agent, refrigerant, and sterilization agent.

In this study, supercritical $CO_2$ will be used to produce Particles-from-Gas-Saturated-Solutions (PGSS). The generated powder is supposed to be used in additive manufacturing (AM), especially within a process that is characterized by directed energy deposition (DED) but also by powder bed fusion (PBF). Due to the difference of viscosity between polymer melt and gas phase, the operating principle of the PGSS plant was adapted to increase the mixing performance. Thus, the polymer granules are melted by a single-screw extruder before being mixed downstream with supercritical $CO_2$ in a planetary roller extruder. Before the gaseous polymer phase is expanded through a nozzle, it is mixed with additional $CO_2$. Due to the plasticization of the gas molecules in the melt, the mixture can be expanded into a spray tower where the melt is torn apart. The resulting polymer droplets are solidified, due to the Joule-Thomson effect.

It is known that $CO_2$ is changing the thermal properties of the polymer, such as glass point, melting temperature, and crystallization temperature. Therefore, to identify the process parameters for the PGSS plant, this contribution is comparing two model polymers by using calorimetric measurements. The measurements were carried out using a calorimeter and a transitiometer, with polylactic acid 3251D (PLA 3251D) from NatureWorks LLC, a biodegradable polymer with a D-Lactid concentration of 1,4 %, and Vestamid® Polyamid 12 L1600 (PA 12) from Evonik, a standard polymer for PBF. It was found that $CO_2$ influences the crystallization behavior in both polymer systems. However, the pressure settings were affecting the melting temperature decrease of PLA 3251D only, an effect not observed in PA 12.

*Keywords: Supercritical $CO_2$, PGSS, Thermal behavior of PLA3251D and PA 12, Polymer powders for AM*

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# EXTRACTION OF PLANT MATERIAL USING SUB- AND SUPERCRITICAL FLUIDS

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Besides providing a range of benefits, supercritical fluid extraction is offering routes to overcome some of the limitations existing with the conventional methods of extraction. Supercritical fluids are so called “green solvents for the future” due to their ecological benefits. The most commonly used are supercritical carbon dioxide and water. One of the main advantages of using supercritical fluids is selective extraction of compounds or fractionation of total extracts. This can be attained by using different gases (propane) for isolation/fractionation of components and by varying the process parameters.

The first part of study includes two stage supercritical carbon dioxide extraction of biologically active compounds from *G. lucidum* fruiting body. Extracts elicited significant targeted activity towards adenocarcinoma cells and had antioxidant and anti-AChE activity. Extractions were carried out in cycles at pressures of 250 bar and 300 bar and temperatures of 40 °C and 50 °C.

In the second part, subcritical fluid extraction from Chia seeds (*Salvia hispanica L.*) has been performed using *n*-propane as a solvent. Influence of elevated operating pressure (up to 300 bar) and temperature (40°C and 60°C) on the extraction yield and extract composition was presented. Compositions of extracts were analyzed by gas chromatography (GC) and the presence of palmitic, stearic, oleic, linoleic and linolenic free fatty acid has been confirmed.

Finally, supercritical fluid extraction has been used for the production of bitter acid hop extracts for the beer brewing industry. Supercritical fluid chromatography was utilized to separate xanthohumol from hops extract. Two different hops extracts, one rich in xanthohumol and another one rich in fatty acids were used. Experiments on fractionation of extracts were performed at three different pressures (220 bar, 250 bar and 270 bar) and three different temperatures (30ºC, 45ºC and 60ºC). The results showed successful isolation of xanthohumol from hop extract.

*Keywords: Supercritical fluids, Supercritical fluid extraction, Natural sources*

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# MEASUREMENT AND PC-SAFT MODELING OF SOLUBILITY OF GALLIC ACID IN AQUEOUS MIXTURES OF DEEP EUTECTIC SOLVENTS

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Deep eutectic solvents have been tested as promissory extracting solvents of polyphenols from plants for food or nutraceutical applications, improving the extraction yields obtained with pure water or other usual solvents. The advantages of using DES for these processes are their good biodegradability and low toxicity because their precursors can be selected among natural compounds. Gallic acid is considered a typical standard for quantifying the total polyphenol content in fruits and vegetable matrices because it is abundant in these sources after the extraction with solvents. However, there are no extensive studies on gallic acid's solubility behavior in different solvents or deep eutectic solvents. Thus, in this work, the solubility of gallic acid is measured in pure water; aqueous solutions of varying hydrogen bond donors as ethylene glycol, levulinic acid, and glycerol; and aqueous mixtures of deep eutectic solvents using choline chloride as the hydrogen bond acceptor, and ethylene glycol, levulinic acid, and glycerol as the hydrogen bond donors. All the measurements were performed from 293.15 K, to 313.15 K, at atmospheric conditions and were validated by comparing the solubility of Gallic acid in water and ethanol from literature. Results suggest that an 50 wt. aqueous solution of deep eutectic solvent based on ethylene glycol or glycerol improves the Gallic acid solubility compared with a 50 wt.% aqueous solution of their corresponding hydrogen bond donor. Solubility results were analyzed in terms of the Kamlet-Taft solvatochromic parameters, concluding that best solvents for solubilizing gallic acid have to act as better hydrogen bond acceptors. For solid-phase study, powder X-ray diffraction was measured for the non-dissolved gallic acid after the equilibrium showing that its structure does not change upon mixing with almost all the aqueous mixtures of this work, but it is modified when using pure ethanol. All the solid-liquid equilibrium results were accurately modeled with PC-SAFT with deviations within 10.55%.

*Keywords: Deep eutectic solvents, Gallic acid, PC-SAFT, Solubility*

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# A COMPARATIVE ASSESSMENT OF ALTERNATIVE SOVENTS FOR CARBON CAPTURE IN A PILOT PURIFICATION UNIT USING CFD AND PROCESS MODELLING TOOLS

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Carbon capture utilization and storage (CCUS) is a promising concept towards the decarbonization of energy intensive industries and long distance transportation (e.g. shipping). The critical factor for optimal CCUS system is the efficient separation of $CO_2$ from the exhaust gas stream. A relatively mature carbon capture technology is the absorption of the $CO_2$ into aqueous MEA solvents using an absorption column followed by their separation in a desorption column, resulting in the purification of carbon dioxide and solvent regeneration. The optimized operation of an absorption-desorption unit depends on the particular column design specifications and operation parameters and the selection of appropriate solvents for gas treatment. Recently, ionic liquid (IL) solvents have attracted considerable interest due to their promising thermodynamic and transport properties. However, their performance under realistic conditions is still at an early stage. The objective of the present work is to develop numerical models for the prediction of exhaust $CO_2$ capture in conventional, industrial scale absorption-desorption packed columns using novel ILs. A Computational Fluid Dynamics (CFD) two-phase reactive flow model is developed incorporating detailed IL thermodynamics and kinetics. Model validation against experimental data from a pilot unit is presented. Further, the results of the coupled hydrodynamic performance are used to suggest possible design specifications directly applicable to industrial settings. Based on the CFD simulations, appropriate reactor models were specified and integrated into an overall process model, developed in ASPEN PLUS, concerning $CO_2$ purification from cement plants. Extensive parametric and sensitivity simulations were performed in order to specify key design and operation parameters towards the optimization of the CCUS process.

*Keywords: Carbon Capture, Ionic Liquids, CFD Modelling and Simulation, Process Simulation*

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# BIOCOMPATIBLE CHITOSAN-STABILISED FILMS INCORPORATING WILD ROSE HIP EXTRACT IN NATURAL DEEP EUTECTIC SOLVENTS

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Wild rose (*Rosa canina* L.) is a plant rich in bioactive compounds (mainly ascorbic acid and flavonoids) with high antioxidant activity. It has been used since ancient times as a medicinal herb for boosting the immune system and fighting off the common cold, while nowadays it is utilized by various industries, mainly in cosmetics.

In the present work the extraction of the bioactive compounds from the plant, was performed by ultrasound assisted extraction (UAE), using different NaDESs as the extraction solvent. The organic acids lactic, citric and levulinic acid were used as hydrogen bond donors (HBD) while betaine, choline chloride, proline and β-alanine were used as hydrogen bond acceptors (HBA) for the preparation of the NaDESs. Total phenolic content (TPC), total flavonoid content (TFC) and antioxidant activity of the obtained extracts were determined. The extracts were then converted into films with the incorporation of chitosan as the stabilising agent. The films were prepared using the casting technique, taking advantage of the high solubility of chitosan in the NaDES extracts. Subsequently, a variety of physicochemical and mechanical properties of the films such as thickness, elasticity, distance to burst, water vapor permeability (WVP) and remaining moisture of each film were measured.

In conclusion, a complete process is presented starting from the raw material to the formation of novel value-added biocompatible films. The direct dissolution of chitosan in a NaDES plant extract, not previously mentioned in the literature, leads to the minimization or elimination of the use of conventional solvents and reagents such us acetic acid or hydrochloric acid. Furthermore, the films' properties differ depending on the solvent used, suggesting there is great flexibility and adaptability regarding the final product.

*Keywords: Wild Rose hip, Natural Deep Eutectic Solvent, Biocompatible films, Chitosan*

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# AN ALTERNATIVE APPROACH FOR THE SYNTHESIS OF TRIAZOLES VIA CLICK HUISGEN CYCLOADDITION REACTIONS USING TASK-SPECIFIC IONIC LIQUIDS AS SOLVENTS AND CATALYSTS

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Ionic Liquids (ILs) are a rapidly growing class of materials that consist entirely of ions. They possess remarkable properties, such as low volatility, chemical and thermal stability, low cost and recyclability, while they that can be used in several applications, including drug formulations, solvents for the solubilisation of drugs and for the synthesis of active pharmaceutical ingredients.

Click reactions have emerged the past decade in the field of synthetic organic chemistry and pharmaceutical science as a group of powerful linking and wide in scope reactions that are fast, simple, easy to purify, efficient, versatile and regiospecific for the synthesis of novel, functional and bioactive compounds.

In this project, a novel green methodology for the synthesis of phenolic acid-triazole hybrids from the Huisgen 1,3-dipolar cycloaddition of azides and alkynes, is presented. Specifically, ascorbic acid-based ILs are synthesized and applied to the reaction, as substitutes of the conventional t-BuOH organic solvent, triethylamine and sodium ascorbate. The novel desired products are produced using high energy techniques, such as microwave and ultrasound radiation, in satisfactory yields and purity, as well as in short reaction times. The innovative and green nature of this method is further enhanced as the ILs can be recycled and reused.

The development and optimization of the aforementioned synthetic protocol is performed via a model reaction between equimolar quantities of carboxamide (**1**), sodium azide and 4-hydroxy phenethyl bromide (**2**), in the presence of copper sulfate and ascorbic acid-based ILs. Product purity, as well as the reaction times and yields, are thoroughly investigated.


Furthermore, in order to investigate the recyclability of ILs, after the workup procedure, the aqueous filtrate is evaporated and the residual IL is dried under high vacuum and reused several times, producing the desired hybrids in good yields and purity. The structure of all the final synthesized hybrids is unambiguously determined using NMR, MS and IR spectroscopy.

The above one-pot-three-component click reaction proceeds in a regioselective manner and is performed in a green and sustainable way, using alternative and recyclable solvents, taking advantage of the benefits of high energy technique and totally excluding organic solvents.

*Keywords: Ionic Liquids, Click Chemistry, Green Synthesis, Recyclability, Triazole hybrids*

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# NATURAL DEEP EUTECTIC SOLVENTS AS GREEN MEDIA FOR THE EXTRACTION OF BIOACTIVE COMPOUNDS FROM OLIVE LEAVES

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Natural deep eutectic solvents (NADESs) are currently emerging as a new class of green solvents that are effectively used as alternative extraction media of bioactive compounds from raw natural materials and biomass. In this context, we present here a greener approach for the efficient extraction of bioactive compounds from olive leaves derived from different varieties of olive trees of Greek flora. Ultrasound Assisted Extraction (UAE) method was used as a high energy technique, in order to simultaneously minimize the extraction time and maximize the yield.

The components of NADESs have significant influence on their physicochemical properties and solubilisation ability which affect their extraction efficiency. Herein, eight NADESs derived from naturally occurring compounds (e.g. betaine, lactic acid, oxalic acid, proline etc.) were synthesised, structurally characterized and tested as extraction media. The implementation of the NADESs screening, indicated the most effective extraction media. The optimum experimental extraction conditions were investigated by performing Design of Experiment (DoE) statistical analysis, applying a symmetrical three-level Box-Behnken design (BBD). The selected independent variables were the NADES-water volumes, the extraction time, the ultrasound power, while the selected responses were the total phenolic and flavonoid content as well as the antioxidant activity of the added value extracts. Moreover, the optimum extracts were further characterized regarding their hydroxytyrosol content by performing by LC/MS/MS analysis.

Overall, the proposed optimized methodology resulted in the efficient extraction of bioactive compounds and could be considered as a competitive alternative to conventional processes.

*Keywords: Natural deep eutectic solvents, Olive leaves, Ultrasound assisted extraction*

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# GREEN SYNTHESIS OF 2.3-DIHYDROQUINAZOLINONE ANALOGUES USING NATURAL DEEP EUTECTIC SOLVENTS (NaDESs) AS SOLVENTS AND CATALYSTS

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Green chemistry is an approach to the design and use of chemical products in order to minimize the impact on the environment. Natural Deep Eutectic Solvents (NaDES) are bio-degradable, non-toxic, recyclable, easy to synthesize from low cost and widely available starting materials and their properties can be tailored to meet the demands of their application. A very promising application is their use as solvents and catalysts in organic synthesis.

In this study, 10 organic acid based-NaDESs were successfully synthesized and characterized and their potential to act as solvents and catalysts for the synthesis of 2.3-dihydroquinazolin-1(H)-one analogues was examined. The synthetic approach involves a multi-component reaction (MCR) using ultrasounds as the energy source. MCRs achieve high atom economy, lower costs, shorter reaction time, and less side products. The developed methodology provided the desired products in high yields, without tedious purification steps. The green character of the developed synthetic approach was further improved by the application of ultrasonic irradiation, leading to even higher yields and significantly shorter reaction times. NaDESs were recovered and re-used for at least three times without loss of their catalytic activity. The choline chloride and lactic acid containing NaDES showed higher efficacy among the ten tested NaDESs and was therefore used as solvent and catalyst for expanding the scope of the reaction, leading to a small chemical library of 2.3-dihydroquinazolin-1(H)-ones possessing diverse substituents.

*Keywords: Natural Deep Eutectic Solvents (NaDESs), 2,3-dihydroquinazolin-4(1H)-ones, Multi-component reaction (MCRs), Ultrasonic irradiation*

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# ENHANCEMENT OF THE SUBCRITICAL WATER EXTRACTION OF CURCUMINOIDS FROM TURMERIC BY PULSED ELECTRIC FIELD

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Turmeric (*Curcuma longa* L.) represents a highly widespread and used herbal spice and traditional medicine across the world. Moreover, its numerous pharmacological activities have been scientifically confirmed so turmeric is a raw material recognised by modern medicine as well. Its biological properties are mostly attributed to the presence of its most significant constituents or curcuminoids which are curcumin and two curcumin derivates, demethoxycurcuminoids (DMC) and bisdemethoxycurcuminoids (BDMC). In addition, turmeric and curcuminoids possess high commercial importance as they are used in the food, chemical, and textile industries.

The goal of this study was to determine the adequate, environment-friendly technological process for achieving the maximum recovery of turmeric's bioactive components. The extraction with water in subcritical state (100-220°C temperature) and liquid state (80°C temperature) under 30 bar pressure was applied. Prior to the extraction, a pretreatment with pulsed electric field (PEF) was applied and the impact of field strength of 2 and 4 kV/cm at constant specific energy input of 14 kJ/kg was investigated. For comparison, an extraction of turmeric powder without the PEF pretreatment was conducted. The extracts were analysed and the total content of curcuminoids was determined.

What favoured the extraction of curcuminoids was the increase in temperature in the range from 80 to 130°C with 130°C being the point where their maximum recovery is achieved and after which there is a significant decrease in the recovery. At the highest extraction temperature (220°C) the curcuminoids degraded and therefore no curcuminoids were detected. While the extracts obtained at 160°C extraction temperature did not have a liquid form as the other extracts but were of semi-liquid and gel structure after cooling. The potential reason could be the Maillard reaction that can cause changes in colour and organoleptic properties considering the complex structure of turmeric and the presence of sugars and starch.

The application of PEF at higher field strength (4 kV/cm) improved the recovery of curcuminoids compared to the control and the lower field strength applied. Therefore, the highest total curcuminoids contents amounted to 253.16 µg/mL where the content of individual curcuminoids was 122.89, 42.60, and 87.70 µg/mL for BDMC, DMC, and curcumin, respectively.

*Keywords: Turmeric, Curcuminoid, Pulsed electric field, Subcritical water*

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# SUPERCRITICAL $CO_2$ EXTRACTION OF COSMETIC AND EDIBLE OIL FROM MOROCCAN ARGAN KERNELS : A NEW PERSPECTIVE FOR INDUSTRIAL APPLICATION

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Argan tree (*Argania spinosa* L.) is an endemic tree from southern Morocco and Algeria. The oil extracted from argan seeds is mainly composed of monounsaturated and polyunsaturated fatty acids, carotenoids, sterols, tocopherols, and squalene. Argan oil is very well known for its antioxidant properties; it is a product of high added value mainly used in food, cosmetic and pharmaceutical industries in Maghreb and Europe. The production of edible oil is performed by mechanical cold-pressing or by traditional hand pressing from roasted argan kernels by using water. Non-roasted argan kernels are used to produce cosmetic oil after grinding and solvent extraction process. For industrial cosmetic applications argan oil is extracted from ground kernels using a lipophilic or halogenated solvent such as cyclohexane, petroleum ether, chloroform or dichloromethane. After solvent extraction process, the extraction yield is about 45-50 %. It is well-known that extraction processes using organic solvents like cyclohexane or dichloromethane which are toxic and non-selective lead inevitably to a separation steps which is time consuming and increase the production costs. A well-known alternative to organic solvent extraction is the supercritical $CO_2$ (SC-$CO_2$) extraction. SC-$CO_2$ is a GRAS (Generally Recognized As Safe) solvent, and thanks to its low critical temperature (304.21 K) it can be used to extract heat-sensitive components. No separation step is needed since $CO_2$ is gaseous at ambient conditions of pressure and temperature and it is recycled at industrial scale enabling a clean and compact process. Experimental and modelling investigations of SC-$CO_2$ extraction of oil from *Argania spinosa L.* unroasted and roasted kernels were conducted. Extraction kinetics and solubility determination were performed at pressure range from 200 to 400 bar, temperature range from 313 to 333 K at a $CO_2$ flow rate of 0.14 kg/h. Whatever the pressure and the temperature, the highest achievable yield was estimated at 0.63 $kg_{oil}/kg_{biomass}$, which is the highest reachable extraction yield (compared to 8 h *n-hexane* Soxhlet extraction). The extraction kinetics were modeled with Sovová's broken and intact cells model. The extraction of type B was found to be the most suited extraction type. Argan oil solubility in SC-$CO_2$ was modelled with the Chrastil equation and compared to empirical correlations. A retrograde solubility behaviour was observed at 200 bar and the most rapid extraction kinetics were found at 400 bar and 333 K leading to an extraction duration of 4 h. The total tocopherols concentration was found between 389.7 and 1688.6 $mg/kg_{extract}$. SC-$CO_2$ extraction kinetic on roasted kernels was slower than the one observed on unroasted kernels, the optimal particle size diameter for extraction kinetics was 750 µm.

*Keywords: Argania spinosa* L., *Supercritical $CO_2$ extraction, Sovová's model, Extraction kinetics, Tocopherols*

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# EXTRACTION OF PALLADIUM PRECIOUS METAL FROM ALUMINOSILICATE-SUPPORTED CATALYST BY SUPERCRITICAL $CO_2$ ASSISTED BY POLYMERS

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Precious metals, especially palladium (Pd), have a crucial role in daily life thanks to their use in a wide range of applications from electronics to automotive catalysts. Spent end-of-life supported catalysts are a strategic secondary resource to ensure the future supply of such critical metals. Nowadays, conventional methods used for the recovery of the metals from spent catalysts are high energy demanding and generate large volumes of effluents to be treated. SUPERMET, European project aims at developing a green process to recycle precious metals, in particular palladium (Pd) and platinum (Pt), especially from spent supported catalysts from petrochemistry and automotive catalysts. The technology consists in metal extraction in supercritical $CO_2$ ($scCO_2$) thanks to $CO_2$-philic complexing polymers bringing the insoluble precious metal into the $scCO_2$ medium (Figure 1).

In this contribution, we will present promising results regarding the polymer-assisted extraction of palladium from aluminosilicate-supported catalysts in supercritical carbon dioxide. We have tested various $CO_2$-philic polymers bearing different complexing units for the metal extraction experiments. One successful polymer was the poly(1,1,2,2-tetrahydroperfluorodecylacrylate-*co*-4-(diphenylphosphino)styrene) copolymer, named P(FDA-*co*-DPPS), which was able to extract up to 70% of palladium from the aluminosilicate support.

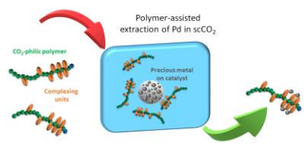


Fig. 1. Extraction of palladium precious metal from supported catalyst by $CO_2$-philic complexing polymers in supercritical $CO_2$

*Keywords: Re-use, Supercritical Extraction, Copolymer, Precious Metal*

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# A FEEDBACK OF TECHNOLOGICAL TRANSFER IN THE FIELD OF SUPERCRITICAL PROCESSES

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Supercritical fluids processes are nowadays coming to a mature level of industrialization in a large range of applications area (Fig. 1) . Indeed, during the latest International Symposium of Supercritical Fluids (ISFF 2018) held in Antibes (France), the different industries case studies very well illustrated the significant number of contributions of SCF fluids in our daily lives (cork stopper, medical patch, food products (sesame oil, ginseng ..), CBD products) coming from all over the word (USA, Europe, Asia).

Supercritical Fluid Innovation (IFS) is a technical R&D Center which treated SCFs projects for industries. IFS is also a cluster that gathers the French Network of both academic and industrial expertizes in SCFs in France.

In this contribution, we will present our vision as an independent technical center of the trend with observed those last 15 years on processes asked by industries (start-up, middles size as well as major group companies), applications fields addressed by those industries (chemistry, food, neutraceutics, waste management). Above, we will make a feedback on the motivations by industries for the employment of supercritical process (environmental, technological goal). We will also draw a sump-up of strengths and weakness to overcome in order to accelerate technological transfer from lab-scale to industrialization.

This vision will be enriched with data coming from the regular supercritical watch report conducted on web since 3 years. This watch-report provides an overview of trends observed on equipment manufacturer, application fields in B to B market as well as B to C market.


Fig. 1: Industrialization of sc $CO_2$ extracts

*Keywords: Supercritical, Subcritical, Technological transfer, Market*

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# CITRIC ACID: TREHALOSE (2:1): ALTERNATIVE TO COMMON SOLVENTS? HARMFULL OR BENING?

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Deep Eutectic Solvents (DES) are a mixture of two or more components where at least one need to be a hydrogen bond acceptor (HBA) and other a hydrogen bond donor (HBD) where the melting point of mixture is lower than melting point of any component individual. These compounds appear as an "green alternative" to organic solvents, and cheaper than ionic liquids. But, at the moment, the number of studies concerning the real biodegradability and biocompatibility is reduced. It is within this context that this work is carried out. With the intuit to study the toxicity of certain DES for animals in two different contexts, in an environmental context where the system was tested at possible environmental concentrations and also in a pharmacological context where the system was tested at different concentrations that can be used in pharmaceutical industry as solvent. These studies were performed with zebrafish, an aquatic animal model recurrently used in pharmacological and environmental tests. These results demonstrated very low toxicity in concentrations tested (up to 12.24 µM) when we tested the system citric acid: trehalose (2:1) in an environmental context and also in a pharmacological context with concentrations up to 1000 µM. The activity of different enzymes involved in antioxidant pathways, protection for toxic compounds, oxidative stress and changes in barrier structure, namely glutathione S-transferase activity, catalase activity, total antioxidant capacity, lipoperoxidation and glutathione peroxidase activity were tested and demonstrate the low toxicity of this system. The promising results herein presented show that in fact DES can be in the future the new class of green solvents, not only used in pharmaceutical industry but also in cosmetic and chemical engineering processes.

*Keywords: Toxicity, Ecotoxicity, Deep Eutectic Solvents, Green Solvents*

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# DES? SOLUTIONS? TOOLS TO CHARACTERIZE THE EFFECT OF WATER IN COMPLEX LIQUID MIXTURES

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Deep eutectic systems (DES) might replace toxic organic solvents in diverse applications. DES have been defined as mixtures of two or more components, where strong interactions cause a huge melting point depression. Thus, DES are liquid at low temperatures, although their pure components might be solids. However, if one of the ingredients is liquid, it is challenging to distinguish a DES from a solution. Some authors defend that DES have a strong non-ideal thermodynamic behavior by presenting stronger and characteristic types of interaction; the consequence is melting at lower temperatures than an ideal solution. In this regard, the effect of the addition of water to this type of mixtures has been investigated. According to the reported definitions, can DES contain water or are they to be considered as solutions? Attempting to clarify this question, the present work explored three characterization tools that can be useful in exploring the nature of these mixtures. As a case study, we explored a mixture of citric acid:L-arginine:$H_2O$, previously reported as DES. Through fundamental equations and a computational tool (PC-SAFT equation of state), it was possible to predict deep melting depressions and much stronger interactions upon water addition. Furthermore, two other tools (FTIR and NMR) were applied to characterize these type of mixtures at a structural and interactional level, and we identified the type of interactions that caused the citric acid:L-arginine:$H_2O$ mixture to become liquid. Moreover, the interactions-network was different from those of individual aqueous solutions. In sum, the explored systems presented a non-ideal behaviour and a type of interactions compliant with the DES definition while refuting the hypothesis of being ideal aqueous solutions. However, the findings are also compliant to a strongly non-ideal regular solution. Although it is still not possible to specifically distinguish DES from non-ideal solutions, given their overlapped definitions, the tools herein explored allow distinguishing the nature of mixtures in regard to their ideal or non-ideal behaviour, potentiated by specific interactions.

*Keywords: Deep Eutectic Systems, Solutions, Water, Characterization*

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# APPLICATION OF APPLE CIDER VINEGAR AS NEW ALTERNATIVE AND FUNCTIONAL SOLVENT FOR EXTRACTION OF BIOACTIVE COMPOUNDS FROM BLACK ELDERBERRY FRUIT

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Apple cider vinegar (ACV) is widely used across the world as a flavoring agent and as a food preservative. Beside of this, its application was suggested in folk medicine as a health beneficial in obesity and overweight, arthritis, asthma, coughs, diarrhea, eczema, diabetes, and high cholesterol, and other disorders and diseases. It is produced by alcoholic and acetic fermentation (double fermentation). The ACV chemical composition is affected by the chemical composition of the apples used as raw material, and by the applied fermentation process. According to the available data, ACV contains various organic acids-dominantly acetic acid, phenolic compounds, minerals (like potassium, sodium, calcium, and iron), vitamins (C and B group), and pectin.

In this study, ACV was applied as an extraction solvent for the extraction of phenolic compounds from black elderberry fruits. As extraction techniques, conventional modified maceration, and ultrasound-assisted extraction were applied. For obtained ACV elderberry extracts analysis of phenolic compounds, flavonoids and anthocyanins were provided. Besides, the impact of extraction of pH change and change of sensory properties was evaluated. The potential of several different ACVs as extraction solvent were investigated. It has been noticed that the capacity of ACV to be applied as extraction solvent depends dominantly on the process of ACV production (industrial or traditional). The process of production affected the ACV pH value, total solids, content of sugars, acetic acid content, the content of initial total phenols, and sensory properties, and these further affect the efficiency of phenolic compounds extraction from black elderberry fruit.

*Keywords: Apple cider vinegar, Black elderberry fruit, Extraction, Phenols, Anthocyanins*

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# PREPARATION OF ENCAPSULATED ADD-VALUE BIOACTIVE PHENOLIC COMPOUNDS EXTRACTED FROM VINE SHOOTS RESIDUES USING SUPERCRITICAL $CO_2$-ASSISTED SPRAY DRYING

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Every year the vine-pruning activity produces a large volume of residues. Around 90% are vine-shoot residues which are highly rich in phenolic compounds and thus have high potentiality to be reused in high added value products, when appropriate extraction techniques are applied. These phenolic compounds have typically very low bioavailability, due to their poor solubility in aqueous media and high susceptibility to thermal and oxidative degradation and consequent loss of bioactivity. The encapsulation of these compounds in suitable excipients can have a positive impact in their bioavailability and bioactivity. Previous data on vine shoot extraction from the BioreVinery project (PTDC/BII-BIO/30884/2017) have identify gallic acid (GA) and resveratrol (RSV) as main phenolic compounds in the extracts. GA is found in high concentrations and RSV has wide therapeutic and cosmetic applications. In this work, model dry powder formulations (DPFs) of GA and RSV using hydroxypropyl cellulose (HPC) as excipient were developed using a green atomization technology, Supercritical $CO_2$-Assisted Spray Drying (SASD). The solids content (maintaining constant the percentage of bioactive compound) and ethanol volume in the solution to be atomized, were studied using a $3^2$ full factorial Design of Experiments (DoE) approach with respect to the process yield, particle size, span and encapsulation efficiency of the bioactive compound in the polymeric matrix. The obtained dry powder formulations (DPFs) were obtained in yields above 60% with encapsulation efficiencies up to 100%, and were further characterized in terms of particle size, morphology, specific surface area, crystallinity, moisture content and antioxidant activity. The SASD has proven to be an efficient encapsulation technique for the phenolic compounds being able to preserve their antioxidant activity with average $EC_{50}$ values of 30.6 µg/mL for GA-DPFs and 149.4 µg/mL for RSV-DPFs assessed by the scavenging capacity for the DPPH radical.

*Keywords: Vine shoots, Phenolic compounds, Supercritical-$CO_2$ assisted atomization, Encapsulation, Antioxidants*

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# FAST DECELLULARIZATION OF TRABECULAR BONE ASSISTED BY SUPERCRITICAL CARBON DIOXIDE

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Decellularization is a process that focuses on the removal of immunogenic cellular material from a tissue or organ. It has become an appealing methodology for the creation of functional and bioactive scaffolds to be implanted with the purpose of restoring of normal tissue function. Several scaffolds deriving from decellularized tissues and organs have been used with varying degrees of success for human clinical applications [1,2].

The present work proposes new methodologies for the decellularization of biological tissues in order to preserve, in the best way possible its properties (Figure 1). For this purpose, the effectiveness of three different decellularization protocols for porcine trabecular bone tissue was investigated using Tri(n-butyl) phosphate (TnBP), supercritical carbon dioxide ($scCO_2$) and, for the first time, a combination of both. TnBP is herein proposed as an alternative decellularization agent to harsh chemicals such as detergents, since it has been reported to better preserve the extracellular matrix (ECM), leading to better biological and mechanical properties of the resulting scaffold [2]. On the other hand, the use of supercritical $CO_2$ is expected to lead to accelerate the decellularization process [3,4], not only reducing the period in which the tissues are exposed to potentially harmful agents, but also resulting in lower costs for the process. $scCO_2$ technology has recently risen as an important sterilization technique [5] due to its appealing properties (inexpensive, low pressure and temperature of operation and non-toxic).

Fresh samples of trabecular bone were here used as a challenging model for testing our proposed decellularization strategies. Trabecular bone samples were extracted from the distal ends of porcine femurs and cut into 6 x 3 mm cylinders, followed by a preliminary cell lysis procedure through 6 cycles of rapid freezing with liquid nitrogen (-196ºC) and rapid melting (room temperature). Three different protocols were implemented: immersion in 1% (v/v) TnBP aqueous solution with agitation, during 48 hours; $scCO_2$ treatment, in a batch mode reactor at 40ºC and 240 bar, for periods of 1 and 3 hours, and $scCO_2$ treatment with 0.1% or 1% (w/v) TnBP, in a batch mode reactor at 40ºC and 240 bar for periods of 1 and 3 hours. Due to the innovative nature of this work, time variants to protocols were implemented to investigate any possible harmful effects caused by prolonged exposure to $scCO_2$ treatment. The samples' structure and morphology were characterized using µ-CT and SEM imaging. Mechanical properties of samples were analyzed using via uniaxial compression testing. Decellularization efficiency was evaluated via hematoxylin–eosin (H&E) staining and DNA quantification.

Results revealed that both TnBP and $scCO_2$ were able to extract the DNA content from the scaffolds, being this effect more pronounced in treatments that used TnBP as a co-solvent. Mechanical analysis of TnBP-treated samples revealed a general increase of the ultimate strength and yield strain, suggesting some degree of crosslinking of collagen fibers occurred. Meanwhile,

# IMPROVING THE ACTIVITY OF HORSERADISH PEROXIDASE IN NADES

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The applications of deep eutectic systems (DES) have grown over the past few years and they have become a viable alternative as media for stabilization of different compounds, such as antioxidants, phenolics or even proteins. Cholinium salts-based systems have been reported as effective media in the stabilization of the enzyme horseradish peroxidase (HRP). These systems, however, face some restrictions when it comes to their application in the cosmetic and pharmaceutical industries, hence the importance of testing alternative DES. In this work, natural deep eutectics systems (NADES) were used to assess the stability of HRP. NADES used were composed of betaine and sugars, in different molar ratios, and phosphate buffer saline (PBS) was used for control experiments. The effect of incubation time and temperature was evaluated through enzyme activity assays. Preliminary results shown that, when incubated in NADES for 6 h, HRP's activity increases, in comparison to control experiments performed in PBS. HRP's structure and conformation were studied through circular dichroism and fluorescence spectroscopy. The possibility to extrapolate these findings to more relevant and sensitive molecules could open new possibilities for the pharmaceutical or cosmetic industry.

*Keywords: Natural Deep Eutectic Solvents, Enzymes, Horseradish Peroxidase, Enzymatic Activity, Stabilization*

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# INFLUENCE OF NATURAL DEEP EUTECTIC SYSTEMS ON WATER THERMAL BEHAVIOR, AND APPLICATIONS IN CRYOPRESERVATION

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Natural deep eutectic systems (NADES), which have applications as solvents for both engineering and life sciences, are mainly composed of sugars, aminoacids or organic acids. In this work, NADES composed by glucose, urea and proline (G:U:P in a molar ratio of 1:1:1) and proline and glucose (P:G 5:3) were prepared and added in different mass fractions to water, from 0.1 to 0.9 wt%. By differential scanning calorimetry (DSC) it was verified that the crystallization tendency of water is modified, even when low fractions of NADES are added. Both NADES G:U:P and P:G alter the water crystallization and melting events, in such a way that high NADES fractions lead to a total suppression of crystallization. A maximum freezing point depression of 22.1 ºC is obtained for $x_{G:U:P}$ = 0.7, and 16.2 ºC for $x_{P:G}$ = 0.6. At intermediate ratios, crystallization occurs on heating. Also, a melting point depression is observed (maximum $\Delta T_c$ ~ 20 ºC), with the respective endotherms shifting progressively to higher temperatures as NADES content decreases approaching to that of bulk water. Calorimetric results show that the crystallization temperature decreases for all P:G mixtures, and this shift is more accentuated for weight fraction of NADES higher than 0.5. These alterations in water thermal behavior also observed by polarized optical microscopy which allowed following the formation of crystals with different crystalline morphologies as bulk water. In particular for P:G aqueous mixture ($x_{P:G}$ = 0.3) rather small crystals were observed. From these results it is safe to say that NADES do have an effect in water thermal behavior, and that this is expressive, even when NADES are present in small amounts. These results prove important for applications of NADES in cryopreservation and storage of food, plants or even animal cells, where the prevention of water crystallization is desired. The cytotoxicity of NADES was evaluated and compared to DMSO, usually used as cryoptectant additive, showing promising results.

*Keywords: NADES, Water, Sugar based-mixtures, Differential scanning calorimetry, Cryopreservation*

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# MULTISTAGE FRACTIONATION OF PINE BARK BY SFE

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Softwood tree bark is still a largely under-utilized by-product from pulp mills. The amount of bark generated per year is estimated to 300-400 million $m^3$. Although the combustion of bark generates heat and energy, a better utilization for this by-product in the future is expected. The bark of softwood trees contains a wide variety of interesting compounds, which could enter into various market segments once isolated. Investigation of extracts in organic solvents of industrially interesting softwood trees like Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) was already carried out in the past and an array of compounds was described. Today, we wish to shift away from organic solvents to more environmentally benign green technologies. The use of supercritical carbon dioxide ($scCO_2$) is fully in line with the aforementioned greener approaches for the extraction of organic compounds. While possessing polarities like unpolar organic solvents, $scCO_2$ is not toxic, relatively cheap and can be recycled infinitely during the extraction process. Supercritical condition refers to a particular state where the fluid is maintained above its critical pressure and temperature. Close to this part of the phase diagram, the surface tension of the fluid is nearly zero since there is no boundary between liquid and gas anymore. These conditions offer interesting possibilities: a small change in temperature and/or in pressure notably changes the density of the fluid modulating solvent power and selectivity. Multistage fractionation of pine bark was investigated in order to extract different classes of bark extractives such as free fatty acids, resin acids, phytosterols, sterol esters, lignans, wax esters and triacylglycerides. The fractions obtained were analyzed using GC-MS/FID.

*Keywords: Bark, biorefinery, Supercritical fluid extraction, Extractives, Gas chromatography*

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# GREENERING CRYOPRESERVATION BY NATURAL DEEP EUTECTIC SYSTEMS AS CRYOPROTECTANT AGENTS

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Dimethyl sulfoxide (DMSO) remains the standard gold cryoprotectant agent in cell banking applications. However, its toxicity remains the main challenge when it comes to post-thawing cell recovery and cell survival. [1] In cell culture, DMSO has to be removed before culture or it will cause cell death; in case of cell therapy DMSO must be washed out before infusion because it can cause nausea and vomiting, headaches, seizures, renal insufficiency and cell death. The removal of DMSO before infusion should eliminate the risk of toxicity effects, however in literature the opposite is often found in data reports [2,3] and alternative methods are required to overcome this major drawback. Natural Deep Eutectic Systems (NADES) have emerged in the last decade as alternative solvents for many applications. [4] The major advantage of these systems is the fact that they are composed by natural components, therefore considered green solvents. Some of their components are found in animals that live in cold environments and known to be involved in their hibernation processes. [5] That fact have encouraged us to test NADES as cryoprotectant agents [6], and our current work is focused on the development of new NADES able to overcome the drawbacks of DMSO. Our latest results have showed that NADES are non-toxic for mammalian cells, that depending on the cell type and cell robustness, NADES can cryoprotect cells more efficiently than DMSO, and one of their most outstanding features is the fact that do not need to be removed during thawing. These results show that NADES are potential candidates to substitute DMSO in regular cell culture. Moreover, our promising results may encourage further studies with other cell types, such as stem cells and red blood cells.

*References: [1] Stokich et al., Cryobiology, 69, 281–290, 2014.; [2] Rowley et al., Cytotherapy, 1 (6), 439-46, 1999.; [3] Fois et al., Bone Marrow Transplant., 40, 831–835, 2007.; [4] Paiva et al., ACS Sustain. Chem. Eng., 2 (5), 1063–1071, 2014.; [5] Gertrudes et al., ACS Sustain. Chem. Eng., 5, 9542−9553, 2017.; [6] Castro et al., Cryobiology, 83, 15-26, 2018.*

*Keywords: Green solvents, Eutectic systems, Cryobiology*

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# EXPERIMENTAL INVESTIGATION ON VOLUMETRIC PROPERTIES OF AN AQUEOUS PHENOLIC DEEP EUTECTIC SOLVENT

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Green solvents are one of the vital materials and tools for researchers in green chemistry. Actually, replacement of conventional solvents by green solvents in chemical industries is one of the basic and fundamental studies of green researchers. Deep Eutectic Solvents (DESs) as a new type of green solvents was introduced to scientific committee in 2003. After this introduction, many various DESs were introduced by researchers with different applications. In 2013, for the first time phenolic DESs were proposed. This type of DESs, were investigated in different applications such as $CO_2$ capturing, liquid- liquid extraction, electronic effect of substitution group and electrolytes of solar cells. However, still many fundamental information about this type of DES is vague. Therefore, in this study, an experimental volumetric investigation has been carried out for aqueous solutions of (1 choline chloride + 4 phenol) DES. Accordingly, volumetric data, excess volume and many derivative volumetric properties of the investigated mixtures have been calculated. By analyzing, calculated properties, it was found that, molecular interactions in mixture are stronger than pure state interactions. Interstitial accommodation was observed in the mixture. Additionally, a remarkable result has been achieved about these systems. In this work we demonstrate that both water and DES tends to be solvated by other molecule, however, this tendency is stronger for water than DES, therefore, probably hydrogen bond networks in the mixture, are established in a manner which water molecules are located at center and surrounded by DES pseudo molecules.

*Keywords: Deep Eutectic Solvent, Water, Density, Volumetric properties, Excess volume*

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# SUPRAMOLECULAR BIOSOLVENTS FOR SEPARATION PROCESSES

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Supramolecular solvents (SUPRAS) constitute a suitable alternative to conventional organic solvents in extraction processes. They are nanostructured liquids synthesized from the self-assembly and coacervation of amphiphiles. First, amphiphiles spontaneously form three-dimensional aggregates (e.g. micelles or vesicles) above a critical aggregation concentration (*cac*) to generate a colloidal system. Secondly, *coacervation* (separation into two liquid phases in colloidal systems) is produced by the growth of the aggregates in the colloid. This is achieved by an external stimuli (pH or temperature change or the addition of a salt or a poor solvent for the amphiphile) that will reduce the repulsions among the amphiphilic head groups or will favour their de-hydration, so that their effective size decreases and they can be packed closer together. As a consequence, oily coacervate droplets are spontaneously produced and form clusters that separate as a new colloid-rich phase (coacervate phase or SUPRAS). SUPRAS have proved unique features as wide scope extractants or organic compounds, metals and proteins from both liquid and solid samples. Their high performance arise from three characteristics: *different polarity microenvironments* (e.g. polar at the head groups and nonpolar at the hydrophobic moieties), *multiple binding sites* owing to the huge concentration of amphiphile in SUPRAS (0.1-1 $mg \cdot \mu L^{-1}$) and *large surface area* arising from the coacervate droplets that make them up. In order to comply with green chemistry criteria, two types of bioSUPRAS were prepared from eco-friendly amphiphiles (high biodegradability, low toxicity, renewable sources) with the aim to extend their applicability to the food and cosmetic industries. BioSUPRAS were made up from i) inverse aggregates of carboxylic acids in mixtures of ethanol:water and ii) normal aggregates of rhamnolipids in salty or mildly acidic water. We determined their synthesis conditions, composition and microstructure. Their applicability to the extraction of polar and no polar compounds was investigated, namely polyphenols, carotenoids and alkaloids from food waste and algae and of soluble dyes from water.

*Keywords: Green solvents, Supramolecular solvent (SUPRAS), Surfactants, Extraction*

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# IMMOBILIZATION CANDIDA RUGOSA LIPASE AND ESTERIFICATION OF RAC-MENTHOL IN DEEP EUTECTIC SOLVENTS

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Menthol is a secondary racemic (*rac*) alcohol that, due to its refreshing and cooling effects, can be used food, pharmaceutical and cosmetic industries. These properties, however, are mainly present in the (-)-menthol enantiomer. Several separation strategies have been studied, in order to obtain an enantiomeric pure product, such as the use of biocatalysts, like enzymes. The separation of rac-menthol can be achieved with Candida Rugosa lipase (CRL) in solvents such as hexane or ionic liquids. This process occurs through an esterification reaction, using eutectic solvents (DES) as solvent media, where (-)-menthol is converted into an ester, and then followed by separation. If species that are enzyme substrates are present in the DES composition, it is possible to envisage a one pot reaction strategy and virtually "solvent free" process.

In our previous work, a DES composed by rac-menthol and lauric acid with a 2:1 composition has proven effective in the esterification of (-)-menthol to (-)-menthyl laurate, having the best results a 37°C and water activity of 0.11. This strategy can be further improved if the enzyme can be reutilized, which can be achieved via enzyme immobilization.

In this work, different immobilization procedures and supports were tested, namely acrylic resins and silica-based materials. The immobilization efficiency in the different supports were assessed as well as the reaction yield *rac*-menthol esterification, and better water activity for the reaction. The results, so far, show that the best solvent for immobilization is acetone and the best supports appear to be XAD7HP and Celite. Regarding the most suitable water activity to perform the reactions, $a_w$ ca. 0.5 appears to give best results. These results allow us to have an efficient *rac*-menthol resolution by designing a reaction-separation strategy that be operated in a continuous mode.

*Keywords: Deep eutectic solvents, Rac-menthol, Candida Rugosa lipase, Immobilization*

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# RATIONAL DESIGN OF NATURAL DEEP EUTECTIC SOLVENTS FOR CHIRAL DRUG PREPARATION

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Designing new, environmentally-friendly, and tunable solvents have been dramatically expanding in popularity in order to overcome the flaws of organic solvents from technological, environmental and economic aspects. Natural deep eutectic solvents (NADES), as a new generation of novel alternative solvents, fully meet green and sustainable technologies principles. Though it is sometimes relatively easy to find an appropriate NADES for certain process, this is occasionally ungrateful procedure. Namely, sometimes is difficult to predict which mixtures and in which molar ratios will originate as a NADES and also which solvent properties crucial will be exerted. Therefore, the composition of NADES and their physical, thermal, chemical or biological properties should be characterized on case-by-case scenario. Abundance of possible NADES formulations, especially when possible addition of certain amount of water is taken into account, makes it impossible to prepare and characterize all of them, pointing out the need for development of predictive NADES structure-activity mathematical models. Approaches used so far for screening appropriate/ideal NADES (out of enormous pool of structural possibilities) have been governed by time consuming empirical methods, while systematic investigation in NADES structure-activity relationship, as a backbone for rational design of these solvents, is still lacking. Current literature suggests COSMO-RS, software that can predict thermodynamic properties and phase equilibrium which would help in designing the best possible solvent for a certain application. COSMO-RS can design new solvent structures with tailored properties and thus the trial-and-error method of NADES preparation can be avoided.

The aim of this work is to design rationally NADES for the preparation of therapeutic deep eutectic solvents and biocatalytic preparation of chiral drug by combining experimental and modelling tools.

*Keywords: Chiral drug, COSMO-RS, Natural deep eutectic solvents, Rational design*

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# DESIGNING A BIOCATALYTIC PROCESS INVOLVING DEEP EUTECTIC SOLVENTS: LIPASE-CATALYSED SYNTHESIS OF (*R*)-1-PHENYLETHANOL AS A CASE STUDY

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The synergistic use of deep eutectic solvents (DES) and biocatalyst fits logically to the efficient and sustainable production of various commercially interesting products. Namely, biocatalysis ensures catalyzing otherwise difficult transformations in high regio-, chemo- and enantioselective manner at mild and economic conditions, whereby DES can serve as strong green support for modulating/directing reaction route for obtaining the desired product. As the number of structural combinations encompassed by DES is tremendous, it is possible to design an optimal DES for each specific enzymatic reaction system. This important feature of DES allows to (i) enhance enzyme stereoselectivity, activity and stability, as well as reaction rate through enhanced substrate solubility; (ii) enhance reaction yield (iii) enhance/modify biocatalyst stereo preference; (iv) contribute to overall greenness of the process (including recycle and reuse). The use of DES for enzyme-catalysed reaction could be considered as “back to the roots”. Namely, when the compounds that constitute the DES are primary metabolites, namely, amino acids, organic acids, sugars or choline derivatives, they can provide cytoplasm-like natural environment for enzymes, meaning that enzymes can transform unnatural substrates in natural environment.

When designing efficient biocatalytic process involving DES, independently of reaction type and enzyme used, the following steps should be included: (i) preparation and characterization of DES (ii) screening of DES for optimal enzyme performance (iii) optimization of the biocatalytic process, and (iv) downstream process design with possible scale-up.

In this work green lipase-catalysed process for obtaining commercially interesting secondary alcohol (R)-1-phenylethanol of high optical purity in DES as medium was development. Several cholinium chloride-based DES were prepared and screened for optimal enzyme performance (enzyme activity, stability and enantioselectivity), followed by optimization of biocatalytic process (substrate and enyzme loading, water content in DES, reaction temperature). Recovery of the products/DES and DES recycling was successfully performed. After laboratory scale, production of (R)-1-phenylethanol was also effectively performed on a preparative scale (half liter batch reactor). The results of this study confirmed the great potential of DES in biocatalytic medium in terms of improved lipase stability and process sustainability.

*Keywords: Biocatalysis, Green chemistry, Natural deep eutectic solvents*

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# SUPERCRITICAL $CO_2$ IMPREGNATION - SELECTION OF SUITABLE POLYMERIC CARRIER FOR HEMP SEED OIL

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Supercritical $CO_2$ impregnation (SCI) process allows incorporation of bioactive components into solid carriers in an environmentally friendly manner. In recent years, SCI was highlighted as a promising method for preparation of added value materials that can protect bioactive components from environment (sun light, air, moisture etc.), stabilise them, and increase their shelf life. SCI process is also suitable for preparation of material with controlled release of bioactive component. Taking into account the above-mentioned, SCI process was employed in this study for incorporation of hemp seed oil (HSO) into biocompatible polymers (starch xerogel, starch aerogel, $\alpha$-cyclodextrin, $\beta$-cyclodextrin, and $\gamma$-cyclodextrin). Given that efficiency of SCI depends on process conditions and affinity of bioactive component towards $scCO_2$ and polymer, it is necessary to optimise process for every individual system. Proposed SCI process was performed at pressure of 30 MPa and temperature of 40 °C during 5 h and 18 h. FTIR analysis confirmed that $scCO_2$ did not have effect on polymer composition nor it remained in polymer after process. Additionally, FTIR and UV-Vis analysis showed that HSO is present in all tested polymers after SCI process. It was shown that impregnation of HSO is highly dependent on selection of polymeric carrier (its chemical composition and morphology) and operating time employed, resulting in loadings from 0.5% to 40%. Chemical analysis showed that HSO is rich in unsaturated fatty acids especially linoleic acid (54-60%) and α-linolenic acid (17-20%). These essential fatty acids have well-established health benefits including protection against cardiovascular, neurodegenerative and inflammatory diseases. Proposed SCI process gave guidelines for development of added-value materials that are solvent free and can be used as phytopharmaceuticals.

*Keywords: Supercritical $CO_2$ impregnation, Hemp seed oil, Starch, Cyclodextrin*

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# FABRICATION OF ULTRAFILTRATION MEMBRANES FROM AN AQUEOUS CELLULOSE NANOCRYSTAL SUSPENSION

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Ultrafiltration is a membrane process that is widely used in water treatment, food and biotechnology industry, as it allows separations with low energy and chemical demand, small footprint and easy scalability. Most ultrafiltration membranes are made of polymers and their fabrication involves use of organic solvents, such as n-methyl pyrrolidone, dimethylformamide and dimethylacetamide. Replacing these solvents with less harmful ones is highly desirable for both environmental and health aspects.

In this study, we showed the fabrication of ultrafiltration membranes by depositing an aqueous suspension of cellulose nanocrystals (CNCs) on a support membrane and causing their irreversible aggregation by increasing the ionic strength within the deposit. CNCs were fabricated from cotton linter by sulfuric acid hydrolysis and showed good colloidal stability in water. The CNC suspension was deposited on a support membrane made of cellulose acetate by dead-end filtration using different permeate volumes to affect the deposit thickness. After CNC deposition, a 200 mM $AlCl_3$ solution, in which the zeta potential of the nanocrystals was close to zero, was permeated through the deposit to cause the irreversible aggregation of the colloids and form a stable membrane layer.

It was observed that increasing the permeate volume during CNC deposition increased the CNC layer thickness and decreased the permeance of the membranes. The pure water permeance of membranes made by depositing 0.12, 0.24 and 0.48 mg CNC/$cm^2$ membrane area were 115, 62 and 41 L/h.$m^2$.bar, respectively. The thickness of the CNC deposit increased from 3.40 to 12.3 µm, as measured with SEM. The rejection of all three membranes for the probe molecule, blue dextran (5 kDa), was all within 91±2%, showing that the pore size of the deposit layer was essentially the same. Stability of the CNC deposit as a membrane layer was assessed by keeping the membranes in water and observing the presence of cellulose on the membrane surface at different times using ATR/FTIR. It was observed that after a week of being kept in water, the ratio of the cellulose peak area (3200 – 3700 $cm^{-1}$) to the cellulose acetate (support membrane) peak area (1750 $cm^{-1}$) was unchanged, showing the stability of the CNC deposit as a membrane.

*Keywords: Cellulose nanocrystals, Ultrafiltration, Membrane*

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# INFLUENCE OF SUPERCRITICAL $CO_2$ ON THE THERMAL PROPERTIES OF POLYLACTIC ACID AND POLYAMID 12

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The increase of concentration of greenhouse gases in geosphere is reported as the main cause of climate change. Air concentration of carbon dioxide ($CO_2$), one of the substances known to show greenhouse gas potential, reached 409 ppm in 2019, equal to an increase of 31.5 % since the beginning of industrialization. However, $CO_2$ is an inert and non-toxic gas, with a critical point of $p_c$=73,75 bar and $T_c$=30,98 °C. Called a green solvent, it has found a wide range of applications in industry as extracting agent, refrigerant, and sterilization agent.

In this study, supercritical $CO_2$ will be used to produce Particles-from-Gas-Saturated-Solutions (PGSS). The generated powder is supposed to be used in additive manufacturing (AM), especially within a process that is characterized by directed energy deposition (DED) but also by powder bed fusion (PBF). Due to the difference of viscosity between polymer melt and gas phase, the operating principle of the PGSS plant was adapted to increase the mixing performance. Thus, the polymer granules are melted by a single-screw extruder before being mixed downstream with supercritical $CO_2$ in a planetary roller extruder. Before the gaseous polymer phase is expanded through a nozzle, it is mixed with additional $CO_2$. Due to the plasticization of the gas molecules in the melt, the mixture can be expanded into a spray tower where the melt is torn apart. The resulting polymer droplets are solidified, due to the Joule-Thomson effect.

It is known that $CO_2$ is changing the thermal properties of the polymer, such as glass point, melting temperature, and crystallization temperature. Therefore, to identify the process parameters for the PGSS plant, this contribution is comparing two model polymers by using calorimetric measurements. The measurements were carried out using a calorimeter and a transitiometer, with polylactic acid 3251D (PLA 3251D) from NatureWorks LLC, a biodegradable polymer with a D-Lactid concentration of 1,4 %, and Vestamid® Polyamid 12 L1600 (PA 12) from Evonik, a standard polymer for PBF. It was found that $CO_2$ influences the crystallization behavior in both polymer systems. However, the pressure settings were affecting the melting temperature decrease of PLA 3251D only, an effect not observed in PA 12.

*Keywords: Supercritical $CO_2$, PGSS, Thermal behavior of PLA3251D and PA 12, Polymer powders for AM*

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# EVALUATION OF BIOLOGICAL ACTIVITY OF PLANT-NADES-EXTRACTS AS READY-TO-USE EXTRACT FOR FOOD AND PHARMACEUTICAL APPLICATION

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Since NADES consist of simple, inexpensive and naturally occurring compounds with an implied high safety profile, it is assumed that extracts obtained by NADES may be directly used in products for human consumption without the need for expensive downstream purification steps. Considering the potential applications of NADES and NADES-based extracts, it is necessary to further evaluate their biological activity. Human cell lines are already widely used in testing biological activity of compounds present in plants and plant's products. The application of *in vitro* cell cultures for this purpose is based on the fact that interaction of the test substance and biological systems occurs preferentially at the cellular level, and has an impact on the whole organism. With such approach a large number of samples, including crude extracts from screening phase, as well as pure fractions obtained during the isolation procedure, could be evaluated. Beyond that, the application of *in vitro* cell cultures is a good choice for preliminary screen of biological activities, which enables faster and more cost-effective studies compared to *in vivo* studies. The findings obtained by *in vitro* tests are valuable and can serve as guidelines for further required *in vivo* and epidemiological studies of biological activity of plants, its compounds, and products.

Based on aforementioned, potential biological activity of plant polyphenolic extracts was evaluated by testing antiproliferative and antioxidant activity. *In vitro* cytotoxicity of prepared extracts was assessed by antiproliferation assay on two tumour cell lines, whereas for investigation of type of cell death and cell cycle arrest a flow cytometric analysis was applied. Antioxidant activity and possibility of extracts to protect cells from oxidative stress was assessed by ORAC method as well as cell-based methods.

*Keywords: Biological activitiy, In vitro testing, Natural deep eutectic solvents, Plant extracts*

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# POTENTIAL APPLICATION OF NATURAL DEEP EUTECTIC SOLVENTS IN FOOD INDUSTRY

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Many industrial processes use large quantities of volatile, flammable and toxic organic solvents based on unsustainable resources such as oil, resulting in significant environmental and economic impacts. Over the past decade, natural deep eutectic solvents (NADES) have become promising alternatives to traditional organic solvents from both environmental and technological perspectives. The choice of a solvent in certain process not only depends on its chemical, and physical properties, but also on its environmental impact (e.g. ecotoxicity and biodegradability), sustainability (possibility of recycle and reuse) and process safety (e.g. flammability and volatility). Therefore, interest for potential application of NADES as solvents and/or supporting medium in different processes has increased significantly, due to their unique physical and chemical properties, and low environmental impact. One of the major attractions of making NADES an alternative to conventional organic solvents lies in the fact that the number of structural combinations encompassed by these solvents is tremendous, thus it is possible to design an optimal one for each specific application. Since the number of possible chemical structures of these solvents is vast NADES are very interesting for use in food industry.

Potential use of NADES for extraction of biological active compounds, preparation of ready-to-use extracts and use of NADES-based extracts for fortification in food industry will be considered herein.

*Keywords: Food fortification, Green extraction, Natural deep eutectic solvents, Polyphenolic compounds*

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# HYDROLYSIS AND FRACTIONATION OF PHENOLIC COMPOUNDS FROM BREWERY'S SPENT GRAIN BY SUBCRITICAL WATER

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Brewery's spent grain (BSG) is the solid by-product generated by breweries accounting for 20 kg per 100 L of beer produced. Integration of this by-product within a biorefinery concept is of great interest to obtain different bioactive compounds, specially taking into account that BSG is a valuable source of phenolic compounds, with ferulic and p-coumaric acids as the primary class of phenolic compounds present in the BSG that have demonstrated antioxidant effects.

Chemical and enzymatic hydrolysis are common methods used to release bioactive compounds. However, chemical hydrolysis is a non-selective method while low yields are usually achieved by enzymatic hydrolysis. In this work, the use of subcritical water (subW) is proposed to hydrolyze the BSG to obtain phenolic compounds bound to the lignocellulosic matrix. The effect of temperature, in the range from 125 ºC to 185 ºC, at constant flow rate (4 mL/min) was assessed in a semi-continuous fixed bed reactor.

Total phenolic compounds (TPC) release increased by increasing temperature with values after 240 min of extraction ranging from 10.3 ± 0.3 to 33.0 ± 0.3 mg GAE/$g_{dry\text{-}BSG}$ at 125 and 185 °C respectively. Compared to enzymatic hydrolysis by using xylanase, TPC initial productivity was higher by subW than by enzymatic hydrolysis with values of 0.087 mg GAE/($g_{dry\text{-}BSG}$·min) and 0.28 mg GAE/($g_{dry\text{-}BSG}$·min) at 185 ºC, respectively.

At 160 ºC and 185 ºC five phenolic compounds were identified: two hydroxycinnamic acids (ferulic and p-coumaric acids) and three aldehydes (vanillin, protocatechuic aldehyde and syringic aldehyde). The maximum individual phenolic release was obtained at 160ºC for hydroxycinnamic acids, while this maximum was achieved at 185ºC for the aldehyde phenolic compounds identified in this work. Based on these results, fractionation of phenolic compounds can be achieved by working under different conditions.

*Keywords: Subcritical water, BSG, Phenolic compounds, Antioxidant activity*

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# A COMPARATIVE ASSESSMENT OF ALTERNATIVE SOVENTS FOR CARBON CAPTURE IN A PILOT PURIFICATION UNIT USING CFD AND PROCESS MODELLING TOOLS

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Carbon capture utilization and storage (CCUS) is a promising concept towards the decarbonization of energy intensive industries and long distance transportation (e.g. shipping). The critical factor for optimal CCUS system is the efficient separation of $CO_2$ from the exhaust gas stream. A relatively mature carbon capture technology is the absorption of the $CO_2$ into aqueous MEA solvents using an absorption column followed by their separation in a desorption column, resulting in the purification of carbon dioxide and solvent regeneration. The optimized operation of an absorption-desorption unit depends on the particular column design specifications and operation parameters and the selection of appropriate solvents for gas treatment. Recently, ionic liquid (IL) solvents have attracted considerable interest due to their promising thermodynamic and transport properties. However, their performance under realistic conditions is still at an early stage. The objective of the present work is to develop numerical models for the prediction of exhaust $CO_2$ capture in conventional, industrial scale absorption-desorption packed columns using novel ILs. A Computational Fluid Dynamics (CFD) two-phase reactive flow model is developed incorporating detailed IL thermodynamics and kinetics. Model validation against experimental data from a pilot unit is presented. Further, the results of the coupled hydrodynamic performance are used to suggest possible design specifications directly applicable to industrial settings. Based on the CFD simulations, appropriate reactor models were specified and integrated into an overall process model, developed in ASPEN PLUS, concerning $CO_2$ purification from cement plants. Extensive parametric and sensitivity simulations were performed in order to specify key design and operation parameters towards the optimization of the CCUS process.

*Keywords: Carbon Capture, Ionic Liquids, CFD Modelling and Simulation, Process Simulation*

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# TOWARDS THE MECHANISTIC UNDERSTANDING OF NATURAL DEEP EUTECTIC SOLVENTS EFFECT ON ENZYME CATALYZED REACTIONS

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Natural deep eutectic solvents (NADES) are a novel class of solvents, offering more benign properties compared to common organic solvents. NADES are mixtures of naturally derived compounds (usually a quaternary ammonium salt and a hydrogen bond donating component, like organic acids or polyols) forming a strong intermolecular hydrogen bonding system. This network stabilizes the liquid mixture, which results in a significantly decreased melting point compared to the initial compounds. This property allows the use of NADES as reaction media/solvents for various chemical reactions. This is typically in the food, feed, cosmetic and pharmaceutical industries, where biocompatibility is required. However, to efficiently design NADES for biocatalysis, a better understanding of their effect on these reactions is needed. Fundamentally, this comes down to the description of the exact hydrogen bonding network and its interaction with the reaction actors. Modeling methods, allowing for such fundamental descriptions (like density functional theory or molecular dynamics), suffer from limitations of accessible time and length scales, which makes their application impractical for bulk media.

We hypothesize that describing the effect that the NADES have on enzymatic reactions is feasible solely through solvation energies of the substrates, medium viscosities and enzyme stability in NADES. If these effects describe indeed their behavior sufficiently, this simpler model could be developed to design neoteric solvents.

As a case study, we monitored the initial enzyme activity and the final conversion rate of lipase catalyzed vinyl laurate transesterification in n-hexane together with various choline chloride based NADES with different compositions and molar ratios. We determined the solubility of substrates and the viscosity of solvents by experimental methods and we used MD based simulation to investigate enzyme stability and to calculate solvation free energies of substrates in NADES. Also, we determined the relationship of these properties to the enzyme activity and conversion rate to evaluate their utility in predicting the reaction parameters.

*Keywords: Naturally derived deep eutectic solvents, Biocatalysis, Molecular dynamics, Reaction modeling, Green solvents*

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# PREPARATION OF A METAL-ORGANIC FRAMEWORK USING SUPERCRITICAL CARBON-DIOXIDE FOR DRUG DELIVERY APPLICATION

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In recent years, MOFs have been considered as promising nanocarriers, due to their high surface area and porosity, well-defined structure and easy chemical functionalization. In particular, MIL-100(Fe) (composed of iron(III) and benzene-1,3,5-tricarboxylate (BTC)), has been studied as a carrier in drug delivery systems because of its biocompatibility, high drug loadings and adaptive mesoporosity. On the other hand, the iron trimesate (FeBTC), composed of the same metal center and organic linker, has been less investigated for this purpose, because of the structural defects and expected lower loading when intended for adsorption and drug delivery applications.

The objective of this work is the the development of an eco-friendly approach based on supercritical $CO_2$ ($scCO_2$) to prepare FeBTC and compare to the conventional approach of the synthesis of MIL-100(Fe). In addition, the study of both MOFs' loading with a model drug, azelaic acid, was carried out using also $scCO_2$ as drug impregnation medium.

MIL-100(Fe) and FeBTC were synthetized following conventional and $scCO_2$ technology, respectively. According to the X-ray diffraction patterns, MIL-100(Fe) reveals a crystalline character, while FeBTC is semi-amorphous; however similar pattern can be observed in both cases, but with broadened peaks for the FeBTC. The presence of an additional amount of BTC was detected in the FeBTC sample by Fourier transformed infrared spectroscopy, by a band appearing at 1700 $cm^{-1}$ corresponding to the carbonyl group. According to low temperature $N_2$ adsorption measurements, high surface area values were reached with both preparation methods (MIL-100(Fe) S.a = 2183 $m^2/g$ and FeBTC S.a = 1418 $m^2/g$). Based on the scanning electron microscopy images, the FeBTC consists of the aggregates of nanoscale particles, while in case of the MIL-100(Fe) cubic shapes with bigger size (< 1 µm) can be observed.

The loading of both matrices with azelaic acid was carried out using $scCO_2$. The amount of the encapsulated drug will be compared to evaluate the adaptability of the MOFs as nanocarriers.

*Keywords: Metal-organic framework, Drug impregnation, Supercritical $CO_2$*

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# METHODS OF ALGINATE AEROGELS IMPREGNATION FOR SUPPORTED IONIC LIQUID PHASE CATALYSIS

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The projected implementation of Carbon Capture, Usage and Storage (CCUS) technologies will open a window of opportunities for captured (and compressed) carbon dioxide to be utilized as a raw material in the production of variety industrial products. One of the promising large-scale applications of waste carbon dioxide is its incorporation into cyclic carbonates via reaction with epoxides. In our work we investigate the use of ionic liquid supported on a porous material (aerogel) under dense carbon dioxide conditions. The supported ionic liquid phase (SILP) brings advantages of both homogeneous (high rates and selectivity) and heterogeneous (easy separation, recyclability, continuous mode of operation) catalysis. Combined with high-pressure carbon dioxide technology, where carbon dioxide serves as both reagent and mobile phase, it allows for almost “solvent-free” process. The choice of aerogel as a supporting material is dictated by its high specific surface area and porosity (mesoporous structure), and yet, low bulk density. The most straightforward procedure of simple deposition of IL/catalyst on a surface of porous aerogel (wet impregnation) suffers from leaching. Therefore, in this study we investigated alternative approaches of impregnation, such as, i.e., ultrasound or vacuum impregnation. These methods relay on physical impregnation mechanism that avoids the complexity related with a chemical modification of support material with covalently bound molecules. Impregnated alginate aerogels were characterized by BET Surface Area Analysis and Scanning Electron Microscopy and tested as a catalyst for the cycloaddition of carbon dioxide to propylene oxide to form propylene oxide.

*Keywords: Aerogel, Supported ionic liquid phase, Impregnation, Dense carbon dioxide, Cyclic carbonate*

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# ZEOLITE FUNCTIONALIZATION IN SUPERCRITICAL CARBON DIOXIDE FOR MIXED MATRIX MEMBRANE PRODUCTION

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A new type of membrane can be produced by incorporating inorganic fillers into the polymeric membranes to form mixed matrix membranes (MMMs) that can be systematically adjusted for a highly selective gas separation. It was shown that zeolite-filled MMMs might achieve a superior separation compared to pure polymeric membranes. Still, the main problem in MMMs fabrication remains the formation of "voids" due to the poor polymer-zeolite interaction. The study reports micro-sized zeolites' surface modification via silanization to obtain better contact between the inorganic and organic phases for the MMMs production. The silanization was performed in supercritical carbon dioxide. The type of contact between phases, reaction time, and curing step were optimized. Cellulose acetate based MMMs were fabricated, and their structural properties were investigated using a two-beam SEM/Xe-PFIB Microscope. Energy focused ion beam of plasma xenon (Xe-PFIB) provided the ability to perform cross-sections of the samples. The results showed that modified zeolites provided better contact between the inorganic and organic phases. A standardized test setup is introduced for screening and qualification of the newly developed membrane material. Preliminary tests are promising.

*Keywords: Supercritical carbon dioxide, Silanization, Mixed matrix membranes*

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# VALORISATION OF FISH WASTES USING SUBCRITICAL FLUID TECHNOLOGIES

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Fish processing generate large amounts of wastes. Fish wastes are discarded at land or sea and they are also used as fertilizer or animal feeds. However, fish wastes contain several high added-value compounds such as oils, amino acids and bioactive peptides, collagen, chitin, hydroxyapatite or pigments that can be recovered/ extracted.

In the present work, cod fish bones were characterized for lipid, sugar, ash, and protein content. The matrix was then extracted with subcritical water (SBW) in order to recover valuable bioactive compounds. The hydrolysis was performed from ambient temperature to 250 ºC, collecting samples at 90, 140, 190, and 250 ºC during 30 min; the pressure was kept at 10 MPa to maintain water in its liquid state. Final yield of extraction was 53.9 %. The collected extracts and the residue left after SBW extraction were analyzed for protein, sugar, and ash content. Based on these results, 89.4 % of initial protein was recovered in the extracts. Molecular weight of hydrolyzed proteins and peptides was characterized by SDS-PAGE. Minerals and metals of the residue left after SBW extraction were also determined. XRD analysis revealed the presence of crystalline hydroxyapatite.

*Keywords: Cod fish, Wastes, Subcritical water, Hydroxyapatite*

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# VALORISATION OF TOMATO WASTE USING SUPERCRITICAL FLUID TECHNOLOGIES

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The main objective of this work is the valorisation of tomato industry wastes, obtaining lycopene enriched extracts using supercritical carbon dioxide ($ScCO_2$) extraction; the effect of different process parameters (temperature and pressure) was studied. Different types of tomato wastes were also studied.

The conventional method for the extraction of carotenoids tested was the Soxhlet extraction method. Soxhlet extraction was performed to be later compared with the supercritical $CO_2$ extraction ($ScCO_2$) results. Soxhlet extraction yields varied between 4 to 14%. $ScCO_2$ extractions were performed at pressures from 200 to 500 bar, and temperatures from 40 to 60 ºC, using lyophilized tomato waste. Higher pressures and higher temperatures increased the yield of extraction of oil by $ScCO_2$.

The extracts were analysed spectrophotometrically at 472 nm to estimate the concentration of lycopene. Lycopene yields ranging from 10 to 200 mg lycopene per 100g of dry material were obtained depending on the pressure/temperature conditions used. Lycopene extracts were further formulated in microemulsions with the aim of developing a topical dosage form, able to supplement the skin with lycopene and treat skin inflammatory disorders.

The degradation rate of lycopene in the tomato waste and in the $ScCO_2$ oil was studied.

*Keywords: Lycopene, Tomato waste, Extraction, Supercritical, $CO_2$*

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# MULTI-PURPOSE CHEMO- AND ELECTROCATALYST MATERIAL FROM AMORPHOUS COBALT METAL–ORGANIC FRAMEWORK

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The notion of M–N–C catalysts, where M is typically Fe, Co, Mn or Ni, is often reserved for the catalysts developed for applications in energy conversion and storage devices. However, recent reports have also emphasized the role of these materials in facilitating heterogeneous organic transformations. There is an accountable divergence in the ways that the M–N–C materials are prepared, and they depend on the ultimate application prerogative. When used in the electrochemical settings, the underlying materials are typically acid-etched to make sure that the additional influence of related nanoparticles (metal and/or that of metal oxides, carbides, nitrides, sulfides and phosphides) deposited directly at the surface of the catalyst is eliminated. In heterogeneous catalysis applications, however, the contribution of these species to the overall chemical reactivity – while being well acknowledged and often relied upon – is not readily distinguished from the instances of single-atom catalysis and the role that nanocrystals protected by graphitic carbon layers might play. Traditionally, carbonaceous materials are developed separately for applications in heterogeneous catalysis and electrocatalysis. Herein, we describe a unique amorphous cobalt metal–organic framework derived material incorporating Co–$N_x$ and Co nanoparticles that acts both as a recyclable catalyst in oxidation and benzylic homocoupling reactions and as an efficient trifunctional electrocatalyst for oxygen reduction (ORR), oxygen evolution (OER) and hydrogen evolution (HER) processes.

*Keywords: Amorphous metal–organic frameworks, Multifunctional catalysts, Heterogeneous catalysis, Electrode materials, Renewable energy*

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# CALCAREOUS DEPOSIT IN DRINKING WATER PIPES AS A HETEREGENOUS CATALYST FOR BIODIESEL PRODUCTION

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The today's civilization is facing a critical transition, as over the next few years there is expected to be a strong growth in demand for energy. This is the result of both the increase in the world's population and the improvement in living standards in world. Despite its development, humanity has not foreseen unprecedented crises that can be accompanied by high energy consumption. The rapid growth in energy needs will be difficult to meet in the medium term due to the currently known fossil fuel reserves.

Morocco is a country with scarce energy resources, namely, those that ensure the majority of the energy needs such as oil, coal and gas. This scarcity situation leads to be dependent on imports of primary sources of fossil origin. However, this non-renewable energy sources result in a high environmental impact. It is important to reverse this trend, making its consumption more efficient and gradually replacing it with clean renewable energy. It was necessary to develop alternatives to petroleum having more suitable for use as fuel. One of the alternatives was biodiesel. It is obtained by processing vegetable oils or animal fats. Chemically, biodiesel is defined as an alkyl ester of long chain fatty acids with physicochemical characteristics similar to mineral diesel.

The present work is devoted to the valorization as a heterogeneous catalyst for biodiesel production of the calcareous deposit present in drinking water pipes. The effects of methanol/oil molar ratio, reaction time, catalyst loading and reusability of the catalyst were systematically investigated.

The catalyst was prepared via thermal treatment at 850 °C for 2 h of the deposit. Characterizations by using X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), Thermo-gravimetric/Differential thermal analyses (TG-DTA), Atomic emission spectrometry ICP-AES and Scanning Electron Microscopy (SEM) have been performed. The effect of catalyst was investigated by variation of catalyst amount from 1 to 5 wt% with respect to the oil weight. The effect of methanol was also studied with different methanol to oil molar ratios between 6:1 and18:1. Under the best transesterification conditions identified as: catalyst amount of 3 wt%, methanol/oil molar ratio of 18, reaction time of 2 h, a methyl ester content of 96% was achieved at 60°C. The produced biodiesel was characterized by FTIR and Nuclear Magnetic Resonance Spectroscopy (NMR). The properties of the prepared biodiesel were investigated according to the Standard Specifications for Diesel Oil and found to be within the limits.

*Keywords: Calcareous deposit, Heterogeneous catalysis, Biodiesel, Transesterification*

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# EFFECT OF TEMPERATURE ON THE GASIFICATION OF OLIVEIRA PRUNE PELLETS

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The present work studied the thermal gasification of olive pruning. Olive pruning from agricultural processes went through a pre-treatment of grinding and pelletizing in order to standardize the raw material. A fixed bed gasifier fed with atmospheric air was used to study the experimental process of gasification of olive pruning pellets, an agricultural residue that is commonly burned in situ. The effect of the reactor temperature on the quality of the syngas produced in a range of 650 to 800 °C was studied. The pre-treatment of grinding, with a 6 mm sieve, transformed the olive pruning into particles smaller than 0.85 mm and pelletizing on pellets with a diameter of 6–16 mm. This raw material was studied in terms of elementary analysis, thermogravimetric analysis and calorific value. During the test, several gas samples were collected and later analyzed by gas chromatography allowing the quantification of CO, $CO_2$, $H_2$, $CH_4$, $C_xH_y$ and $N_2$. The reaction mechanism of the gasification process is decisive in the syngás composition. The experimental results presented that the relatively lower temperatures favor the production of gas and the calorific value, mainly due to the capitalization in light hydrocarbons. The best results were obtained for a bed temperature of 650 °C, with the syngas presenting a Lower Calorific Power of 5.35 $MJ.kg^{-1}$ with a flow rate of 26, 3 $m^3.h^{-1}$. The thermal gasification process is a viable alternative for the energetic recovery of lignocellulosic waste, namely olive pruning pellets.

*Keywords: Gasification, Olive waste, Energy recovery*

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# ANAEROBIC DIGESTION OF CORK BOILING WASTEWATER - LABORATORY SCALE

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The main objective of the work was to perform the energy recovery of cork boiling wastewater (CBW) through anaerobic digestion process. The experiments were performed in reactors of work volume of 6 liters and different substrate and cosubstrate ratios, with temperature control and mechanical agitation, for obtaining greater biogas and biomethane amounts. The operational temperature was mesophilic (38 °C) with the agitation of 15 rpm being carried out for five minutes three times a day. The reactors were fed with different ratios of Inoculum (IN), CBW, cow manure (CM), and lignocellulosic biomass (LB). Two mixtures under different ratios were performed, namely IN:CBW:CM with the ratios of 0.5:2:0.5 and 0.5:2.2:0.3, and IN:CBW:LB with the ratios of 0.5:2:0.5 and 0.5:2.2:0.3. The process of anaerobic digestion of IN:CBW:LB had an accumulated biogas production of 55.26±1.56 $mL.gSVadd^{-1}$ and volume of 1.62 $mLCH_4.gSVadd^{-1}$ for the biodigester with the ratio of 0.5:2:0.5, on the other hand, the ratio of 0,5:2,2:0,3 for the same mixture, presented a reduction of biomethane production to 0.05 $mLCH_4.gSVadd^{-1}$, what is justified by the increase in the amount of cork effluent. For the mixture IN:CBW:CM, there was no production of biogas for the ratio of 0.5:2:0.5 due to the high conductivity and excess production of volatile fatty acids. When the amount of CM was reduced (ratio 0.5:2.2:0.3), the biogas production was 124.3 $mL.gSVadd^{-1}$ and the biomethane production was 72.16 $mLCH_4.gSVadd^{-1}$. With the tests performed, it can be concluded that the process of anaerobic digestion of CBW can be a viable alternative for energy recovery.

*Keywords: Cork boiling wastewater, Anaerobic digestion, Biogas, Cow Manure, Lignocellulosic Biomass*

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# COMBINING BIOENERGY WITH CARBON UTILIZATION AND POWER-TO-GAS STORAGE FOR EFFICIENT CLIMATE NEUTRAL TRANSITION

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The transformation of global energy system towards carbon neutrality is sorely needed to mitigate the environmental effects of climate change. The Power-to-Gas technology offers effective decarbonization potentials and balances the intermittent nature of variable renewable energy sources, i.e., wind and solar power in large scale. However, approximately only the one third of the input renewable energy can be gained back in the process. In the present work a bioenergy-based storage cycle is introduced that combines the biofixation and utilization of carbon dioxide and the storage of fluctuating renewable electricity by interconnecting the conversion stages with co-hydrothermal gasification. Wet microalgae biomass was converted into a hydrogen and methane rich fuel gas mixture by co-gasifying hydrochar and wet biomass feedstocks above the supercritical point of the applied water solvent (T>374°C, p>22.1 MPa). The thermochemical process is characterized by high carbon conversion ratio (>75%) and enhanced total fuel gas yield (>30 mol $kg^{-1}$). The C1-C2 and H2 rich fuel gas was valorized further into high quality synthesis gas. It is obtained that the bio-synthetic hybrid conversion system outperforms conventional chemical processing pathways maintaining high round-trip efficiency (>41%) and low greenhouse gas footprint (<120 g CO2,eq $kWh^{-1}$) in a cradle-to-grave framework.

*Keywords: co-Hydrothermal Gasification, Power-to-Synthesis Gas, Response Surface Methodology, Life Cycle Assessment, Climate neutrality*

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# MECHANOSYNTHESIS OF BIOMETALLIC COMPLEXES FOR COSMECEUTICAL APPLICATIONS

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Cosmeceuticals are a growing market, with a high demand especially in the last decade. This may be explained by an increase of consumers looking for enhanced beauty products, able to extend skin protection, anti-aging, whitening and anti-wrinkling. Cosmeceutical formulations may incorporate natural products (*e.g.* plant extracts) or synthetic ingredients. However, for many reasons (*e.g.* seasonal or regional availability, large scale production), the cosmetic industry is highly interested in the synthesis of new bioactive molecules.

Mechanochemistry is a solventless, emergent green methodology that enables the preparation of new bioactive molecules by a simple and scalable process, both in batch and continuous mode. Herein, we disclose a straightforward protocol for the synthesis of biometallic complexes under very mild conditions, short reaction times and high yields. The new complexes showed to be non-cytotoxic, stable under sunlight, laser irradiation and high temperatures, thus fulfilling the required performance for potential cosmeceuticals.

*Keywords: Mechanosynthesis, Cosmeceutical, Ascorbic acid, Stability Studies, Cytotoxicity assay*

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# SFE, SFC-MS AND THEIR HYPHENATION : FROM PLANT EXTRACTION TO CHEMICAL CHARACTERIZATION

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The world cosmetics market is in perpetual growth despite the current health climate. At the same time, natural products are becoming more and more popular. In the future, this will lead to the transformation of industrial tools for a more environmentally friendly operation. The use of supercritical fluids for extraction (SFE) has been well known since the 1960s and is perfectly in line with this green chemistry approach. However, its full potential has not been fully realized. In a logic of continuity, supercritical fluid chromatography for the analysis of the extracts obtained is logically essential. Our research is also based on the coupling of both technologies. Here are three concrete examples illustrating our work:

1) The extraction of different peppers and their characterization by gas chromatography coupled with mass spectrometry (GC-MS),

2) SFE-SFC-ESI-MS on-line coupling for fatty acid extraction and characterization,

3) SFC-EI-MS on-line coupling for the analysis of volatile compounds (terpenes and terpene derivatives).

*Keywords: Supercritical fluids, Extraction, Chemical characterization, Hyphenation*

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# MICROCAPSULES FORMULATIONS FOR ECOLOGICAL AGRICULTURE AND FUNCTIONAL FOOD PRODUCTION

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The simultaneous encapsulation of microorganisms and agrochemicals is a beneficial tool of nutrient delivery and protection for ecological and sustainable plant production. The advantages of the bioactive agent encapsulation are slow and controlled release, more efficient use of agrochemicals with higher environmental protection. Since several microorganisms, particularly the ones related to roots, can increase plant growth and productivity, *Trichoderma viride* (*T. viride*) was used in this research. *Trichoderma* species are some of the most frequent culturable fungi in soils, based upon the frequency of isolation on appropriate media. The twin roles of antagonistic activity in opposition to plant pathogens and the promotion of soil fertility make *Trichoderma* species a promising opportunity for traditional plant protection and nutrition technologies. Recently, microparticles containing each biological and chemical agents have been investigated in terms of microparticles physicochemical properties, morphology, and release kinetics. The outcomes of various cations ($Ca^{2+}$ and $Cu^{2+}$ ions), microparticle size, the presence of the outer chitosan layer on the release of the active agents from alginate-based microcapsules have been investigated. Optimization was achieved to produce microparticles by delivering active agents to the plants at the rate that carefully approximates plant needs over a prolonged period. The investigation pointed out that proper selection of agroformulation variables helps in designing microcapsules/microspheres with the desirable release of *T. viride* spores and copper/calcium ions for plant nutrition and protection. After the optimization, microparticles containing different combinations of $Ca^{2+}$/$Cu^{2+}$ ions, *T. viride*, alginate and chitosan were applied to the soil in the conventional/hydroponic planting of lettuce (*Lactuca sativa L.*) and tomato (*Solanum Lycopersicum L*). The application was performed just before planting. After the lettuce/tomato harvest, fresh samples were used for the preparation of extracts. Extracts were analyzed in terms of biological activity, with regards to the total polyphenols, antioxidant activity, lycopene, chlorophyll, total sugars as well as the $Ca^{2+}$/$Cu^{2+}$ ions content. Results revealed significant improvements when comparing the treated lettuce/tomato to the control (untreated) with regards to almost all of the measured parameters, *i.e.* the obtained biomass yield, rosette diameter, and height as well as the content of bioactive compounds and antioxidant activity. Bioencapsulation alongside the presence of chemical agents revealed a promising, sustainable, environmentally friendly, rapid, convenient, economical and efficient delivery of biological and chemical agents for plant nutrition and protection as well as production of plants with increased nutritional quality.

*Keywords: Microcapsules, Green chemistry, Food, Tomatoes, Lettuce*

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# CHEMICAL STRUCTURE OF PHENOLIC ACIDS DURING THE ADSORPTION PROCESS ONTO β-GLUCAN

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Polyphenols are large groups of secondary plant metabolites. They showed many bioactivities like interactions with dietary fibre. These interactions can influence their accessibility for absorption (bioaccessibility) and their amount that is being absorbed (bioavailability). Interactions between polyphenols and dietary fibre like β-glucan can be studied through adsorption process. Many factors can have influence on adsorption process like chemical structures of polyphenols. The aim of this study was to investigate the adsorption between phenolic acids (gallic acid, *p*-coumaric acid, caffeic acid and chlorogenic acid) and β-glucan and to see how chemical structure influenced the adsorption process. Adsorption was carried out at 25 °C and pH 5.5 for 16 hours. The non-linear Dubinin-Radushkevich model was applied in order to analyze the data and to obtain the informations about chemical bounds between phenolic acid and β-glucan. The results showed that hydroxybenzoic acid (gallic acid) showed the higher adsorption capacity than hydroxycinnamic acids (caffeic, *p*-coumaric and chlorogenic acid). This could be related to the chemical structure of polyphenols. The order of adsorption capacity can be connected with the chemical structure of polyphenols. The higher number of hydroxyl groups can favor the adsorption of phenolic acids onto β-glucan. Gallic acid has the highest number of hydroxyl groups attached on the ring of all phenolic acids and showed the highest adsorption capacity, followed by caffeic acid and *p*-coumaric acid. The chlorogenic acid showed the lowest adsorption capacity. In this case the esterification between caffeic acid and quinic acid which are the building blocks of chlorogenic acid could lowered the adsorption capacity on β-glucan. From the Dubinin-Radushkevich model the bonds between phenolic acids and β-glucan could be physical bonds like hydrogen bonds and Van der Waals forces.

*Keywords: Adsorption, Chemical structure, Polyphenols, β-glucan*

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# ZETA POTENTIAL OF SOME HYDROXYCINNAMIC ACIDS

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Polyphenol acids are plant metabolites found in food. They contain a phenolic ring and at least one organic carboxylic acid function. Caffeic, chlorogenic, ferulic acids are some of the hydroxycinnamic acids. In food, hydroxycinnamic acids are found in the form of esters. *β*-glucan is a polysaccharide that belongs to the group of soluble fibres. Zeta potential is also called electrokinetic potential, which represents a physical property on the surface of a macromolecule. Also, zeta potential is defined as the potential at the distance of the shear surface. Knowing the zeta-potential allows predicting the long-term most stable behaviour of a macromolecule. Stability of a macromolecule depends on the zeta potential and the charge on the surface and the macromolecule. One of the aims of this work is to determine the zeta potential of hydroxycinnamic acids solutions, *β*-glucan solution and hydroxycinnamic acids and *β*-glucan model through different concentration ranges. The second aim is the prediction of the most stable behaviours of hydroxycinnamic acids and *β*-glucan models at different pH values. In addition, absorption spectra were recorded. Zeta potential of hydroxycinnamic acids and *β*-glucan model had shown in acidic medium positive values and alkali medium negative values. The highest zeta potential value of hydroxycinnamic acids and *β*-glucan model had reached in pH 10. According to the stability criteria, hydroxycinnamic acids and *β*-glucan model had shown the most stable behaviour at pH 10. The change of pH value had a great influence on the chemical structure and the zeta potential value of analyzed models.

*Keywords: Zeta potential, Caffeic acid, Chlorogenic acid, β-glucan*

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# INFLUENCE OF $SO_2$ REDUTION ON TWO WHITE WINES AGING ON VOCs AND AMINOACIDS

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EU countries are in the top 16 of the world's wine producers. To respond to a public health concerned, caused by $SO_2$ excessive exposure, EU has required a warning in the products indicating that sulphites are present if concentrations are higher than 10mg/L and its reduction or replacement whenever possible. This additive is used as a preservative agent in winemaking process, due to its anti-oxidative and anti-microbial properties. Wine aroma depends on many factors, being grape variety and winemaking process that most contributes to VOCs found in wines where aminoacid composition due to their biosynthetic products play an important role. Also, during wine ageing volatile composition can change depending on many factors such as temperature, pH or oxidation process. The aim of this work was to evaluate the impact of $SO_2$ on the VOCs composition of two white wines (one varietal and one blend) during ageing and the amino acids (AAs) composition. $SO_2$ was added between 0 and 120 mg/L to wines and VOCs were analysed after three and six months of storage. All experiments were performed in duplicates. The VOCs were analysed by HS-SPME-GC/MS. VOCs were tentatively identified by matching mass spectra with spectra of reference compounds in NIST library and LRI calculated and compared with the literature. The AAs composition after three months of aging were quantified by HPLC-DAD using standards. It was observed that when different doses of $SO_2$ were applied, a distinct VOCs profile are obtained. impacting the aroma of the final product. AAs present distinct concentrations according to $SO_2$ added. These results should be taken in consideration by winemakers when reducing $SO_2$ additions to wine in order to maintain or improve the quality of the final product produced.

*Keywords: Sulphur Dioxide ($SO_2$), Volatile organic compounds (VOCs), White wine, Aminoacids*

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# MENTHOL-FATTY ACIDS DEEP EUTECTIC SYSTEMS AS WOUND HEALING AGENTS

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Deep eutectic systems (DES) have emerged as promising alternative systems that fully comply with the green chemistry standards, comprising advantages such as low toxicity, renewability, biodegradability, as well as low cost of production. DES are a mixture of components which at an adequate molar ratio lead to a strong depression in the melting point, resulting in a liquid functional system with a tailor-made design for a particular application. DES composed by natural occurring molecules are defined as natural deep eutectic systems (NADES).

This work is part of a wider study to unravel the therapeutic potential of NADES based on menthol and fatty acids to work as wound healing agents. Fatty acids are commonly present in vegetal and animal fats and have a contribution on human skin natural disinfection and regeneration. Menthol is a well described terpene extracted from Mentha species with anti-inflammatory, anesthetic, antimicrobial and a transdermal permeation enhancer.

From the evaluation of the antimicrobial, biological performance, and safety of NADES composed by menthol:lauric acid and menthol:myristic acid, our results have revealed that these systems present promising antimicrobial and antibiofilm activities, while not compromising the normal migration and proliferation of human keratinocytes. Further work on the assessment of the anti-inflammatory activity of these systems is currently ongoing. It is expected eutectic systems able to cope with microbial invasion and biofilm formation, while dealing with inflammation, and thus providing a suitable wound healing agent based on natural compounds.

*Keywords: Green chemistry, Deep eutectic systems, Natural bioactive compounds, Antimicrobial, Wound healing*

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# FORMULATION OF POLYMERIC NANOPARTICLES USING A BIOACTIVE EXTRACT OF THE INVASIVE BROWN SEAWEED *Sargassum muticum*

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Drug delivery systems have been increasingly the focus of research topics, and nano and microparticles gather great attention for the delivery of molecules with therapeutic potential. Natural resources, such as seaweeds, evidence great potential to provide materials, owing to their bioactive properties. Despite the complexity of the composition, the major polysaccharide present in brown seaweeds is fucoidan, which is mainly comprised of fucose units and sulphate groups, and the polymer has been attributed relevant activities. *Sargassum muticum* (Sm) is an invasive brown seaweed in the Atlantic coast. Green extraction technologies such as subcritical water extraction (SWE), ultrasound assisted extraction and microwave assisted extraction provide advantages towards biorefinery concept when it comes to work with natural materials. These extracts may find applications in food, pharmaceutical and/or cosmetic industries. The aim of this work was to produce nanoparticles (NP) using a Sm extract obtained by SWE, by polyelectrolyte complexation (based on electrostatic interaction between oppositely charged materials).

The extraction process was performed using a solid:liquid ratio of 1:30. The reactor was heated up to 170 °C and quickly cooled to room temperature. The liquid phase resulting from the process was used to formulate the NP, where sulphate groups provide negative charges. Chitosan (CS) was used as counterion, providing positive charges, and different Sm/CS mass ratios (4/1 to 1/4) were tested. The order of polymer mixing (Sm onto CS or CS onto Sm) was tested as variable. Polymeric NP were characterised regarding size and zeta potential. Antioxidant activity, phloroglucinol content, sulphate content and cytotoxicity of Sm extract were evaluated.

The proposed extraction process was adequate to produce an extract suitable for NP preparation. NP of smaller sizes (≈300 nm) were obtained when Sm extract was the predominant component. Natural Sm extracts obtained by SWE are suggested to be adequate for the formulation of NP with potential application in drug delivery.

*Keywords: Bioactive compounds, Chitosan, Fucoidan, Green extraction, Polymeric nanoparticles*

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# THERAPEUTIC DEEP EUTECTIC SYSTEMS AS PROMISING NEW TOOLS IN THE ANTICANCER BATTLE

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Cancer remains a major health problem worldwide, with colorectal cancer being the third most incident and lethal, and the second most prevalent. Inflammation has been highly associated with cancer development and maintenance; therefore, the reduction of the inflammatory microenvironment represents a promising therapeutic target. The use of nonsteroidal anti-inflammatory drugs (NSAIDs) to reduce colorectal cancer risk has already been described, however NSAIDs have poor solubility and consequently poor bioavailability.

Deep eutectic systems (DES) are based on the combination of two or more components that, in a certain molar ratio, present a lower melting point than its individual components. These systems often present less volatility and toxicity, are biodegradable, and have low production costs, thus representing a promising alternative to conventional solvents, while being in compliance with the green chemistry metrics. When an active pharmaceutical ingredient is part of the system it is designated by therapeutic deep eutectic system (THEDES). In order to discover new therapeutic agents, THEDES were synthetized combining natural occurring molecules with anticancer properties, such as terpenes, with NSAIDs, namely ibuprofen, flurbiprofen and ketoprofen. Our previous results have unraveled that THEDES present promising therapeutic activity towards colorectal cancer cells. This has been attributed to solubility and permeability increase, resulting in improved drug bioavailability, but also its selective cytotoxic action towards cancer cells without compromising normal cell viability. In conclusion, this THEDES represent a promising therapeutic agent with the environmental concerns of a green solvent.

*Keywords: Colorectal cancer, THEDES, NSAID, Terpenes*

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# GREENING ORGANO CATALYSIS: NOVEL IMMOBILIZED ORGANO CATALYSTS FOR SUSTAINABLE CHIRAL API PRODUCTION

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Catalysis plays a major role in the manufacture of many chiral APIs, agrochemicals, fragrances, etc which can be achieved using chemocatalysis. Moreover, industry constantly strives to achieve this goal in the most sustainable and efficient and continuous manner possible. Therefore there is clearly the need for eco-friendly, sustainable and economically advantageous processes. One way, to achieve this objective is through organocatalyst recycling via immobilization. The catalyst is linked to an appropriate support employed in the reaction in question and then separated from the product via simple filtration and utilized in further reactions. Hydrosilylation reactions are clean processes that provide amines from imine substrates (Figure 1).

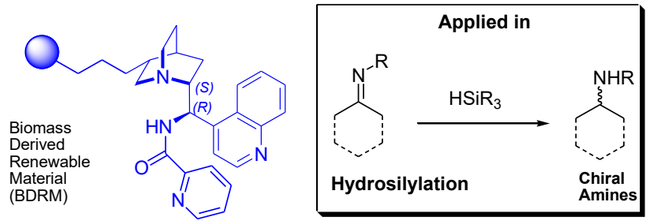


**Figure 1. Our immobilized Organocatalysts**

In this communication we will present our results on the development of immobilized cinchona organocatalysts derived from biomass sources (Fig. 1) in hydrosilylation reactions, this will include a comparative discussion on the effectiveness of these catalysts as regards: yield, enantioselectivity, stability and recyclability.

*Keywords: Organocatalyst, Chiral amine, Catalyst recycling, Heterogeneous catalysis*

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# SOLIDS TURN INTO LIQUIDS. EUTETIC MIXTURES OF PHARMACEUTICS TO IMPROVE DRUG SOLUBILITY

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Active Pharmaceutical Ingredient (API) lower solubility is one of the current problems in pharmaceutical development. Several methodologies can be used to improve API solubility among them are the use of the concept of deep eutectic solvents (DES) in which one of the constituents is the API. This class of compounds is commonly called Therapeutic Deep Eutectic Solvents (THEDES). DESs are a mixture of a hydrogen bond acceptor, with a hydrogen bond donor, which at a certain molar ratio leads to a system with a melting point close to ambient temperature and lower than those for the pure compounds. DESs have being gaining attention from the academic and industrial research due to their properties such as non-toxicity, biodegradability, being non-expensive and easy to prepare.

The strategy proposed in this work is to improve the solubility of chlorpropamide and tolbutamide, by preparing THEDES. Both APIs are sulfonylurea compounds used for treatment of type 2 diabetes mellitus and have low solubility in water. To prepare the THEDES several molecules were tested, namely, tromethamine, L(+)-arginine, L-tryptophan, citric acid, malic acid, ascorbic acid and *p*-aminobenzoic acid, in a molar ratio of 1:1. To improve the eutectic mixture viscosity water was added in different molar ratios to all systems. The mixtures that formed THADES were characterized by mid-infrared spectroscopy, Raman spectroscopy, and differential scanning calorimetry. Their viscosity and solubility were also determined. Since it is known that THEDES may have different toxicity than the parent compounds, cytocompatibility was performed by metabolic activity and cell lysis evaluation, according to ISO10993-5:2009.

*Keywords: Deep Eutectic Solvents, Therapeutic Deep Eutectic Solvents, Diabetes, Solubility, Green Chemistry*

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# BIOCATALYTIC PROMISCUITY OF LIPASES IN CARBON–PHOSPHORUS BOND FORMATION

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α-Hydroxy phosphonates have become increasingly important for their agricultural and pharmaceutical properties and as suitable materials in the synthesis of other α, and γ-substituted phosphonates. α-Hydroxyalkyl phosphonic acids and their esters exhibit a wide spectrum of biological activities such as antibacterial, fungicidal, anticancer, potent renin inhibitory and HIV protease inhibitory effects. A large number of methodologies for the synthesis of various α-hydroxy phosphonates compounds have been extensively developed under various conditions. The majority of these processes suffer some drawbacks such as stoichiometric amount of catalysts, costly metal ion and the use of highly toxic catalysts. Thus, it seems significant to find a method to overcome these limitations. Moreover, due to pharmacopoeia limits of heavy metal contaminations (below 5 ppm) reported methods cannot be used in the pharmaceutical and cosmetic industry.

*Keywords: Promiscuity, Biocatalysis, Lipases, Sustainability, Bond formation*

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# SUPERCRITICAL IMPREGNATION OF POLYSACCHARIDE AEROGELS: FEASIBLE TECHNIQUE FOR VARIOUS DRUGS

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Having unique properties such as extremely low densities, large open pores and high inner surface areas, aerogels are classified as materials with high added values. Since natural materials can take place of synthetic materials, bioaerogels have gained increasing attentions as promising candidates for use in pharmaceutical formulations as well as drug delivery systems. Polysaccharide based aerogels as well as aerogels based on natural proteins are providing opportunities for life science and food applications due to their biocompatibility and bioavailability. Supercritical impregnation is a promising technique with a great potential in the preparation of new polymeric systems, such as aerogels. Due to the cost and environmental regulations, food and pharmaceutical industries are in a need of a new, alternative technologies and processes. The process of impregnation is intensified with considerable savings of both energy and raw materials, by tuning the specific properties of supercritical fluids. It is a promising technique for improving the dissolution and adsorption of poorly water-soluble drugs, where more than 40% of newly discovered drugs is poorly or practically insoluble in water.

The following work deals with the supercritical impregnation of various drugs such as fat-soluble vitamins (vitamin $K_3$ and vitamin $D_3$), nifedipine, fenofibrate into polysaccharide aerogels, such as pectin, alginate, and chitosan. The technique proved to be successful overcoming the disadvantages of the slow diffusion processes and long times in the case of impregnation from the liquid solutions. Achieved loading varied, depending on the nature of used drug and polysaccharide. To name just a few, the loadings as high as 20% were achieved in the case of vitamin $D_3$ for alginate aerogels. Textural properties ($N_2$ adsorption-desorption analysis), surface morphologies (SEM), thermal properties (TGA/DSC) and functional groups (FTIR) of prepared formulations were determined.

The applicability of prepared formulation was checked through *in-vitro* dissolution tests. Release of impregnated drugs from aerogels was compared with the release of pure drugs. By impregnating drugs into aerogels, the dissolution and bioavailability of drugs was significantly improved, in most cases achieving controlled release.

*Keywords: Aerogels, Supercritical impregnation, Polysaccharides, Vitamin $D_3$*

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# THE INFLUENCE OF SUPERCRITICAL HEMP EXTRACT ON THE METABOLIC ACTIVITY OF METASTATIC CELLS

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Antioxidants have an important role in the body, being balanced with the free radicals. As the human body is becoming increasingly resistant to drugs, there is an emerging need for new drug development. Lately, the use of natural remedies is increasing. Some of them are already in use as anti-cancer ("antineoplastic" or "cytotoxic") chemotherapy drugs. Literature suggests natural extracts containing several antioxidants (such as flavonoids, polyphenols), cannabinoids, terpenes, various vitamins (vitamin E), etc. This leads to restoring the balance between antioxidants and free radicals in the body, simultaneously using them as a prevention for cancer. One of the most popular plant nowadays is hemp (*Cannabis sativa L.*). Hemp contains several chemical compounds (terpenes, carbohydrates, fatty acids, phytosterols, phenolic compounds, cannabinoids, etc.). However, cannabinoids are the most favoured. The most known cannabinoids are Δ9-tetrahydrocannabinol (THC) and cannabidiol (CBD), which have many positive properties such as anticancer, anti-inflammatory, anti-oxidative, analgesic, antiepileptic, anti-nausea, neuroprotective, antibacterial, antidiabetic, anti-ischemic, anti-seizure, antiepileptic, sedative, stimulating bone growth, etc.

Aim of the research was to investigate the optimal conditions for supercritical fluid extraction of cannabis. Extraction experiments were performed with supercritical carbon dioxide in a temperature range of 40 °C to 80 °C and a pressure range of 150 bar to 350 bar. The highest contents of antioxidants (A = 45%), phenols (TP = 628.676 mg GAE / 100 g material) and cannabinoids (THC = 0.1%, CBD = 28.2%, CBG = 2.5% CBC = 3.2% and CBN = 0.4%) were found in extracts processed at a temperature of 60 °C and a pressure of 300 bar. The decarboxylation was performed at 115 °C before extraction. C cannabinoid levels were visibly higher (THC = 0.2%, CBD = 47.9%, CBG = 3.8%, CBC = 5.8%, and CBN = 0.9%). The effect of decarboxylation was also expressed in the inhibition of cancer cell function. For the non-carboxylated extract, it was measured that the inhibition of cancer cell division required an extract concentration of c = 1 mg/mL, while the decarboxylated extract required a lower concentration of the applied extract (0.5 mg/mL).

*Keywords: Hemp, Metastatic melanoma cells WM-266-4, Microorganisms, Antioxidants*

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# GREEN DEVEPOMENT OF MEFENAMIC ACID-AFFINITY POLYMER FOR WASTEWATER PURIFICATION STREAMS

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Pharmaceutical pollution is becoming a global concern, especially due to its impact in the water and environment lifecycle. Drugs are released in high amounts to the environment during their consumption, between 30 and 90% of an oral dose is excreted in urine as an active substance. More than 600 different drugs have been detected in drinking water, wastewater, sewage sludge and soils. Typically, the wastewater treatment facilities are not equipped to remove these active ingredients from sewage. The improper disposal of drugs and the low efficiency in the removal of these compounds from wastewater treatment streams are leading to their persistence in the environment.

Mefenamic acid (MFA) is a non-steroidal anti-inflammatory drug indicated for relief of mild to moderate pain, and for the treatment of primary dysmenorrhea. This drug has been detected in wastewater treatment effluents with concentrations between 87-163 ng/L. However, these treatments are not specific and have not been efficient in the removal of MFA from wastewater streams. Synthetic affinity polymers with molecular recognition ability have been advanced for a wide range of processes where high-affinity, robustness and reusability are an added value.

Synthetic affinity polymers like molecularly imprinted polymers (MIPs) have been developed using supercritical carbon dioxide ($scCO_2$), a green technology. MIPs are obtained as dry-powders, in high yields, stable, ready-to-use, with controlled morphology, reusable, robust and with similar binding properties in comparison with natural molecules.

Herein, anadsorbent polymeric material with affinity to MFA was developed in $scCO_2$, using 2-vinylpiridine as monomer, ethylene glycol dimethacrylate as crosslinker and AIBN as a free-radical initiation. The materials were characterized by FTIR, average particle size as well as particle size distribution. The MFA-MIP and their control (non-imprinted polymer) were then loaded into a Solid Phase Extraction column and evaluated as adsorption materials for MFA mimicking a wastewater crude solution. MFA-MIP was able to absorb 26 % more than the control material revealing high potential to be used as adsorbent in wastewater purification streams.

*Keywords: Green chemistry, Supercritical carbon dioxide, Molecularly Imprinted Polymer, Affinity purification, Waste treatment*

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# EUTECTIC ASSISTED MECHANOCHEMICAL FORMATION OF A NOVEL SALT OF PROPRANOLOL

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Salt formation is a commonly used strategy to improve solubility of poorly soluble active pharmaceutical ingredients. Salt crystallisation often requires the use of environmentally unfriendly solvents. Other techniques such as hot melt extrusion and ball milling have been studied in the context of possible solvent-free salt crystallisation. However, little is understood about the mechanisms which govern the mechanochemical salt preparation. Here we report on eutectic-assisted salt formation of propranolol and capric acid in a 1:1 molar ratio. The formation of the salt – propranolol caprate (PRC) from solvent has been previously reported by Stott et al. [1] We have resolved the crystal structure of PRC by single-crystal X-ray diffraction. The possibility of PRC formation in the solid-state has been studied by optical microscopy. When crystals of propranolol and capric acid were brought into contact at ambient conditions, formation of a liquid phase was observed under the light microscope. Once the sample was fully in the liquid state, nucleation followed by crystal growth was induced with a spatula. Immediately, the crystallisation of a new phase was observed. The crystal form of the new phase was undoubtedly different from the crystal shapes of pure propranolol and capric acid. The sample was then heated to confirm the presence of the salt. The newly formed crystals began to melt at around 99°C which is higher than that of propranolol (m.p. 91.8°C) and capric acid (m.p. 31.85°C), which agreed with melting point of PRC, found at 100.8°C by differential scanning calorimetry. Furthermore, a physical mixture of propranolol and capric acid was prepared by co-grinding the starting materials in an agate pestle and mortar in the 1:1 molar ratio. During grinding a liquid-intermediate was observed. Powder X-ray diffraction pattern of the physical mixture matched the one obtained for pure PRC crystallised from ethanol, thus confirming the salt formation in the solid-state. The liquid-intermediate phenomena can be attributed to formation of submerged eutectic which facilitates the formation of the salt. Similar observations were made and reported for the formation of several co-crystals.

*References: [1] Stott et al., Int. J. Pharm., 161–17, 2001.*

*Keywords: Propranolol, Capric acid, Salt synthesis, Mechanochemistry, Solid-state reactions*

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# GREEN SYNTHESES OF IMPORTANT PHARMACEUTICAL INTERMEDIATES *VIA* ENZYMATIC KINETIC RESOLUTIO

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Chiral carboxylic acids esters are important intermediates in the synthesis of pharmaceutical intermediates. Common methods for the synthesis of these class of compounds consists kinetic resolution and dynamic kinetic resolution of respective ester by enantioselective hydrolysis. We will report the results of our studies on the first example of dynamic kinetic resolution (DKR) of chiral unsaturated carboxylic acids. The application of tandem metal−enzyme DKR was found to be a powerful tool for the manufacture of high-value pharmaceutical commodities. This new protocol of kinetic resolution was based on irreversible enzymatic esterification of 3-aryl-4-pentenoic acids with *ortho* esters and was introduced to obtain optically active unsaturated carboxylic acids [1]. This procedure was combined with metal-catalyzed racemization of the target substrate, providing the optically pure *S* enantiomer of ethyl 3-phenylpent-4-enoate with very high isolated yield (98%). A substantial influence of organic cosolvent and metal catalyst on the conversion and enantioselectivity of the enzymatic dynamic kinetic resolution was noted.

*References: [1] Ostaszewski et al., ACS Catal., 6, 3287−3292, 2016.*

*Keywords: Kinetic resolution, Dynamic kinetic resolution, Enzymatic reaction*

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# THEDES-LIKE MIXTURES INFLUENCE IN THE BIOAVAILABILITY OF NSAIDS

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Non-steroidal anti-inflammatory drugs (NSAIDs) are commonly administered for the symptomatic treatment of inflammatory diseases, such as osteoarthritis (OA). OA is a musculoskeletal inflammatory disease affecting almost 4% of the world population and associated to cartilage loss between junctions, pain, bone changes, stiffness and loss of joint function. Most of the NSAIDs administered for OA symptomatic control present poor bioavailability, requiring high-dose intakes to reach short therapeutic effect, associated to several adverse and systemic effects. A biocompatible formulation to enhance the bioavailability of these drugs is of great importance for oral and intra-articular OA treatments, as it can improve their efficiency and safety while avoiding the long-term development of new drugs associated to the regulatory entities. In this sense, therapeutic deep eutectic solvents (THEDES) and other liquid formulations with similar properties have been emerging as highly promising vehicles to improve drugs bioavailability, by facilitating their dissolution, permeation and absorption. These liquids are easily produced by mixing two or more components whose hydrogen-bonding interactions liquefy the mixture, yielding a 100% atom economy and purity. Furthermore, these systems are commonly recognized as non-toxic, biodegradable and biocompatible liquids.

In this work, two THEDES-like liquid formulations with potential to improve OA therapies where characterized in terms of their physicochemical properties, evaluated in terms of cytotoxicity and their influence in the solubility of NSAIDs in physiologic media was studied. The properties of these liquids regarding polarity, pH and solvent intermolecular forces in respect to different NSAIDs showed to influence their solubility in physiological media. Some of the studied NSAIDs showed improved solubility by the THEDES-like formulations studied. This might be promising for enhancing their bioavailability and thus their efficiency in the treatment of inflammatory diseases, as OA.

*Keywords: THEDES, NSAIDs, Bioavailability, Osteoarthritis*

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# CARBON DOTS NANOCOMPOSITES AS PHOTOCATALYSTS IN THE REDUCTION OF ANTIBIOTICS' CONCENTRATION ON AQUACULTURE EFFLUENTS

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Contamination of surrounding waters with antibiotics by aquaculture effluents can be problematic, due to the possible increase of bacterial resistance. Thus, cost-effective water treatments for the removal of these compounds before effluents discharge should be investigated. Photodegradation is an important mechanism in the degradation of compounds containing aromatic rings or photoactive functional groups, as is the case of most of antibiotics. On the other hand, the use of carbon dots (CDs) and CDs-nanocomposites as photocatalysts to produce reactive oxygen species can be a strategy to enhance these pollutants' photodegradation rate. In this work, the synthesis of four materials (CDs, $TiO_2$ and CDs-nanocomposites: CD@$TiO_2$ and CD/$TiO_2$) and their application on the photodegradation of two aquaculture antibiotics (sulfadiazine (SDZ) and oxolinic acid (OXA)) was evaluated. CDs were produced using citric acid and glycerol, while $TiO_2$ was obtained from the precursor titanium butoxide. For the synthesis of the CDs-nanocomposites, two approaches were used: the simultaneous synthesis of CDs and $TiO_2$ from citric acid, glycerol and titanium butoxide (CD@$TiO_2$), and the synthesis of $TiO_2$, from titanium butoxide, in presence of previously synthesized CDs (CD/$TiO_2$). All the four materials favored photodegradation; however, the response of the two antibiotics was different in terms of the most efficient photocatalyst and its concentration. For SDZ, the faster photodegradation rate was attained with CD@$TiO_2$ at the 500 mg $L^{-1}$. Meanwhile, for OXA, photodegradation was faster using CD/$TiO_2$ and the lowest catalyst concentration (5 mg $L^{-1}$). Using these conditions, kinetic studies were performed in ultrapure water and in aqueous solution of synthetic sea salts (30‰). For SDZ, the presence of CD@$TiO_2$ decreased the half-life time ($t_{1/2}$) in both water samples, with a higher reduction in the synthetic sea salts. In what concerns OXA, a decrease in $t_{1/2}$ was only observed in ultrapure water. These results highlight the important effects of the environmental water characteristics in the photodegradation behavior of antibiotics and in the performance of photocatalysts.

*Keywords: Remediation, Water treatment, Photodegradation, Solar radiation*

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# THE POTENTIAL OF THERAPEUTIC LIQUID MIXTURES ON TUBERCULOSIS THERAPY

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Tuberculosis disease appeared around 3 million years ago, however its outbreak happened in the 1800s. This disease is characterized by an airborne infectious disease caused by *mycobacterium tuberculosis complex*. Despite this disease is considerable treatable and the numbers of cases by tuberculosis infection have been falling slowly along the years, this disease is still considered the deadliest infection worldwide with and average of 1.2 million deaths in 2019. The current treatment for tuberculosis is based on a combination of multiple antibiotics that have to be administered for several months, with several adverse effects that will, for instance, affect the compliance to the patient to the treatment and enhance the incidence of drug-resistance. The development of green chemistry approaches for pharmaceutical industry is essential for reducing costs, toxicity and reduce the risk of contamination the environment. Therapeutic liquid mixtures represent an alternative and sustainable strategy that may tune the properties of these anti-tuberculosis drugs. One of the main goals of this project is formulate therapeutic liquid mixtures with drugs used in first-line treatment of tuberculosis and/or reported adjuvants and, then evaluate their properties, their bioavailability and activity in *mycobacterium tuberculosis* strains. Our previous studies resulted in formulation of therapeutic liquid mixtures with citric acid:ethambutol:$H_2O$ and citric acid:arginine:$H_2O$ in different molar ratios and it was observed that these mixtures could improve the solubility of ethambutol, when present as one of the components of the liquid mixture and pyrazinamide, when solubilized in therapeutic liquid mixtures made with ethambutol and arginine.

*Keywords: Therapeutic liquid mixtures, Tuberculosis, Bioavailability, Green chemistry*

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# GREEN PROCESSING OF LIDOCAINE-LOADED SOLID LIPID MICROPARTICLES AND *IN VITRO* EVALUATION USING 3D-BIOPRINTED HUMAN SKIN SUBSTITUTES

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Wounds, especially chronic wounds, are painful to patients and susceptible to infection. Local anesthetics, such as lidocaine hydrochloride, can alleviate pain during debridement and prevent bacterial growth, however, they present a limited duration of action. In this work, the Particles from Gas-Saturated Solutions® (PGSS®) technology was used to produce solid lipid microparticles (SLMPs) of glyceryl monostearate (GMS) loaded with lidocaine. PGSS® technique is a green technology based on the use of compressed or supercritical $CO_2$ for the melting and subsequent atomization of a mixture at low temperatures and avoiding the use of solvents. The obtained SLMPs were tested for the controlled release of the lidocaine at the wound site.

SLMPs were obtained as a fine powder consisting in non-spherical, porous particles with particle sizes between 20–120 µm. Physichochemical characterization revealed that the chemical structure of GMS was not modified upon PGSS® processing, while lidocaine experienced a reduction in its crystallinity. The encapsulation efficiency of lidocaine in the SLMPs was high (60–80%) for all the tested concentrations of lidocaine (1, 2, 4 and 10 wt.%). Drug release tests in Franz cell experiments showed a sustained release of lidocaine for 24 h. Drug permeation tests were carried out in Franz cells using a novel method based on a 3D-bioprinted human skin substitute mimicking the human epidermal and dermal layers. The SLMPs delayed drug penetration with respect to pure lidocaine powder. Antimicrobial tests against relevant bacterial strains found in wound infections (*Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Escherichia coli*) showed that SLMPs were able to inhibit bacterial growth in all cases, proving useful in preventing wound infections.

*Keywords: SLMPs, Drug delivery, PGSS® technique, Wound healing, Pain treatment treatment*

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# DEVELOPMENT OF LABORATORY DEPTH FILTER FOR SCALE-UP &-DOWN ACTIVITIES

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Residual coloration of chemical intermediate or final product in fine chemicals or pharmaceutical industries is critical. Therefore, the residual coloration has to be removed at the right chemical step with a straightforward, efficient and cost-effective technology. Carbon depth filtration is often use in chemicals industries in particular because it is greener towards free carbon treatment since it allows to considerably reduce carbon loading for a higher discoloration efficiency. Nevertheless, it is challenging to implement depth filtration at commercial scale because there are currently no laboratory tools to establish scalable process parameters. As part of this project, we have developed a state-of-the-art laboratory depth filter tools which allows to calibrate at laboratory scale production parameters. Since the miniaturization of the system brings technical constraints and requires precise management of various operational parameters, in order to achieve representative and reproducible results, this project is highly challenging.

*Keywords: Laboratory depth filtration, Activated coal, Discoloration, Scale-up*

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# ENVIRONMENTALLY-FRIENDLY METHOD BASED ON SUPERCRITICAL $CO_2$ FOR THE STERILIZATION AND MANUFACTURING OF POYMERIC SCAFFOLDS

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Medical device-associate infections, mainly from catheters and prosthesis, represent a common healthcare scenario that affects the lives of million patents worldwide. Severe complications may arise from this initial situation, being the primary cause of prothesis failure and replacement. There is not a universal sterilization procedure suitable for the processing of all types of medical devices or biological tissues. This scenario represents the major pitfall in the development and commercialization of new generation biomedical products (scaffolds). In this work, an efficient and green supercritical (sc-) $CO_2$ sterilization method was developed compatible with the processing of thermosensitive materials. In addition, the method was further modified to integrate the manufacture and sterilization of poly (ε-caprolactone) (PCL)/poly(lactic-co-glycolic acid) (PLGA) scaffolds through sc-$CO_2$ technology.

By the addition of low contents of hydrogen peroxide (1200 ppm) at warm temperatures (39ºC) and moderate pressures (140 bar), the sc-sterilization method successfully achieved SAL-6 against three biological indicators of standard sterilization procedures; *Bacillus stearothermophilus (*steam), *Bacillus pumilus* (radiation) and *Bacillus atrophaeus* (ethylene oxide). On the other hand, sterile and highly porous scaffolds (>70%) matching those of trabecular human bone were obtained in a one-pot process. The presence of cytotoxic $H_2O_2$ residues in the scaffolds was indirectly measured by incubation with fibroblast, a particularly sensitive cell line towards this additive. These results place great value on the supercritical technology to address some of the current major challenges of tissue engineering: sterilization of biomaterials and process integration.

*Keywords: Sterilization, Scaffolds, Supercritical $CO_2$*

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# DEEP EUTECTIC SYSTEMS AS POTENTIAL SOLUBILIZATION VEHICLES FOR MOMETASONE FUROATE AND DEXAMETHASONE

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Mometasone furoate (MF) and dexamethasone (DEX) are corticosteroids widely used in the treatment of allergies, skin diseases and autoimmune diseases due to their anti-inflammatory properties. Recently, DEX has been endorsed by the European Medicines Agency in the treatment of patients with severe cases of COVID-19. Despite their widespread use these corticosteroids are hindered by their low water solubilities, 1 µg/mL and 89 µg/mL respectively.

Deep eutectic systems (DES) are defined as a mixture of two or more compounds, which at a specific molar ratio present a strong depression of the melting point when compared with those of its individual components. DES which are liquid at room temperature can be used as solvents. These systems are advantageous because they can be easily prepared in high purity at low cost, and, when composed by natural compounds, are inherently biodegradable and have low toxicity. DES have been successfully employed in the solubilization of several active pharmaceutical ingredients (APIs) due to their high stabilization and solubilization power. In addition, by changing the components of the eutectic system, the solubility, permeation and absorption of APIs can be increased by several folds, when compared with water, or tuned to suit the specific needs of each application. The APIs can even be used as one of the components to create a novel eutectic system with therapeutic activity.

Herein, we report the use of DES based on natural organic acids and terpenes for the solubilization of MF and DEX. In some cases, DES are able to dissolve up to 2.3 times the amount of drug observed for Transcutol® P, one of the most commonly used co-solvents in pharmaceutical formulations. These systems also exhibit interesting antimicrobial activities and can potentially be used as preservatives. As proof of concept, MF solubilized in DES was used to prepare o/w emulsions for skin delivery. The study included optimization of the emulsions and subsequent characterization, namely pH, droplet size, rheology and *in vitro* permeation studies.

*Keywords: Deep Eutectic System, Active Pharmaceutical Ingredients, Solubility, Emulsions*

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# ANTIMICROBIAL ACTIVITY OF ORGANIC SALTS AND IONIC LIQUIDS

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Organic salts and ionic liquids based on active pharmaceutical ingredients and their derivates (OSIL-APIs): ampicillin (Amp), penicillin G hydrolysate (seco-Pen), amoxicillin hydrolysate (seco-Amx) and amphotericin B were prepared in moderate to high yield using buffer procedure. The prepared OSIL-APIs were tested against sensitive and resistant gram-positive and gram-negative bacteria as well as other pathogens. They show good solubility and significant increase of antibiotic activity particularly against resistant species with relative decrease of inhibitory concentration in respect to parent antibiotics (RDICs) up to >1000 for [$C_{16}$Pyr][Amp] against *E. coli* TEM CTX M9 and [$C_{16}$Pyr][seco-Amx] against MRSA ATCC 43300. The gathered data suggest that the adequate ionic pairing is vital to enhance or promote antibiotic activity, with possible alterations in their mechanism of action according to the selected counter-ion. Recently was suggested that combination of antimicrobials with non-active compounds can provide a promising strategy to address bacterial resistance and, in this respect, OSIL-APIs can provide ideal platform for drug modification.

*Keywords: Organic salts and ionic liquids with active pharmaceutical ingredients (OSIL-APIs), Bacterial resistance, Beta-lactam antibiotics, Sntiprotozoal agents*

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# THIOSULPHATE: A GREEN SOLVENT FOR GOLD EXTRACTION

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Cyanide leaching has been the most common (>%59-90) industrial method used for the extraction of gold from its ores since the late 19th century. Yet, there are severe environmental concerns for its use due to the high toxicity of cyanide. A general ban on the use of cyanide in gold extraction was even considered by the European Union (EU) in 2010. However, the EU could not force the producers to ban cyanide due to the lack of an alternative reagent which can compete with cyanide owing to its economic and technical advantages. Many studies have been carried out on the development of alternative lixiviants to replace cyanide. Among them, thiosulphate ($S_2O_3^{2-}$) is the most prominent environmentally friendly alternative. Thiosulphate leach system commonly uses cupric ion ($Cu^{2+}$) as an oxidant/catalyst and ammonia to mitigate excess consumption of thiosulphate by complexing with copper over a neutral-alkaline pH range of 8-10. Alternatives to copper such as cobalt ($Co^{2+}$) and nickel ($Ni^{2+}$) appear to be tested.

Thiosulphate has fast leaching kinetics (6-12 h. *vs.* 24-48 h.), low unit cost (300-400 US$/t (ammonium thiosulphate) *vs.* 2500-3000 US$/t) and low toxicity (452-625 times less) compared with cyanide. High gold extractions from certain type of refractory gold ores which are not amenable to cyanide leaching can be readily achieved by thiosulphate leaching. However, thiosulphate leaching has also some shortcomings such as its complex leach chemistry and the need for an efficient method of solution purification and metal recovery. Several methods including precipitation with sulphide salts and cementation are suggested for recovery of gold from pregnant leach solutions. After several years of R&D studies, a commercial thiosulphate leaching process was developed and a plant was commissioned in 2015 by Barrick Gold Co. This process involves thiosulphate leaching ($Cu^{2+}$-$CaS_2O_3$) of a double-refractory gold ore followed by resin in leach (RIL) and electro-winning stages for recovery of gold from leach solutions. There have been also recent attempts in worldwide for implementation of thiosulphate leaching of gold from ores. Exploiting thiosulphate as a green solvent in gold leaching is expected to reduce the potential environmental concerns associated with the use of toxic cyanide and hence contribute to the environmental sustainability of the gold industry.

*Keywords: Gold ore, Leaching, Cyanide, Thiosulphate, Environment*

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# FRACTIONATION OF DIFFERENT WOOD SPECIES INTO HIGH-VALUE LIGNOCELLULOSIC MATERIALS

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In recent years, the implementation of cellulose nanofibers has been gaining interest due to their great potential in various advanced applications, besides broadening the uses of the highly exploited cellulose. The Basque Country has many small-sized forests in which native and foreign introduced species tend to regrow randomly. Aiming to solve this problem, the objective of this work is to boost the forestry management by revalorizing their comprehensive source of lignocellulosic raw materials by a robust thermochemical process.

Six different wood species were characterized and fractionated to provide an alternative to the traditional Atlantic mixed forests management. The species used were Northern red oak, common oak, common ash, Iberian white birch, sweet chestnut, and black locust. All the samples were treated by an organosolv delignification process and elemental chlorine-free (ECF) bleaching to fractionate them into their main components, recovering as main streams cellulose and lignin. This work is focused on the production and characterization of cellulose nanofibers (CNF), which were obtained by the defibrillation of the cellulose via high-pressure homogenization and characterized by FTIR, XRD, and AFM.

The CNF obtained from Northern red oak, and common oak had the best results because of the total defibrillation and lack of entanglement visible in the AFM images. Concerning the crystallinity calculated by XRD, the differences between the obtained cellulose nanofibers were minimal. Therefore, the same process can be suitable for different lignocellulosic raw materials, considering that the products obtained have similar properties. With this consideration, a mix of hardwoods could be used as feedstock for the same process to elaborate CNF.

*Keywords: Cellulose nanofibers (CNF), Elemental chlorine-free (ECF) bleaching, Organosolv delignification*

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# A HIGHLY SENSITIVE AND SELECTIVE COLORIMETRIC AND FLUORESCENT SENSOR FOR PHOSGENE DETECTION

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Phosgene is a highly toxic and reactive gas used in World War I as a chemical weapon. Despite its toxicity, phosgene is vastly employed as a starting material in the chemical industry for the production of pharmaceuticals and isocyanates [1]. Hence, its fast and precise detection is of high importance not only for the protection of the operators involved in the industrial processes, but also for the general safety in case of terrorist attacks or accidents.

We have developed a highly sensitive and selective phosgene sensor based on a carboxylic acid derivative of phenyl 5,6-pinenepyridine (**1**), which shows fast response in solution and solid state (Figure 1A). The sensor displays both colorimetric and fluorescent response in the presence of phosgene (Figure 1B), leading to an isoindolone-derivative (**2**), as demonstrated by single-crystal X-Ray diffraction (Figure 1C). The proposed mechanism for the synthesis of **2** involves the formation of an acyl chloride, followed by a nucleophilic attack from the pyridine. This is the first example of such a sensing reaction for phosgene detection, as most of the reported sensors are based on the formation of urea derivatives starting from diamines [2].

With a limit of detection in solution in the order of 1 ppb, our phosgene sensor is one of the most sensitive reported up to date. In addition, a range of chlorinated compounds was tested and the compound **1** has shown to be very specific in its response towards phosgene. In this contribution, we will present complete studies on the synthesis of the sensor as well as the analytical and photophysical details of the sensing reaction.

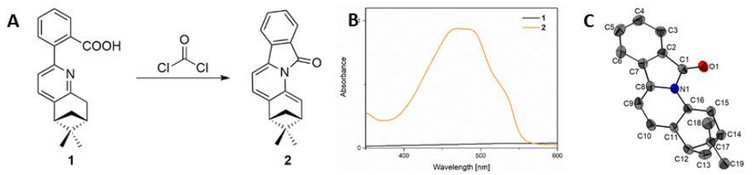


*Figure 1. The sensing reaction (A). UV-Vis spectra of 1 and 2 in THF, at 0.1 mM concentration (B). X-ray structure of **2**, with thermal ellipsoids at 30% probability (the hydrogen atoms were omitted for clarity) (C).*

*References: [1] Collins et al., J. Occup. Environ. Med., 53, 239–244, 2011.; [2] Chen et el., Anal. Chem. 89, 12596–12601, 2017.*

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# ENHANCED DISPERSION OF NANOFIBRILLATED CELLULOSE IN POLY (BUTYLENE SUCCINATE) MATRIX VIA COMBINATION OF SOLVENT CASTING AND MELT BLENDING FOR FUNCTIONAL GREEN NANOCOMPOSITES

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The last decade has seen rapid implementation of various sustainable technologies based on renewable resources to counter the global warming and the pollution problems. Transition to bio-based economy requires suitable materials with comparable properties to conventional oil-based ones. Poly (butylene succinate) (PBS) is bio-based, biodegradable polyester compatible with conventional polymer processing technologies and has excellent properties that are often compared with polyethylene and polypropylene. Nanofibrillated cellulose (NFC) has gained popularity due to renewability and existing preparation methods, that yield material with high mechanical strength, large specific surface area, barrier properties and non-toxicity. Owing to the recent advances in biopolymer field the production of functional materials in from of biocomposites is growing exponentially. We used conventional solvent casting method as reference and reduced solvent amounts by dispersing highly loaded films into polymer matrix with secondary melt processing step. Loadings from 5 to 15 wt.% were prepared, analyzed and compared. Tensile test, dynamical mechanical analysis, differential scanning calorimetry and thermogravimetric analysis were performed while biodegradation was studied under composting conditions. Introduction of the melt blending increased elastic modulus, storage and loss modulus but reduced maximum elongation, both methods yielded improved disintegration in the soil with total time of around 2 months. Thermal properties were preserved or slightly reduced compared to pristine PBS, and SEM images showed good filler dispersion.

*Keywords: Biodegradation, Composting, Physical-mechanical properties, Crystallization, Thermal properties*

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# OLIVE PITS- AN ATTRACTIVE SOURCE OF VALUABLE COMPOUNDS

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One of the most widespread crops in the Mediterranean basin is the olive grove. The crop and the industry associated with it generate a large amount of waste and by-products. One of these is the olive pit (OP), which is the most abundant solid by-product, representing between 10-15% of the olive. In recent years, it has begun to be separated for use as a fuel, due to its high calorific value.

The OP is a lignocellulosic material rich in polysaccharides (cellulose and hemicellulose) and lignin (33%). It is mainly composed of cellulose (21%) and hemicellulose (25%), with xylose (24%) being the most abundant sugar in this fraction. OP is a renewable and abundant material, which has an advantage over other subproducts, since its location is centralized in the mills and associated industries. Due to this, it is an ideal material for obtaining high added-value products, framing it within the concept of biorefineries. One of its most outstanding uses is to obtain fuel-ethanol, this compound is a key element to ensure an alternative to fossil fuels. It is also a source of other products, such as antioxidants, biopolyols, protein, lignin and xylitol.

Therefore, OP is a lignocellulosic material with great potential to be exploited in a biorefinery, since it allows the use of its different fractions to obtain multiple products with high added value. It can be adapted to the demand for products and to the existing technological infrastructures. This work presents the main uses and application, as well as the products that can be obtained from OP.

*Keywords: Olive pits, Biorefinery, High valuable compounds*

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# GREEN EXTRACTION OPTIMIZATION OF PHENOLIC COMPOUNDS FROM OLIVE POMACE BY PRESSURIZED ETHANOL-WATER

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Hydroxytyrosol (HT) and Oleuropein (OL) are major olive phytochemicals with antioxidant and anti-inflammatory properties. Olive pomace (OP) is the main by-product of the olive oil industry and an environmental threat due to its high organic/phenolic load. Its valorization as source of bioactive compounds is paramount for the sustainable growth of related industries. This work proposes an intensified process to maximize the recovery of these compounds from OP with hydroalcoholic mixtures, by a Pressurized Liquid Extraction (PLE) optimization. A Central Composite Design was selected, setting as factors the temperature (65-185º C), the percentage of EtOH in water (8-92%) and the solid/liquid ratio (0.2-0.8 $g_{OP}/mL_{SOLVENT}$). Freeze-dried OP was pre-treated with supercritical $CO_2$ to minimize its lipophilic content and enrich the Dry Extract (DE) in polyphenols. Different optimal conditions were found to boost each response compared to conventional solid-liquid extraction: i.e. the DE richness in OL and HT reached 13.8 $mg_{OL}/g_{DE}$ (475% increase) and 9.5 $mg_{HT}/g_{DE}$ (428% increase). Also, the Decarboxymethyl oleuropein aglycone dialdehyde (3,4-DHPEA-DEDA) was identified by HPLC-DAD-MS/MS as the most abundant polyphenol and was studied for the first time for this material. Also, it was found to correlate with the antioxidant activity (AA), both with similar optimal extraction conditions. Thus, an efficient, selective, sequential, scalable and green extraction process was established

*Keywords: Olive pomace phenolic compounds, Antioxidant capacity, Oleuropein, Hydroxytyrosol, Decarboxymethyl oleuropein aglycone dialdehyde*

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# TREATMENT OF REVERSE OSMOSIS CONCENTRATES OF LANDFILL LEACHATE BY WET AIR OXIDATION

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Nowadays, in most developed countries, the major way to deal with municipal waste is sanitary landfill. This practice generates leachate as rainwater percolates through waste. Whilst leachate ages, its composition varies and tends to be heavily polluted with hazardous and bio-refractory organic compounds. Reverse osmosis (RO) is already used in sanitary landfills since it generates good quality permeate. However, one of the main drawbacks of RO is the production of highly polluted concentrate that cannot be discharged in the environment or reused.

Wet air oxidation (WAO) is widely studied for the mineralization of effluents containing non-biodegradable compounds. Oxidation is a great destructive reaction that transform recalcitrant organic pollutants into carbon dioxide and water when complete. This process may require a high-energy consumption, but it can be autothermic in a certain range of chemical oxygen demand (COD) (10 – 100 $g.L^{-1}$). Relevant COD loads for autothermicity are reached in RO concentrates of landfill leachate. Consequently, the aim of this work is to evaluate the performances of WAO on RO concentrates to degrade bio-refractory compounds. In previous works, the coupling of RO/WAO has shown promising results on synthetic effluents in terms of total organic carbon (TOC) degradation by WAO and retention by RO.

Non-catalytic WAO with air injection was performed in a lab-scale autoclave (1 L) on different RO leachate concentrates that were collected in a sanitary landfill in southern France. Different operating conditions were studied (P = 15-20 MPa ; T = 200-300 °C ) depending on seasonality of leachates to evaluate effluent mineralization through pH, conductivity, turbidity, COD, TOC and inorganic carbon analysis. COD and TOC abatements of at least 70 % attested the possibility to treat RO leachate concentrates with WAO. In order to meet French regulations for discharge in the environment, further tests and analysis will be performed.

*Keywords: Landfill leachates, Hybrid process, Reverse osmosis, Wet air oxidation, Process intensification*

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# WASTE PAPER CONVERSION TOWARDS "GREEN" PACKAGING

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The modern scientific multiscale approach of chemical engineering “the green approach of process engineering” that combines both market pull and technology push is strongly oriented on raw materials and process intensification and on the couple - green products/green processes “to produce much more and better in using much less”, and to sustainably produce products responding to the society needs. Products designed to be used time and time again, packaged in sustainable, recyclable, and reusable materials represent a commitment to a sustainable future. Paper is one of the few truly sustainable products and is highly recyclable and biodegradable. Paper is recycled more than any other commodity in the solid waste stream and is often the dominant raw material used in paper production. The largest share of produced paper and cardboard is for packaging. This investigation describes ideas together with experimental results for applying biodegradable chemical additives as starch for retaining fibers and fines together with achieving improved hydrophobicity and strength in the production of packaging paper from recycled fibrous material.

*Keywords: Waste, Paper, Packaging, Biodegradable*

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# SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC EVALUATION OF SILVER DOPED ZINC STANNATE (Ag-$ZnSnO_3$) FOR REMOVAL OF CAFFEINE UNDER UV IRRADIATION

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Facile less energy intensive hydrothermal method was used for the synthesis of silver doped zinc stannate (Ag-$ZnSnO_3$). Structural and morphological characterizations were performed via XRD, FTIR, TEM, SEM-EDX, $N_2$ adsorption-desorption at 77K, XPS, and UV-Visible spectroscopy. Employed for photocatalytic degradation of caffeine, the photocatalyst material removed after 4 hours of 365 nm UV irradiation almost 100% caffeine amount. Effects of hydrogen peroxide ($H_2O_2$), ions and humic acid (HA) towards caffeine removal were also investigated. Reactive oxygen species (ROS) probe was performed employing chemical scavengers for the detection of probable species of either superoxide anion ($O_2^{\cdot-}$), hydroxyl radical ($^{\cdot}OH$), holes ($h^+$), and electrons ($e^-$) driving the photochemical degradation process and based on this related surface charge mechanism was proposed.

*Keywords: Advanced oxidation processes (AOPs), Heterogeneous photocatalyst, Doping, Water purification, Caffeine*

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# PERFORMANCE AND PERMEATE QUALITY OF ULTRAFILTRATION AS TERTIARY URBAN WASTEWATER TREATMENT FOR WATER REUSE

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Among possible processes for wastewater reclamation, ultrafiltration (UF) is an interesting option because it can theoretically retain suspended solids and microorganisms. The objective of this study is to find out the optimized operating conditions of UF to perform municipal wastewater reuse cost-effectively. A semi-industrial and fully automatic UF pilot plant with periodic classic backwashes (CB) and air backwashes (AB) was settled to filtrate the secondary effluent from a French urban wastewater treatment plant. The UF system was operated under constant flux mode. This study compared 15 filtration conditions each for more than 40 hours to investigate the impacts of flux, filtration cycle time, and air backwash frequency on the membrane hydraulic filtration performance, membrane fouling management, and permeate quality. The pilot plant worked in stable and sustainable state, with periodic and effective backwash sequence resulting in slow decrease of permeability during the whole process. Due to higher water recovery rates (>90%), better irreversible fouling control, stable permeability variation, and less chemical washing occurrences, the best sustainable conditions were a flux of 60 $L \cdot h^{-1} \cdot m^{-2}$, a filtration time of 60 min, and air backwash frequency of 1AB every 3CBs. For all tested conditions, the permeate water quality met the water reuse guidelines of the World Health Organization and the last regulation adopted in May 2020 of the European Parliament setting minimum requirements for water reuse in agriculture. For instance, the parameters of permeate quality including total suspended solids <2 $mg \cdot L^{-1}$, biochemical oxygen demand ≤10 $mg \cdot L^{-1}$, turbidity < 0.5 NTU, and *Escherichia Coli* >5 log removal, all reached the highest level of EU regulation (Level A). In addition, considering the presence of microplastics in the secondary effluents and the actual health crisis due to the virus SARS-CoV-2 responsible for Covid-19 disease, the evaluation of the retention of SARS-CoV-2 and microplastics by UF as tertiary treatment will also be carried out to possibly open more reuse applications.

*Keywords: Tertiary treatment, Ultrafiltration, Water reuse, Backwash, Covid-19*

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# PRESSURIZED LIQUID EXTRACTION (PLE) OF INDUSTRIAL HEMP RESIDUE AND PURIFICATION OF THE EXTRACTS

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Waste treatment is always an open question for any industrial process. In the case of plant-based processing, for example after separation of the seeds, the remaining biomass still contains several valuable components. An appropriately planned design resulting in zero waste of the harvested biomass along with the concept of the circular economy may even prove to be economically reasonable.

Apart from the historical reluctance, several kinds of cannabinoids prove to be a viable option for treating numerous mental and physical diseases without imposing high risks for the patient. One of the popular cannabinoids is the 2-[(1R,6R)-6-isopropenyl-3-methylcyclohex-2-en-1-yl]-5-pentylbenzene-1,3-diol (common name: CBD), which has been under investigation in the special emphasis of therapeutic use.

In this work, solid industrial hemp, harvested for its fibre, trashing residue was extracted with ethanol at elevated temperature and pressure. An experimental design with three levels for each independent variable (T=323-333-343 K; P= 8-10-12 MPa) was applied for the optimization of the pressurized extraction process of CBD. The kineteics of each extraction experiments was measured and both the total and the CBD yields were sufficiently modeled with the Brunner equation. At the best PLE conditions, from approx. 7 gr of solid hemp residue -without drying- resulted 52 mg of CBD after a 5 minute extraction with 1,5 ml/min flowrate of ethanol.

The resulting extract needs to be purified before any final use. Liquid-liquid extraction is one of the promising purification techniques, thus equilibrium distribution rations of the CBD starting from the obtained extract was measured the obtained extract in a methanol-water-hexane biphaseic system at atmospheric pressures and room temperature. The distribution ratio significantly changed depending on the molar composition of the solvent mixture with special regard to methanol content suggesting the relevance of liquid-liquid extraction-based refining of the extracts, including back extraction steps as well.

*Keywords: Extraction, Hemp, Waste treatment*

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# PERFORMANCE AND PERMEATE QUALITY OF ULTRAFILTRATION AS TERTIARY URBAN WASTEWATER TREATMENT FOR WATER REUSE

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Among possible processes for wastewater reclamation, ultrafiltration (UF) is an interesting option because it can theoretically retain suspended solids and microorganisms. The objective of this study is to find out the optimized operating conditions of UF to perform municipal wastewater reuse cost-effectively. A semi-industrial and fully automatic UF pilot plant with periodic classic backwashes (CB) and air backwashes (AB) was settled to filtrate the secondary effluent from a French urban wastewater treatment plant. The UF system was operated under constant flux mode. This study compared 15 filtration conditions each for more than 40 hours to investigate the impacts of flux, filtration cycle time, and air backwash frequency on the membrane hydraulic filtration performance, membrane fouling management, and permeate quality. The pilot plant worked in stable and sustainable state, with periodic and effective backwash sequence resulting in slow decrease of permeability during the whole process. Due to higher water recovery rates (>90%), better irreversible fouling control, stable permeability variation, and less chemical washing occurrences, the best sustainable conditions were a flux of 60 $L \cdot h^{-1} \cdot m^{-2}$, a filtration time of 60 min, and air backwash frequency of 1AB every 3CBs. For all tested conditions, the permeate water quality met the water reuse guidelines of the World Health Organization and the last regulation adopted in May 2020 of the European Parliament setting minimum requirements for water reuse in agriculture. For instance, the parameters of permeate quality including total suspended solids <2 $mg \cdot L^{-1}$, biochemical oxygen demand ≤10 $mg \cdot L^{-1}$, turbidity < 0.5 NTU, and *Escherichia Coli* >5 log removal, all reached the highest level of EU regulation (Level A). In addition, considering the presence of microplastics in the secondary effluents and the actual health crisis due to the virus SARS-CoV-2 responsible for Covid-19 disease, the evaluation of the retention of SARS-CoV-2 and microplastics by UF as tertiary treatment will also be carried out to possibly open more reuse applications.

*Keywords: Tertiary treatment, Ultrafiltration, Water reuse, Backwash, Covid-19*

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# SEPARATION OF FLUORINATED GREENHOUSE GASES USING ALTERNATIVE SOLVENTS AND ADVANCED MATERIALS

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Fluorinated greenhouse gases (F-gases) are a family of synthetic gases, including hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride ($SF_6$), used in a large range of industrial applications, such as air conditioning and refrigeration systems. They are powerful greenhouse gases with a global warming potential (GWP) up to 23000 times greater than $CO_2$ and with long atmospheric lifetime.

The research on green and sustainable technologies to efficiently capture, separate, and recycle F-gases is vital to reduce the environmental impact of these gases and to accomplish the European target of cutting their emissions by 2/3 by 2030, compared to the levels of 2014.

We investigated alternative solvents, such as fluorinated ionic liquids (FILs) and deep eutectic solvents (DES), activated carbons, and metal-organic frameworks (MOFs) for the selective capture of the most used HFCs in refrigeration: difluoromethane (R-32), pentafluoroethane (R-125), and 1,1,1,2-tetrafluoroethane (R-134a).

The commercial refrigerant R-410A (a blend of R-32 and R-125) is one of the most used refrigerants and is under the spotlight of the EU HFC phase-down. However, since it is a near-azeotropic system, the separation in its HFC components is not feasible by conventional distillation. Therefore, this refrigerant was chosen as case study for the development of technologies based on alternative solvents and advanced materials for the selective separation of value added pure HFC from refrigerants with high GWP. The azeotropic mixture of R-32 and R-125 was efficiently split into its constituents, with high purity, using an adsorption-based separation process.

*Keywords: Fluorinated Ionic Liquids, Activated carbons, MOF, F-gases, Adsorption*

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# PROCESSING STABILIZATION OF POLYETHYLENE WITH NATURAL EXTRACTS FROM GRAPE POMACE

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Presently polyethylene is one of the plastics produced and applied in the largest quantity in the world. The polymer is exposed to heat, shear and oxygen during its processing, both granulation and the manufacturing of the final product. After primary use, during the recycling of the polymer, it may be subjected to further processing steps. Adequate stabilization is essential to protect the polymer and hinder degradation resulting in the deterioration of properties. However, the currently applied synthetic phenolic antioxidants and their degradation products may leak into the environment and their possible effect is not fully understood yet. Consequently, we aim to replace synthetic stabilizers with natural extracts originating from agro-food industrial wastes. Winery by-products are rich in value-added bioactive molecules such as phenolic acids, flavonoids, anthocyanins and *trans*-resveratrol.

An oil-rich extract from grape peel was produced by supercritical carbon dioxide extraction. The extracted residue, which was rich in phenolics, was treated further with 96% ethanol in Soxhlet, stirred tank and ultrasound assisted extraction. The resulting three extracts were characterized by LC-MS/MS and the DPPH method using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical. The content of total phenolics was quantified using Folin-Ciocalteu's phenol reagent and the thermal stability of the products was determined by thermogravimetric analysis (TGA). The Tipelin FS 471-02 grade Phillips type polyethylene powder (MOLGroup Chemicals, Hungary) was processed by six consecutive extrusions at 260 °C. Each antioxidant package contained 1000 ppm extract and 1000 ppm Sandostab PEPQ (Clariant) secondary antioxidant. For comparative purposes the polymer was stabilized with 1000 ppm Irganox 1010 (I1010, BASF Switzerland) in combination with and without PEPQ. Stability was characterized by the measurement of the melt flow rate (MFR) and the oxygen induction time (OIT) of the polymer. The functional groups (unsaturated and carbonyl) of polyethylene were determined by FTIR spectroscopy, while the color of the samples was characterized by the yellowness index (YI) and the optical L* parameter measured using a Hunterlab Colorquest 45/0 apparatus.

The large polyphenol content (~20 %) and small $IC_{50}$ (~14 μg/ml) value ("efficient concentration" from DPPH measurement) of the extracts indicated remarkably strong antioxidant activity. LC-MS/MS measurement revealed that the extracts contain ~0.02 w/w % of *trans*-resveratrol and 0.4 w/w % of quercetin, but other antioxidants, such as myricetin, isorhamnetin and their derivatives could be detected in the extracts as well. The efficiency of the grape peel extracts during six consecutive extrusions is larger than that of the synthetic phenolic antioxidant used as reference, although the extracts discolor the polymer in some extent. Differences between the extracts produced by the three extraction methods are not very significant.





# APPLICATION OF SUBCRITICAL WATER EXTRACTION FOR PROCESSING MICROALGAE BIOMASS FROM WASTEWATER TREATMENT

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The application of microalgae in wastewater treatment demonstrated to be an effective and sustainable biological treatment for removing nutrients and other contaminants while reducing chemical oxygen demand. Moreover, microalgal treatment overcomes the biggest drawbacks of conventional purification procedures which are large chemical and energy consumption. Additionally, the obtained biomass can be used further for the creation of fertilizers, feed for animal, biostimulants, biopolymers, and so on. As the microalgae biomass contains bioactive components, it has the potential to be applied in pharmacy and cosmetics. However, the presence of contaminants and pathogens in the biomass poses a limit to these kinds of applications.

Therefore, the aim of this study was the valorization of the *Scenedesmus obliquus* microalgae biomass obtained from the purification treatment of brewery wastewater. Furthermore, subcritical water extraction was applied to obtain extracts at temperatures 120, 160, and 200°C for 10 min and pressure of 30 bar. After extraction, the used biomass, obtained liquid extracts, and solid residues were investigated in terms of the organic profile and the content of heavy metals. In addition, their microbiological profile and the content of polyphenols in liquid extracts were also investigated.

In the lyophilized biomass, the most dominant compounds were the hydrocarbons with saturated and unsaturated bonds. A significantly lower number of identified compounds in these samples belong to the group of alkylated hydrocarbons, ketons, phenols, alcohols, and organochlorine compounds. Compared to the biomass, the residue samples contained a significant amount of esters. Moreover, it was recorded that their percentage slightly increases with the increase in extraction temperature.

An increase in the content of Cr, Zn, Ni, and Fe was recorded in liquid extracts with the rise in temperature. The content of metals in residues rises with the temperature increase up to 160°C and then it decreases. However, metals content is higher at all temperatures compared to the starting biomass. With regard to the microbiological profile, it was determined that there was a complete elimination of microorganisms at all temperatures, and that the content of polyphenols is in positive correlation with the temperature.

*Keywords: Subcritical water extraction, Scenedesmus obliquus, Wastewater*

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# VALORIZATION OF *Rosa canina* BY-PRODUCTS THROUGH APPLICATION OF SUPERCRITICAL FLUID EXTRACTION

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The importance of agro-industrial by-products reutilization has remarkably increased due to their potential to fortify different products and foodstuffs. The conversion of agro-industrial by-products into the novel natural formulations addresses environmental and economic issues caused by discarding waste material and resulting in the development of cost-effective waste treatment. In the filter tea factory, the significant amount of by-products and wastes is generated in the form of herbal dusts. The herbal dust is herbal material grinded to the particle size lower than the size of pores of the filter tea bag. The quality of generated herbal dust depends on the properties of processed herbal materials and usually ranges from 10 to 35% of inlet material.

Rose hip (*Rosa canina* L.) herbal dust, obtained as a by-product from the filter-tea factory, was subjected to the supercritical carbon dioxide extraction (SFE-$CO_2$) at pressures of 200 and 300 bar and temperature of 60 ºC. The extraction yield was measured after 0.5, 1, 1.5, 2, 3, 4, and 5 h of extraction, being the highest after 5 h of extraction in the extract obtained at 300 bar (9.67±0.03%). Efficiency of extraction was compared to the results obtained in Soxhlet extraction of the same material. Chemical composition of supercritical extracts was assessed by GC-FID and GC-MS identifying different compounds including saturated long-chain hydrocarbons, sterols, and tocopherols. The main compounds detected in the extracts were identified as γ-sitosterol, α-tocopherol, γ-tocopherol and nonadecane. According to the results, this modern extraction technology has a great potential in the exploitation of rose hip herbal dust as a source of bioactive compounds and applications in pharmaceutical industry.

*Keywords: Rosehip, Herbal dust, Supercritical fluids, Gas chromatography, Tocopherols*

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# ECOTOXICITY ASSESSMENT TO SUPPORT THE SELECTION OF TECHNOLOGY ALTERNATIVES FOR SCANDIUM EXTRACTION FROM BAUXITE RESIDUE IN SCALED-UP EXPERIMENTS

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Technology alternatives for scandium production were assessed based on the ecotoxicity of the residues produced by the leaching of bauxite residue (BR) with various technological approaches. Leaching is the first technological step producing the largest amount of waste in the technology chain of the SCALE project. Therefore, the selection of the most environmentally sustainable technology alternative was crucial from the point of view of the generated waste. Leaching procedures at laboratory scale included: leaching with various concentrations (1–4 M) of sulphuric acid at ambient and high temperature (95°C), leaching with ionic liquid (HbetTf2N) and mechanochemical leaching (3M $H_2SO_4$, 1 h milling). The results were verified by samples from a pilot experiment. For the ecotoxicity assessment testorganisms from three trophic levels were applied to the water extract of the solid wastes: *Aliivibrio fischeri* (bacteria) bioluminescence inhibition test, *Sinapis alba* (plant) root and shoot elongation test, *Daphnia magna* (crustacean) immobilization test. Effective Concentrations ($EC_{20}$ and $EC_{50}$, concentration causing 20/50% inhibition) were calculated and the residues were categorized into acute aquatic toxicity classes and potential environmental effect categories (based on an eco score system). The results on the high sulphuric acid concentration samples (2–4 M) indicated that the ecotoxicity of the residues from the various technologies increased in the following order: ionic liquid leaching (LIL) < high temperature mineral acid leaching (HT MLA) < ambient temperature mineral acid leaching (AT LMA) < mechanochemical leaching (LPC). At lower (1 M) acid concentration the ecotoxicity of the HT LMA residue was lower than of the AT LMA residue. However, when the low acid concentration was applied in two cycles, the residue from the second cycle had the same ecotoxicity as the HT LMA residue. These residues had similar ecotoxic effects as the original BR with slight acute aquatic toxicity and a potential weak effect on the aquatic environment. The results from the pilot tests confirmed that the residue from the scaled-up leaching technology had slight acute aquatic toxicity and a potentially weak effect on the environment.

*Keywords: Ecotoxicity assessment, Bauxite Residue, Leaching technology, Scale-up, Wastes*

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# HYDROXYTYROSOL EXTRACTION FROM OLIVE OIL BY-PRODUCTS: FROM UNIVERSITY REASEARCH TO AN INDUSTRIAL PLANT

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Hydroxytyrosol is an important natural bioactive polyphenol found in olives, and its consumption has been linked to the benefits of the Mediterranean diet, and in particular to the protection against cholesterol oxidation and cardiovascular disease. The growing interest in hydroxytyrosol has prompted the development of methods for the separation, concentration and purification of this substances and its derivatives from various materials derived from the olive tree, especially those with less economic value, such as olive pomace and olive mill wastewaters. Indeed, only 2% of the phenolic fraction found in the olive fruit ends in the olive oil, while 98% is retained in the sub products.

Zeyton Nutraceuticals is a spin-off company focused on the production of 100% natural hydroxyltyrosol-rich extracts from olive oil industry by-products. Zeyton uses an internationally patented, environmentally friendly, membrane-based technology to obtain hydroxytyrosol-rich extracts. It is a low energy consumption process with an easy operation/maintenance, low investment and area requirement. Furthermore, since it does not involve the utilization of solvents and high temperatures, original molecular structures present in the mixture are preserved during the process.

Products under development include, hydroxytyrosol capsules for oral administration and hydroxytyrosol enriched olive oils.

*Keywords: Hydroxytyrosol, Olive pomace, Nanofiltration*

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# ASSESSMENT OF THE ANTIOXIDANT PROPERTIES OF ULTRASOUND-TREATED CHONDRUS CRISPUS RED SEAWEED

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Carrageenophyte red macroalgae are used mainly industrially for the extraction of gelling or thickening biopolymers. Nevertheless, this type of algae is composed of a variety of high value compounds with nutritional, functional or biological properties. In the context of sustainability and bioeconomy, the valorization of algae components with bioactive properties of interest for food, nutraceuticals, cosmeceuticals or pharmaceuticals should be further studied. In this work, the potential of ultrasounds-assisted treatment of Chondrus crispus red seaweed for the recovery of bioactive properties is proposed.

Chondrus crispus used as raw material was gently supplied by Compañía Española de Algas Marinas (CEAMSA) (Pontevedra, Spain). All samples were sonicated using an ultrasound bath at fixed temperature (80 ºC) and frequency (80 kHz) and varying some other relevant processing conditions such as time, alga/water ratio or ultrasounds amplitude. The total phenolic content, antioxidant capacity or protein content of the soluble extracts was carefully determined using well-known standard procedures.

Results indicated that the selection of the adequate ultrasounds conditions allowed obtaining extract from Chondrus crispus containing around 22 mg/g extract of protein, 13 mg gallic acid equivalents/g extract of total phenolic content and 180 mg Trolox equivalents/g extract of antioxidant capacity. In general, ultrasounds treatment at the selected conditions favored the recovery of high value bioactive compounds when compared with conventional procedures where organic solvents and long processing times are required.

*Keywords: Green technology, Bioactive compounds, Ultrasounds-assisted extraction, Red macroalgae*

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# ANALYSIS OF POSSIBILITY OF DESIGNING GREENER CEMENTITIOUS COMPOSITES

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Nowadays, $CO_2$ emissions to the atmosphere have been growing steadily for several decades. Environmental protection has become one of the priority tasks of scientists from around the world. Researchers are trying to find ways to produce the most important materials that way, to reduce $CO_2$ emissions to the atmosphere. Cement is one of them. Cement production is one of the most adverse $CO_2$ emissions in the world (ca. 8% $CO_2$ emission in the world). Looking for opportunities to improve the natural environment, we should look for alternative material solutions (for example marble and limestone powders). Now, researchers are trying to reduce the amount of cement in cementitious mixes by replacing it with supplementary cementitious materials (SCM's). One of the most commonly used SCM in cementitious mixes are fly ash and mineral powders (f.e. fly ash).

Granite powder waste is a waste material generated by crushing granite rocks or cutting granite rocks. Fly ash is a co-product generated in coal burning process (mainly in energetic industry). So far, both of these materials have been treated as waste, but the search for new SCM's means, that they are increasingly used to reduce the amount of cement in cementitious mixes.

The main aim of the article is to determine the possibility of reducing the environmental footprint of cementitious composites produced with the use of SCM's (fly ash and granite powder). Paper presents the results of research related to the characteristics of these materials. The chemical composition of these materials was determined and their influence on the properties of cementitious composites. Based on calculation algorithms, the amount of $CO_2$ emitted to the atmosphere was determined depending on the composition of cementitious composites. The ratio of the cost of producing a cement composite and the amount of $CO_2$ emitted during its production was also compared.

The article is a comprehensive analysis of profits related to the possibility of changing the cement industry according to green technology requirements. It also indicates the directions of development in the design of more green cementitious composites.

*Keywords: Green cementitious composites, Supplementary cementitious materials, Fly ash, Granite powder*

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# PHOTOCATALYSIS AND BIOCHARS: A COMBINATION TOWARDS REMEDIATION AND CIRCULARITY

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Antibiotics are widely used in aquaculture, which may lead to environmental pollution concerns and cause bacterial resistance, considered a massive health threat. Therefore, the development of sustainable strategies for the remediation of aquaculture effluents before their release into the environment is mandatory. Photocatalysis is considered a green and effective process for water remediation, employing semiconductor materials and light for the removal of organic pollutants. Among photocatalysts, titanium dioxide ($TiO_2$) has been extensively used due to its availability, cost-effectiveness and properties as photocatalytic active crystal phases. On the other hand, the conversion of pulp and paper mill sludge into biochar (BC) to be used in water remediation ultimately constitutes an implementation of circular economy. In this work, BC was used as $TiO_2$ substrate (providing a solid surface for the generation of highly oxidizing species). Furthermore, BC was magnetized (harboring the magnetic particles into its porous framework) allowing for the simple after-use recovery of the material. Four materials were synthesized: BCMag (magnetized BC), BCMag-$TiO_2$ (BCMag functionalized with $TiO_2$), BC-$TiO_2$-$Mag_{in\text{-}situ}$ and BC-$TiO_2$-$Mag_{ex\text{-}situ}$ (BC functionalized with $TiO_2$ and afterwards magnetized by *in-situ* and *ex-situ* approaches, respectively). The application of the produced waste-based magnetic biochar/$TiO_2$ composites on the photodegradation of two antibiotics widely used in aquaculture (sulfadiazine (SDZ) and oxolinic acid (OXA)), was assessed. BCMag-$TiO_2$ and BC-$TiO_2$-$Mag_{ex\text{-}situ}$ were selected to undergo kinetic studies after preliminary studies of photocatalytic performance and characterization. For SDZ, half-life time ($t_{1/2}$) noticeably decreased from 11.2 ± 0.5 h in absence of material, to 2.9 ± 0.1 h and 3.3 ± 0.1 h, in presence of BCMag-$TiO_2$ and BC-$TiO_2$-$Mag_{ex\text{-}situ}$, respectively. For OXA, even though the differences were not so substantial, the presence of the photocatalysts also revealed a decrease in $t_{1/2}$ (from 1.21 ± 0.08 h, in absence of materials to 0.46 ± 0.01 and 0.71 ± 0.03 h, in presence of BCMag-$TiO_2$ and BC-$TiO_2$-$Mag_{ex\text{-}situ}$, respectively). Therefore, the application of these materials offers a wide range of advantages going from the sustainability and the cost lowering of the treatment process to the implementation of circularity.

*Keywords: Aquaculture, Antibiotics, Photosensitizers, Removal strategies*

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# VALORIZATION OF CORK USING SUBCRITICAL WATER

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Granulated cork was submitted to subcritical water extraction/hydrolysis in a semi-continuous reactor at temperatures in the range of 120−200 °C and with a constant pressure of 100 bar, with the goal of obtaining extracts enriched in different value-added compounds. The influence of temperature on the composition of the cork extracts obtained was assessed - namely, their content of carbohydrates and phenolics. The extraction yield increased with the temperature, and this was associated with the decrease in the dielectric constant of water and the increase in its ionic product. Extracts composed of up to 36% phenolics were obtained at temperatures of up to 120 °C, with an antioxidant activity only two times lower than that of pure gallic acid, but in low amounts, showing potential for applications in the cosmetics, food, and pharmaceutical industries. Assays at higher temperatures generated extracts richer in carbohydrates and with a phenolics content of ca. 20 wt.% in comparatively far higher amounts. Neither the amount of suberin nor its structure were affected by the subcritical water treatment, thus it can be used like the original material in many sectors.

*Keywords: cork; Quercus suber L., Subcritical water, Phenolic, Carbohydrates*

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# TOWARDS THE RECYCLING OF WASTE MINERAL POWDERS BY USING THEM AS AN ADDITIVE TO EPOXY RESIN COATINGS

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The wastes from the extraction and processing of mineral resources are not re-used and are one of the largest waste streams in Europe. These wastes contain quartz, alumina or limestone fine powders and are extremely hazardous. Because they often float in the air, get into the soil and water the waste mineral powders have the potential to cause pneumoconiosis, respiratory failure, idiopathic pulmonary fibrosis, cancer in humans and affect the nervous system in animals. Furthermore, its disposal leads to water pollution and plant pollination. These powders will not be harmful for humans when incorporated in solid epoxy resin in floors. Thus, the main goal of the work is to investigate the possibility of decrease the hazardous effect of waste mineral powders thanks to its utilization in hardened epoxy resin coatings. It should also be noted that epoxy resins are very harmful to the environment. Long-term work on the production and application of epoxy resins can cause severe allergies. Compounds contained in the epoxy resins can persist in the environment for a very long time. Therefore, there is a need to find a solution to reduce the total mass of these resins used to make the coatings. The work presents the elaboration of the current state of knowledge on the modification of epoxy resin with mineral powders. The main aim of the work is to show the potential of using waste mineral powders as a promising additive to epoxy resin coating and to identify research gaps. Due to the usage requirements and durability of the epoxy resin coating, as well as the ease of application of liquid epoxy resin, appropriate values of its fundamental properties are required. The work contains a review of the research carried out so far on the influence of mineral powders on the fundamental properties of epoxy resins, such as: density, viscosity, contact angle, hardness, impact resistance, compressive, tensile and flexural strength, glass transition temperature and pull-off strength. Waste mineral powders are not commonly used in the epoxy resin coatings. Of the mineral powders, only quartz and granite mineral powders have been used so far. There is no knowledge of the properties of epoxy resins modified with other mineral powders. However, the research done so far gives promising evidence that the addition of the adequate mineral powder and its amount for the epoxy resin coatings could improve their properties. The problem of a large amount of mineral waste affects almost all of Europe and epoxy resin coatings are very popular throughout Europe. The solution of using waste mineral powders as an additive to the epoxy resin coatings could contribute to solving the problem of mineral waste recycling.

*Keywords: Coating, Epoxy resin, Waste, Mineral powder*

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# SEQUENTIAL ORGANIC SOLVENT EXTRACTION AND CHARACTERIZATION OF KRAFT AND ORGANOSOLV LIGNINS

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The production of high added value materials derived from waste or renewable resources is largely promoted by environmentally friendly policies worldwide. In order to fulfill sustainable developments, products obtained from biorefineries of lignocellulosic biomass can significantly contribute, especially lignin, the most abundant aromatic natural compound on earth. It is highly available and has a low price. However, its main drawback is its heterogeneity, which leads to variations in the properties, and consequently, possible applications.

Consequently, to improve and increase the industrial applicability, a solution to minimize these unfavorable properties is the separation of lignin into fractions using different organic solvents. This work aims to design a suitable process of sequential organic solvent extraction (SOSE) for both organosolv and kraft lignin, while performing the greenest and most sustainable process possible. Therefore, it is of great importance to choose the most suitable organic solvents for the lignin solvolysis, prioritizing the least harmful solvents that provide with good solubility yields and different chemical properties interesting for diverse applications.

Yield of the process, purity, molecular weight, S/G ratio and phenolic hydroxyl group content of the fractions obtained were measured and calculated by various methods. Yields were obtained gravimetrically, purity and chemical characterization were obtained following the standardized method of Quantitative Acid Hydrolysis, mean molecular weights and polydispersity index were obtained by Gel Permeation Chromatography, and S/G ratio and hydroxyl content were obtained by $^{31}$P NMR spectroscopy analysis, as well as concurrently using Py-GC/MS for the S/G ratio determination and Folin-Ciocalteau method at the UV-vis spectrophotometer for the total phenolic content.

The SOSE designed successfully separated lignin into fractions of low polydispersity index, different molecular weights and varied chemical composition. However, noticeable differences between both technical lignins could be observed, the main one being the considerably lower solubility capacity of the organosolv lignin in the chosen solvents.

*Keywords: Sequential organic solvent extraction, Kraft lignin, Organosolv lignin, Py-GC/MS, $^{31}$P NMR*

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# HYDROLYSIS OF THE PROTEIN FRACTION OF THE INDUSTRIAL SOLID RESIDUE FROM RED ALGAE AFTER AGAR EXTRACTION

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The industrial process to produce agar from red algae generates a solid residue that still contains valuable compounds that can be recovered reducing the environmental impact by incorporating this by-product within a circular economy concept. The amount of protein fraction from this solid residue accounted up to 21 % (w/w) in a dry basis with 172 ± 9 mg amino acids/g, being aspartic acid the major amino acid 20.4 ± 0.8 mg/g.

In this work, the use of subcritical water (subW) is proposed to valorize this solid waste biomass by hydrolysis and fractionation of the different biomass compounds, mainly the protein fraction. The effect of operating temperature on protein hydrolysis and free amino acid release has been studied in a semi-continuous fixed-bed reactor, in the range from 129 to 200 ºC, at constant flow rate (2 mL/min). A maximum in the protein yield, nearly 70%, was reached at 185 ºC. An increase in temperature led to an increase of the ionic product of water with higher levels of hydronium and hydroxide that favors biomass hydrolysis. Higher operating temperatures led to lower protein fraction yield. At these conditions, the residence time of water with the hydrolyzed and soluble products in the reactor is long enough to cause protein degradation.

The total content of free amino acids in the subW extracts followed the same trend as the protein fraction determined in the subW extracts. At 200 ºC, lower content of free amino acids was determined due to the degradation of amino acids at this temperature and residence time. Serine, and aspartic and glutamic acids have been found the most temperature sensitive amino acids that are degraded faster than low molecular weight amino acids such as glycine and alanine. Correlation between antioxidant capacity and different components determined in the subW extracts (total phenolic compounds, protein fraction and free amino acids) showed that the strongest correlation was obtained for TPC and antioxidant capacity.

Analysis of the solid residue after subW treatment showed that ashes were not solubilized being possible their application as fertilizers.

*Keywords: Subcritical water, Macroalgae residue, Protein, Free amino acids, Antioxidant activity*

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# STRATEGIES FOR THE SCALE UP OF NADES AS AN EXTRACTION AND STABILIZING AGENT

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Residues of the food and agricultural industries are rich in phytochemicals of interest that possess high antioxidant, anti-carcinogenic, anti-inflammatory, among others beneficial properties that can be used for the creation of products of added value such as nutraceuticals, cosmetics and pharmaceuticals. Conventional extraction solvents constitute health hazards, both in their handling and if ingested. Since the final goal of the extracted phytochemicals is human consumption a rigorous purification process is needed which increases the processing costs of the overall process. As an alternative, green solvents such as Natural Deep Eutectic Systems (NaDES), could be used. NaDES have proven to be efficient extraction medias as well as stabilizing agents and due to their formulation, their use in the final product is possible thus removing the need for extensive purification steps. However, there are still some issues associated with the use NaDES such as their viscosity. This work intends to explore strategies to translate the use of NaDES in a laboratory scale to an industrial scale and what issues need more attention.

*Keywords: Extraction, NaDES, Residues, Scale-up*

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# DESIGN, CONSTRUCTION, AND INITIAL TESTING OF AN ELECTROCHEMICAL TESTING STAND FOR THE STUDY OF DIFFERENT ELECTROLYZERS

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Electrochemical methods are environmentally friendly technologies used for the decontamination of many wastewaters containing organics and persistent pollutants such as herbicides, pesticides, pharmaceuticals, and others. Integrating these technologies for wastewater management in agroindustry's has recently become a promising alternative to help alleviate economic and environmental issues by coupling wastewater treatment with hydrogen evolution. This study introduces a novel electrochemical testing stand (TRL - 4) equipped with a low-cost Arduino-based data acquisition system for online parameter estimation, data storage, and processing that can be used for the analysis of different reactor designs. Electrochemical characterization of a prototype reactor at different temperatures and flow rates showed promising results with an overall increase in power density from 1.07 W $cm^{-2}$ at 15 °C and no recirculation to 9.82 W $cm^{-2}$ at 45 °C and 6 L $min^{-1}$ flow rate for the same input voltage. These findings revealed the great potential of wastewaters from agro-industrial origin to be used as electrolytes for electrochemical applications.

*Keywords: Electrochemical treatment, Wastewater, Hydrogen production, Reactor Design*

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# WASTE IS THE NEW WEALTH - RESOURCE RECOVERY FROM POULTRY WASTEWATER FOR MICROALGAL BIOREFINERY

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Sustainably providing goods and services across economic sectors is essential to meet the increasing demands of the growing population and to cope with the challenges of climate change. To this end, both the production of biological feedstock and the recovery of recyclable natural resources play a critical role. In recent years, microalgal biomass has been advocated as a promising source of renewable feedstock for a range of economic sectors. Microalgae farming starts to gain traction globally, but the culture process needs large amounts of water and nutrients and, consequently, its economic viability is hampered by high production costs. Laboratory studies suggest that resource recovery from wastewater for algae cultivation may reduce these costs while simultaneously providing a cost-effective and sustainable means of wastewater treatment. Nevertheless, implementing this on pilot and industrial scale requires a better understanding of which wastewater conditions favor microalgal biomass production. Using a battery of microalgae species, we assessed the algal growth potential on a range of sterilized and non-sterilized dilutions of wastewater from poultry farming. Besides species differences, we observed that wastewater dilution may positively affect biomass productivity. In addition, the results suggest that while wastewater sterilization is overall beneficial for rapid microalgal growth, it is not strictly necessary if wastewater is sufficiently diluted. Overall, this study is an important step to facilitate the translation of controlled laboratory experimentation on algae cultivation in wastewater to more realistic scenarios on pilot scale.

*Keywords: Circular economy, Bioeconomy, Sustainability, Bioresource, Biotechnology*

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# ENZYMATIC MODIFICATIONS OF WATERMELON RIND PECTIN FOR TAILORED APPLICATIONS

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Pectin is widely used in the food industry as a gelling agent, thickener and stabilizer. Increasing demand has prompted the search for new pectin sources and the improvement of their physicochemical properties by chemical modifications. However, chemical modifications are non-selective and often result in pectin degradation and low reaction rates, hampering the targeted modification to accomplish the desired properties. Therefore, enzymatic treatments are gaining interest as a green alternative to conventional chemical modification. Engineered watermelon rind pectin (WRP) could be a good alternative compared to conventional pectins, due their inherent interesting properties and composition and good yield from thisdisposal waste which could be valorized. This work reports on the relationship between pectin structure and functionality. To this end, two type of pectins were previously extracted using mathematical models in order to obtain the parameters of optimized yields and high yield with high arabinose content. Then, different enzyme treatments were applied to both pectins using pectin methyl esterase (PME), endo-1,5-α-arabinanase (EA), endo-1,4-β-galactanase (EG), and their combinations (PME+EA and PME+EG). The influence of eliminating the pectin-protein complexes with the addition of pepsin and protease was also evaluated. Samples were heated and dialyzed with 3.5 kDa molecular weight cut off. Structural characterization of pectin was inferred from the sugar composition (HPAEC-PAD) and their molecular weight (HPSEC). Then, the effect of pectin composition on the gelling capacity was evaluated, showing that removal of ester groups from the pectin structures was a good strategy to improve gelation properties. This work points out the potential of enzymes to tailor the structural properties of pectin obtained from watermelon rind for different food applications.

*Keywords: De-esterification, endo-Arabinanase, endo-1,4-β-Galactanase, Pectin methyl esterase*

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# PREPARATION OF HIGLY SPECIFIC SURFACE AREA ACTIVATED CARBONS FROM AGRICULTURAL WASTES AND LIGNITE

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The preparation of activated carbon from various carbonaceous sources using the process of chemical activation was examined. The carbonaceous precursors that were used are zero-cost sources as agricultural peels (tea stalks, orange peels, kiwi peels) and mined lignite ($C_{39}H_{35}O_{10}NS$). The activation agents were phosphoric acid ($H_3PO_4$) and potassium hydroxide (KOH). The pyrolytic experiments, in all cases, were carried out at 650 °C (temp. rate 10 °C/min) for 1 h, under $N_2$ (99.999 % pure) flow of 30 $cm^3$/min STP. After the process of pyrolysis, the solid residues were washed with HCI 15% and deionized water in order to obtain neutral pH (6-7). After BET characterization it was found that the tea stalk, orange peel, kiwi peel and lignite activated carbon materials presented specific surface area (SSA) equal to 1976, 1446, 1287 and 240 $m^2$/g, respectively, and total pore volume of 1.38, 0.81, 0.783 and 0.41 $cm^3$/g, respectively. It's worth to note that the activation agents for tea stalks, orange peels, kiwi peels and lignite were KOH, KOH, $H_3PO_4$ and $H_3PO_4$, respectively, with impregnation ratio 3.3/1, 3.3/1, 12.5/1 and 1/1, respectively. The overall %yield for all cases was 9% while in the case of activated carbon derived from lignite was 71%. The results of yield (%) may range ± 5-10% due to the process of precipitation and decantation, for all synthesis cases. The characterization of activated carbon materials was achieved using BET, FTIR XRD and SEM techniques.

*Keywords: Activated carbon, Agricultural wastes, Lignite, Characterizations*

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# VALORIZATION OF AGROFORESTAL RESIDUES FOR THE SYNTHESIS OF BIOBASED MULTIFUNCTIONAL POLYMERS

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In the last years, there have been a growing tendency in the study and utilization of different types of renewable sources, especially biomass, owing to its convenient environmental and socio-economic features. Lignocellulosic biomass is the most representative type, due to its significant abundance (70% of total plant biomass). Generally, the valorization of this kind of source is carried out by the extraction of its single components. Lignin, which represents one of them, is attracting a great deal of attention lately for being a natural and polyphenolic polymer with a wide range of applications in a variety of fields such as materials, energy, chemicals etc. One of the most remarkable features of lignin is its polyphenolic nature, which makes it a good alternative to other synthetic compounds such as phenol in the formulation of materials. Nevertheless, lignin presents less active sites within its structure compared to phenol, thus having lower reactivity. Therefore, a prior activation stage via chemical modification is generally required. In addition to that, certain properties of lignin such as mechanical strength or thermal stability can be also improved by the combination with inorganic compound as clays or silicates. Moreover, those compounds are able to provide various advantages such as the introduction of several functional groups, creating multifunctional materials.

Thereby in this study, the valorization of two different lignocellulosic biomass sources namely almond shells and maritime pine wood residues was carried out as raw materials in the synthesis of biobased multifunctional polymers. In a first step, the two biomass sources were valorized by means of the extraction of lignin via organosolv process. Following to that the two lignins extracted namely lignin from almond shells (LAS) and lignin from maritime pine (LMP), were chemically modified implementing a glyoxalation process. In the final stage, organically modified montmorillonite (nanoclay) was added into the lignin matrix via inorganic functionalization (hybridization). The results showed that the biomass sources significantly influenced the chemical properties of the lignins extracted and the later process of chemical modification performed. Concerning the glyoxalation process, it was observed an increase in the amount of hydroxyl groups within the lignin structure and the formation of condensates between lignin small units by means of methylene bridges as showed by FTIR and $^1$H-NMR analyses. On the other hand, after the process of inorganic functionalization it was confirmed by XRD analysis the introduction of the inorganic nanoclay and their substitution into the lignin structure. The nanoclay introduced into the lignin structure proved to enhance the thermal behavior of the nanocomposite as seen in the TGA analysis. Thus, it was confirmed, the possibility of valorizing efficiently the sources of lignocellulosic biomass as raw materials for the synthesis of biobased multifunctional polymers. Moreover, these polymers showed a great potential for further applications owing to their improved reactivity and thermal performance.

*Keywords: Biomass, Lignin, Nanoclay, Glyoxalation, Hybridization*

# CHEMICAL PRECURSORS FROM RENEWABLE RESOURCES: PRODUCTION OF LEVULINIC ACID

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Within the last century, the global consumption of conventional fuels and chemicals has increased significantly at expenses of the productivity of our ecosystem due to take-make-dispose mentality which lead fossil fuels reserves to a rapid depleting. As consequence, an increase of environmental concern has increased in the las decades scoping the sustainable production a use of the resources. As solution, circular economy system has emerged as a sustainable alternative to the consumption society having biorefinery as main pilar.

Biorefinery is the sustainable processing of biomass into a spectrum of biobased products, which can replace those that are nonrenewable. In this work, the production of levulinic acid (LA) from bleached cellulose has been investigated. LA market along with most organic acids, is getting bigger due to its potential application as precursor of many other chemicals, involving applications such as polymers, herbicides, fuels, food industry, etc.

In this work, the reaction was carried out in microwave reactor using an acid hydrolysis co-catalyzed by a metal Lewis acid together with organic acids. A screen of different solvent and catalyst was performed to select the best solvent and catalyst. The optimum conditions were selected using Design Expert 11 software after several experiments. Selected conditions were used with many other catalysts to compare their efficiency.

In overall, a novel green route using organic acid, catalyst and microwave heating has been designed to produce levulinic acid from cellulose. A yield of 39.14 % was achieved under optimal conditions for LA in a one pot procedure.

*Keywords: Levulinic acid, Organic acid, Biorefinery, Cellulose*

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# VALORIZATION OF OLIVE-DERIVED BIOMASSES THROUGH A TWO-STEP CASCADE BASED ON ULTRASOUND-ASSISTED EXTRACTION

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Besides olive oil, olive leaves and fruits extracts are currently applied as key ingredients of nutraceuticals and dietary supplements due to their cardiovascular health promoting properties, among other effects. Among the bioactive compounds, these extracts present phenolic compounds, such as hydroxytyrosol and its derivatives, which have shown therapeutically potential. Nevertheless, there are untapped olive-derived wastes that are generated in high amounts, but little information has been reported on their chemical composition, including valuable minor compounds such as phenolic compounds.

In this context, an integrated valorization scheme was applied to two olive-derived biomasses: a new byproduct obtained after the cleaning of the olive pits recovered from the olive pomace and the exhausted olive pomace (EOP), which is generated after the extraction of the residual oil contained in the olive pomace. This scheme consisted of ultrasound-assisted extraction (UAE) as first step to recover phenolic compounds and an alkaline treatment as second step to fractionate the residual lignocellulosic fraction. The chemical characterization showed that these byproducts contain a high amount of extractives, up to 52.9%. The solubilization of phenolic compounds from this fraction by UAE was much higher for EOP, correlating well with the extractive content, the total yield of extracted solids and the antioxidant activity. Moreover, the phenolic profiles were different.

The second step enabled to recover a liquid fraction, which contained also valuable components, i.e. proteins, sugars, and soluble lignin, which conferred antioxidant properties to these extracts, and whose content depended on the biomass and conditions applied. Furthermore, the solid fraction could be destined for other purposes, such as fuel production.

*Keywords: Exhausted olive pomace, Olive-derived biomass, Ultrasound-assisted extraction, Valorization*

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# VALORIZATION OF EXHAUSTED OLIVE POMACE THROUGH AQUEOUS EXRACTION AND ORGANOSOLV PRETREATMENT

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Exhausted olive pomace (EOP) is generated in huge amounts after obtaining the residual oil contained in the olive pomace, the main byproduct of the olive oil industry. Thus, the valorization of this residue is attractive from an environmental point of view and to generate an extra income. In this work, a valorization scheme has been proposed. For that, EOP was firstly subjected to water extraction at 85ºC for 90 min in a thermostatic water bath at 200 rpm. It enables the recovery of valuable compounds, i.e. hydroxytyrosol (0.6 g/L) and mannitol (4.8 g/L), in the aqueous extract. Then, as a second step in the valorization scheme of EOP, the recovered solid fraction was subjected to several pretreatments using a laboratory scale 1-L stirred tank reactor: liquid hot water and organosolv pretreatment with 50% or 60% ethanol (catalysed and uncatalysed with 1% sulfuric acid). The best conditions that enable to reach the highest delignification and facilitated the enzymatic hydrolysis to recover glucose were: 50% ethanol-1% sulfuric acid at 130ºC for 60 min. From the pretreatment liquor, an organosolv lignin (OL) with antioxidant properties was obtained through acid precipitation. Moreover, the lignin-rich residue obtained after enzymatic hydrolysis also presented antioxidant properties but lower than the former.

In conclusion, this works give new insights into the valorization of EOP through an integrative process to recover valuable bioactive compounds, antioxidant lignins and fermentable sugars.

*Keywords: Biorefinery, Exhausted olive pomace, Lignin, Natural antioxidants, Organosolv*

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# XYLAN / LIGNIN MODIFIED BIOCOMPOSITES FROM LIGNOCELLULOSE WASTE

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Nature is a source of inspiration for many material scientists to develop high-performance and functionality materials and composites. Lignocellulose is one of the most common and prolific materials that attracts scientists because of their properties and accessibility. Lignocellulose materials have significant advantages, such as renewability, biodegradability, excellent rigidity and new functionality. The preparation of tree and wood imitating material, based on lignocellulose, has attracted a high interest in the field of scientific research over the last ten years.

Current work includes approaches and research pathways for the preparation of cellulose film and aerogel. Here we report the production, characterization, and comparison of nanofibrilated lignocellulose composite materials derived from different sources of lignocellulose. Nanofibrils were obtained from several sources of lignocellulose waste - wood flour, hemp fibers and paper powder using the microfluidization process. The dispersions of 1% lignocellulose concentration have been processed for the preparation of samples. Beechwood Xylan (Hemicellulose source) and lignin were additionally used for wood-mimic composite preparation. The particle size was measured with SEM and DLS measurements. Composite films were obtained by simple casting and evaporation in a petri dish; while freeze drying technology was used for aerogels. The structure and properties of the received composite materials were studied by mechanical testing, XRD, SEM and TGA analysis. The results received are highly promising, which promotes the new composite's simple manufacturing method with a controlled structure hierarchy.

*Keywords: Lignocellulose composites, Fibrillated cellulose, Aerogels*

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# COMPARISON OF BLEACHED AND UNBLEACHED NANOPAPER FROM PISTACHIO SHELLS

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Cellulose and lignocellulose nanofibrils were extracted from pistachio shells utilizing environmentally friendly pulping and totally chlorine-free bleaching. The extracted nanofibers were used to elaborate nanopaper, a continuous film made by gravimetric entanglement of the nanofibers and hot-pressed to enhance intramolecular bonding. The elaborated nanopapers were analyzed through uniaxial tensile test, color properties, water contact angle (for surface-free energy), to analyze the influence of non-cellulosic macromolecules in the final properties of the nanopaper. Results showed that the presence of lignin augmented the viscoelastic properties of the nanopapers in ≈25% compared with fully bleached nanopaper; moreover, the hydrophobicity of the lignocellulose nanopaper was achieved, as the surface free energy was diminished from 62.65 to 32.45 $mNm^{-1}$ with almost non-polar component and a water contact angle of 93.52°. On the other hand, the presence of lignin had an apparent visual effect in the color of the nanopapers, with a ΔE of 51.33 and a ΔL of -44.91, meaning a substantial darkening of the film. In general, the presence of lignin resulted in the enhancement of selected properties, which are desirable for packaging materials, which makes pistachio shell nano-lignocellulose an attractive option for that field.

*Keywords: Pistachio shells, Organosolv, Environmentally friendly bleaching, Nanofibers*

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# SUSTAINABLE IRON-CARBON MAGNETIC COMPOSITES FOR THE REMOVAL OF PHARMACEUTICALS FROM WASTEWATER

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Highly porous activated carbons (AC) represent an attractive option for advanced wastewater treatment, due to their ability to efficiently adsorb pharmaceuticals and other contaminants. Nevertheless, some flaws are reported regarding the application of AC in wastewater treatment plants (WWTP), including: 1) high price, which is mostly derived from the use of unsustainable materials/methods in their production; 2) difficult after-use separation and regeneration of spent AC for reutilization, particularly for powdered AC, limiting their life-cycle. In order to overcome these gaps, an industrial waste was used in this work to sustainably produce magnet-responsive iron-oxide functionalized AC, which can be efficient in the adsorption of pharmaceuticals from wastewater, easily recovered from treated aqueous phase and further reutilized. Two waste-based AC were first prepared by chemical activation and two different pyrolysis methods (conventional and microwave heating) and later, loaded with magnetic iron oxide nanoparticles. The kinetic and equilibrium adsorptive performance of the produced magnetic activated carbons (MAC) were evaluated towards the removal diclofenac (non-steroidal anti-inflammatory) and venlafaxine (antidepressant) from different matrices (ultrapure water and real WWTP effluents). Furthermore, for a better evaluation of the applicability of these MAC, the competitive effects in binary systems containing diclofenac and venlafaxine were evaluated in both the studied water matrices. Finally, depleted MAC were recovered magnetically, regenerated by microwave heating, and successfully applied in a second adsorption cycle. The obtained results revealed the feasibility of producing waste-based magnetic composites that simultaneously combine high efficiency for pharmaceuticals removal with easy retrievability and successful regeneration/ reutilization.

*Keywords: Adsorption, Emerging contaminants, Magnetic carbon materials, Microwave pyrolysis*

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# WASTE PAPER CONVERSION TOWARDS "GREEN" PACKAGING

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The modern scientific multiscale approach of chemical engineering “the green approach of process engineering” that combines both market pull and technology push is strongly oriented on raw materials and process intensification and on the couple - green products/green processes “to produce much more and better in using much less”, and to sustainably produce products responding to the society needs. Products designed to be used time and time again, packaged in sustainable, recyclable, and reusable materials represent a commitment to a sustainable future. Paper is one of the few truly sustainable products and is highly recyclable and biodegradable. Paper is recycled more than any other commodity in the solid waste stream and is often the dominant raw material used in paper production. The largest share of produced paper and cardboard is for packaging. This investigation describes ideas together with experimental results for applying biodegradable chemical additives as starch for retaining fibers and fines together with achieving improved hydrophobicity and strength in the production of packaging paper from recycled fibrous material.

*Keywords: Waste, Paper, Packaging, Biodegradable*

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# FISHERIES AND AGRIFOOD INDUSTRIES WASTE STREAMS VALORIZATION AT iBET

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iBET is a private not for profit research centre in the area of biotechnology and life sciences based in Portugal. Food & Health Division has strong competences studying food products, considering aspects related to their quality, safety, authenticity, sensory and functionality. One of the core areas of the division is the efficient extraction of high added-value products from agro- and food industry related waste.

By products from fisheries wastes (e. g. blue shark, crab, shrimp, codfish) and agro-industries (e. g. brassica, citrus, apple, olive, grape) among others have been explored as sources of health-related molecules. Focused on the bioactivity of the target extract or purified compounds, clean and sustainable extraction processes are designed. Supercritical $CO_2$, pressurized liquids and alternative solvents, such as deep eutectic solvents, are used for the recovery of bioactive compounds.

Chemical, enzymatic and cell-based assays are used to evaluate potential of the obtained compounds for further use in food, nutraceutical and cosmetic application. Antioxidant, anti-inflammatory, anti-cancer, anti-fungal, antimicrobial anti-obesity, anti-hypertension, wound healing and anti-aging effect among others are some of the bioactivity tests available at iBET.

*Keywords: Circular Economy, Waste Valorization, Green Extraction Technologies, Sustainability, Bioactivity*

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# BRINGING LIFE TO INDUSTRIAL WASTES THROUGH THE PRODUCTION OF CARBON ADSORBENTS

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Solid industrial wastes generated from pulp and paper industry are produced in the order of dozens of millions per year, with their sustainable management being environmentally and economically challenging. Most commonly, and particularly in the case of primary paper mill sludge, these residues are incinerated or landfilled according to applicable legislation. These practices are discouraged even by the Confederation of European Paper Industries, in line with the Waste Framework Directive (2008/98/EC), which highlights the importance of finding alternative management strategies. The use of paper mill sludge as a secondary raw material for the production of carbon adsorbents is an interesting option, which, in line with the Circular Economy paradigm, involves the transformation of these cellulosic wastes into added-value products, improving resource efficiency by extracting extra value from an end-of-line waste. This work aimed at using primary paper mill sludge as precursor of carbon adsorbents, namely biochar, activated carbon (AC), and magnetic iron-carbon composites to be applied in the adsorptive removal of pharmaceuticals from water. For this purpose, primary paper mill sludge was subjected to pyrolysis (biochar), to pyrolysis combined with chemical activation (powdered AC), and to pyrolysis combined with both chemical activation and grafting functionalization (functionalized AC), agglomeration (granular AC) or magnetization (magnetic AC). The different production schemes, evidencing different levels of complexity, allowed to obtain materials with very distinct properties and suited for application in different operation modes. The adsorptive capacity of the resulting materials was evaluated for the removal of a group of pharmaceuticals, both in ultrapure water and in effluent from a Sewage Treatment Plant, considering batch and continuous systems. The obtained results are indicative of the adequacy of this secondary raw material as precursor of highly efficient carbon adsorbents, capable to attain performances that are comparable to, or even surpass, the ones of commercial AC.

*Keywords: Cellulosic industrial wastes, Circular Economy, Adsorption, Water treatment, Pharmaceuticals*

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# WHITE WINE GRAPE POMACE AS CARBON SOURCE FOR CAROTENOID-PRODUCING OLEAGINOUS YEASTS

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Oleaginous yeasts are a group of yeasts that can accumulate more than 20% of cell mass as lipids, and some species can reach 70%, under specific conditions. Most of the accumulated lipids are triglycerides (TAGs). *Rhodotorula babjevae* is an oleaginous red yeast that during lipids accumulation also synthesizes carotenoids. Carotenoids are natural lipid-soluble pigments used in the food industry as a coloring agent, and in the pharmaceutical industry as an additive to cosmetics, due to their antioxidant activity.

Grapes are one of the major crops worldwide, ca. 78 tons having been produced in 2019, of which about 52% were used in the winemaking process. Grape pomace (GP) is the by-product generated in the winemaking process, representing ca. 15% of the grape total input. GP is essentially composed of lignocellulose, also containing some proteins, lipids, and phenolic compounds. In the case of white winemaking, GP is separated from the juice before fermentation, leaving this residue with a high amount of soluble sugars (mostly glucose and fructose), which can easily be extracted.

Soluble sugars from white wine grape pomace (WWGP) were used as alternative carbon source for the growth of *Rhodotorula babjevae* under nitrogen limitation. Growth with either WWGP sugars or with a conventional glucose-fructose mixture reached similar contents of biomass, lipid accumulation and carotenoids, showing that WWGP sugars are a viable alternative carbon source. Fatty acid profile analysis showed oleic acid to be the main component of the microbial oil produced.

*Keywords: White wine grape pomace, Oleaginous yeasts microbial oil, Carotenoids*

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# VALORISATION OF POMEGRANATE BY-PRODUCTS WITH A BIOREFINERY CONCEPT

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The need to increase circularity of industrial processes as limited resources are available has triggered the development of the food by-products biorefinery concept. To develop sustainable industrial processes, the valorization of available by-products is crucial as well as the analysis of processes which can be feasible scaled up. In this work the possible valorization pathways of pomegranate by-products, peel and seed are summarized through the evaluation of the optimized extraction processes in lab- and pilot plant scales, and characterization of the obtained extracts by their bioactivities (quantitative analysis of constituents, antioxidant and antimicrobial activities). Pomegranate (*Punica granatum* L.) is widely cultivated in Mediterranean part of Europe, Asia and South America to produce juice, jams and wine. Turkey is one of the biggest pomegranate grower country in Europe, with a production mass more than 500 000 tonnes annually. Pomegranate peel and seed remains in large quantities (42% of whole fruit) after juice pressing containing phenolics and high valued seed oil which possessing high nutritional and medicinal values.

Soxhlet-, stirred-, and ultrasound assisted extraction and supercritical $CO_2$ extraction in lab- and pilot plant scales were studied. Solvents, and process parameters of extraction (extraction time, temperature and feed-to-solvent ratio) were optimized for pomegranate peel and seed separately aiming for the highest extraction yield with the highest concentration of the targeted bioactives in the extracts. Individual phenolic compounds were quantified by HPLC. The fatty acid content of seed oil was quantified by GC-MS. The peel extracts showed stronger antioxidant activities than the synthetic alternatives (BHT, BHA) analysed by the DPPH (2,2-diphenyl-1-picrylhydrazyl) method. The different peel extracts showed strong antibacterial properties in standard *in vitro* tests in the presences of different strains of Gram-negative and Gram-positive bacteria. Furthermore, peel extract was applied as stabilizer in polyethylene processing, showing promising results in replacing synthetic industrial polymer stabilizer (Irganox 1010).

*Keywords: Pomegranate peel and seed, Biorefinery, Extraction, Supercritical $CO_2$, Scale up*

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# ADVANCED VALORISATION FOR CORK WASTEWATER

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The cork manufacturing process involves several stages with waste generation, mainly industrial water from boiling of cork planks. Cork boiling water (CBW) is characterized by high COD, BOD, total solids and phenolic compounds content. The main aim of this study is the advanced valorisation of these spills by removing organic matter as measured by reductions in chemical oxygen demand (COD) and total phenolic compounds (TPC), in order to obtain valuable by-products. CBWs samples were collected from several cork factories and characterized by HPLC/DAD/FLD. They were treated by calcium in alkaline media according to a methodology developed by CICYTEX what led to the precipitation of most of phenolic compounds, along with the isolation and/or concentration of the remaining ones. Up to 26 phenolic compounds presented in crude cork were analyzed after and before the treatment and the results compared.The resulting depuration rates were in the ranges 34-46% for COD and 80-91% for TPC. Besides, this treatment reduced the pollution of CBWs and the decanted suspension can produce biogas by biodigestion, according with studies carried out in CICYTEX. On the other hand, the digestate could be used as a fertilizer but it is necessary an addition of K and P. With reference to treated CBWs: some phenolic compounds remained practically without precipitating and even with a preconcentration.

In conclusion, a good yield of depuration is obtained by removing organic matter with this efficient and green methodology. This organic matter can be transformed into by-products with interest for several industrial sectors: biogas, fertilizers. Besides, some interesting phenolic compounds can be extracted from the purified effluent, so this advanced depuration proposed is according with the concepts of biorefinery and circular economy.

*Keywords: Cork, Wastewater, Advanced, Depuration, Biorefinery*

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# SUBSTITUTION OF HAZARDOUS CHEMICALS IN FUR PROCESSING INDUSTRY

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Chemicals are widely used in many aspects of human living, right from household utilities to food products. The range of chemicals is huge that is used in the technological processes. Fur industry is one of the most polluting industries across world. Still, many fur industries practice conventional chrome tanning processes. The chemicals used for leather processing is often considered harmful and toxic to human health and environment based on their properties. Moreover, the industry also produces a huge amount of effluents and wastes during each stages of the production. The improper treated wastes impose severe environmental and human health risks in long term.

According the European policy - REACH regulation (EC 1907/2006), substances of very high concern to be replaced with non-toxic or less hazardous substances of same functionality. The study focusses on the finding an alternative substance to substitute the most toxic chemicals used for fur processes. The identified alternatives were assessed with various criteria such as hazard, legal requirements, CMR properties etc. A comparative evaluation was carried out for both conventional chrome tanning and identified alternative tanning agent.

The analysis of the fur industry has shown that the industry remains still most polluting industries that use potentially toxic chemicals which impose a huge risk to human health and environment. After analyzing the list of identified substances based on the literature study, the alternatives were chosen and assessed using the Life cycle assessment (LCA). By substituting with proposed alternative, the conventional system reduces the impact of human health by 30%. Expected benefits for the company: the proposed alternative does not have CMR properties, it helps to reduce impact for environment by eliminating the chromium waste, improve workers health and enhance company's image.

*Keywords: Hazardous chemicals, Substitution, Processing industry, CMR, REACH*

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# BIOCOMPOSITE COATINGS – A SUSTAINABLE ALTERNATIVE FOR PAPER PACKAGING FUNCTIONALISATION

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The actual trends in packaging are directed towards sustainable materials which replace the plastics and synthetic polymers and develop functional properties (i.e. antimicrobial, gases barrier etc.). in coatings or surface treatments of the packaging material. Therefore, nowadays it is of great practical interest to develop an efficient process to impart functional properties (antibacterial, barrier) to conventional paper materials to obtain a sustainable package and high protection of foods. At the global level, the packaging paper is an important growing area, i.e.: paperboard is accounted for 35.7% of world food packaging consumption in 2016, followed by flexible packaging (plastic, paper and foil) with 23.3%, rigid plastic packaging with 18.2% and metal with 12.2%. The advantages of paper/paperboard as packaging material are based on: paper is obtained from renewable raw materials; after use, paper products are recyclable, biodegradable and compostable - in Europe, 72% of used paper is recovered for recycling in new paper products; paper/paperboard can be converted into containers with specified strength and stiffness, is more resilient than glass/plastic over a wider temperature range, it is lighter and more easily printed on than other materials. However, as food packaging material paper/paperboard is limited due to its porous structure and hydrophilic character of cellulose fibres that give the poor barrier properties (i.e. low water and grease resistance, high permeability to gases and water vapours) and sensitivity to microbial attack. Current solutions to obtain paper with adequate barrier properties (to be used for food packaging) are based on oil-derived polymers, which inevitably increase carbon footprint of packed product and endanger recyclability and biodegradability of used packages.

In this paper are presented some investigations regarding the development of (bio)composite coatings based on natural polymers (starch and chitosan), natural zeolites and silver nanoparticles (AgNPs) and their applying onto paper surface to obtain specific properties for food packaging applications. The obtained coated papers have been assessed regarding the antimicrobial activity, water and air barrier properties as well as mechanical strength. The obtained results demonstrated that the composite coatings based on starch: chitosan: zeolites: AgNPs exhibit improved barrier and mechanical strength properties as well as the inhibition effect on pathogenic microorganisms for food alteration *E. coli* and *S. aureus*.

*Keywords: Composite coatings, Paper packaging, Coatings, Biopolymers, Food packaging*

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# A GREEN APPROACH FOR ALGINATE EXTRACTION FROM BROWN SEAWEED USING A HIGH-PRESSURE-ASSISTED METHOD

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This work reports on the production and characterization of alginate-based extracts from *Saccharina latissima* and *Ascophyllum nodosum* by means of a novel green approach based on a high-pressure (HP) assisted pre-treatment prior to conventional extraction. The alginate extracts were characterized in terms of composition and structure by ATR-FTIR, NMR, HPAEC-PAD, and RAMAN, and in terms of functional properties, including a rheological characterization of the extracts as well as evaluation of their antioxidant properties and polyphenol content. The HP pre-treatment affected differently depending on the macroalgae used. Although the alginate extraction yield and extracts properties were not significantly altered in *Saccharina latissima,* higher yields were obtained from the alginate extracts obtained from *Ascophyllum nodosum,* which, in addition to the conventional alginate yield, contained low molecular weight polysaccharides, proteins, and polyphenols which conferred them a high antioxidant capacity and led to the production of brownish alginate extracts with different rheological behavior. These results show the efficiency of the HP pre-treatment method to produce cost-effective alginate-based extracts with potential applications within the food industry.

*Keywords: Alginate, Bioactive compounds, Brown seaweeds, Green extraction, Pressurized liquid extraction*

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# BIO-BASED POLYMER NANOCOMPOSITE FOR PHOTOPOLYMERIZATION APPLICATIONS

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Even though bio-based polymer materials are not considered a new phenomenon, petroleum-based polymers still hold the major part of the polymer market. That is not even including the fact that most bio-based polymer systems still contain petroleum-based components for better performance or price. Therefore, polymer industry is still in dire need of “greenering” through more use of bio-based materials and not only that. More environment friendly production of products as well. One good option is to supersede meltprocessing, that requires huge amounts of energy with photopolymerization.

We report photopolymerization investigations of bio-based polymer resins enhanced with natural fiber nanoparticles. Thorough investigation of photopolymerization process under UV-irritation is offered.

While neat resins formulation adjustments were performed most importantly discussed is natural fiber nanoparticle impeccable affect on mechanical properties of the prepared samples. Prepared resins neat and composite have been validated for UV-assisted 3D printing and coating applications showing promising results in aspect of resolution and stress and strain properties enhancement. In some cases, addition of nanoparticles improved tensile and flexural stress resistance by two-fold. Kinetics of UV-curing process, mechanical and thermal properties are discussed.

*Keywords: Biopolymers, Bio-composites, Nanocomposites, Photopolymerization*

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# SOLVENT FREE COATINGS BASED ON RECYCLING PRODUCTS

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In fact, the existing and future processes will sooner or later be forced to gradually adapt to the principles of "green chemistry", which includes a modern approach to chemical engineering that meets both market requirements and the social and environmental constraints of sustainable industrial processes. In this study, a new type of paper protective self-healing coating is reported. Thus, the coating systems are based on a recycling product (i.e. from the chemical recycling of flexible polyurethane foams), on polythiols, and on trimerized aliphatic diisocyanates and designed to react with the surface atoms or oxidized products by two different mechanisms thus forming chemical bonds between the paper surface and the coating. By this and the adjustment of the coating system to extremely low water uptake or water vapor penetration and oxygen penetration the paper surface is protected from the most aggressive environmental species. Further, the coatings are produced without the use of solvents so that a very smooth surface is formed and this is very hard (Shore D hardness of > 80) but as well elastic (elongation at break > 4%). Such type of coated paper could have many applications such as in the printing and packaging industry but also others. In addition, its production process combines the spray coating and UV curing process following each other within a few seconds.

*Keywords: Coatings, Paper, Self-healing, UV curing*

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