

6<sup>th</sup> International Conference on Chemical Engineering

# ICCE 2022

International Conference on Chemical Engineering

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Romania, Iași, October 05 – 07, 2022



## Book of Abstracts



“Gheorghe Asachi” Technical  
University of Iași

“Cristofor Simionescu”  
Faculty Of Chemical Engineering and  
Environmental Protection

6<sup>th</sup> International Conference on Chemical Engineering

**Innovative Materials and Processes for a Sustainable Development**

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Romania, Iași, October 05 – 07, 2022

# ICCE 2022

## BOOK OF ABSTRACTS

*Organized by:*

**“GHEORGHE ASACHI” TECHNICAL UNIVERSITY  
of IAȘI**

**“CRISTOFOR SIMIONESCU”  
FACULTY OF CHEMICAL ENGINEERING and  
ENVIRONMENTAL PROTECTION**

**ASOCIATIA RADU Z. TUDOSE A CADRELOR DIDACTICE SI A  
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**BOOK OF ABSTRACTS**

**Section 1 Advanced Materials, Manufacturing and Processes**

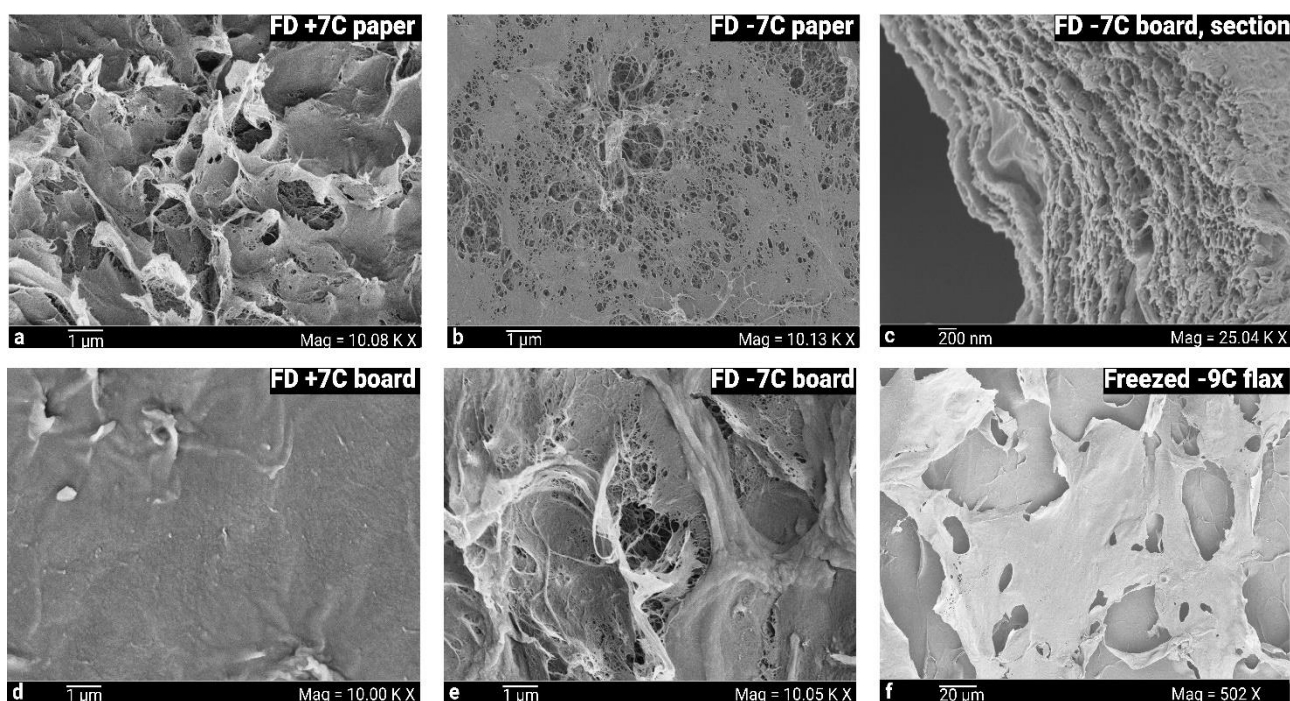
# Microstructure of as-prepared and dried hydrogels made from waste paper, flax and hardwood pulp

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Novel hydrogels with high contents of bound water were synthesized from waste paper and cardboard, flax and hardwood pulp due to self-organization in solution of DMAc/LiCl. The hydrogels should be carefully post-processed to characterize and to control of their properties. The microstructure of the hydrogels after various unconstrained drying protocols (ambient at room temperature, oven at 100 °C, freezing in the freezer and freeze-drying) was studied by scanning electron microscopy (SEM) and FTIR. After drying with all methods, there was a sharp loss of water as it evaporated and a strong thickness decrease of the samples. However, the microstructure of the samples differed significantly depending on the drying protocol. As revealed with SEM, the hydrogels after drying at ambient conditions and in the oven had a very dense web of cellulose fibres. In view of this, irreversible evaporation was observed and the water-retention capacity was not restored when re-hydration was attempted. After freezing the hydrogels both in refrigerator (-9 °C) and freeze-dryer (FD) at (+7 °C) and (-7 °C) (initially freezing at (-20 °C)), the microstructure of the dried samples was highly porous (Fig. 1).



**Fig. 1.** SEM images of freeze-dried hydrogels obtained from waste newsprint paper and cardboard freeze-dried at (+7 °C) (a and d, respectively) and at (-7 °C) (b, c and e); hydrogel obtained from flax freeze-dried in the refrigerator (f)

The implication of the different drying methods showed that the protocols impacted strongly the way how the water was removed from the highly swollen hydrogels and determined the final sample properties.

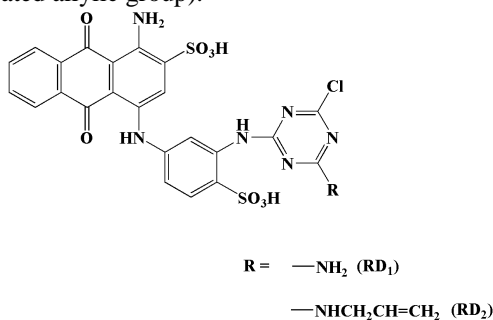
# Applicability of anthraquinone reactive dyes for paper dyeing

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Reactive dyes are widely used in the textile industries for dyeing of cotton, wool, silk, polyamides and other synthetic fibres. Recent investigations with reactive dyes are focused on dyeing of cotton of reactive dyes' removal from wastes and have only limited use on practical application in the papermaking process and single reports on laboratory experiments (Dai et al., 2022). Two anthraquinone reactive dyes (Fig. 1) have been synthesized (Konstantinova et al., 2009). Reactive dye 1 - RD1 is monochlorotriazine reactive dye and reactive dye 2 - RD2 is bifunctional (contains two reactive groups – one is chlorine atom and one unsaturated allylic group).



**Fig. 1.** Chemical structure of the investigated anthraquinone reactive dyes

The synthesised reactive dyes have been used for investigation of its applicability for paper dyeing through a comparative analysis of the paper slurry, white water and paper sample properties, with cationic and anionic direct dyes. Aiming to prepare woodfree paper for printing and packaging, wet-end chemical additives have been added, in the following sequence: dye fixative - 1% of o.d.f., two direct and two reactive dyes - 0.2%; 0.4%; 0.6% of o.d.f., sizing agent - 1% of o.d.f. and retention additive – 0.05% of o.d.f.. The drainage ability of paper slurries has been determined; turbidity, conductivity, pH and dye concentration in the white waters; strength properties and colorimetric data of dyed paper samples were examined in the CIELab system and colour stability by conducting accelerated thermal and light aging. The results for the white water properties of undyed and dyed with reactive dyes paper slurries, shown in table 1, confirmed the applicability of the used reactive dyes for the papermaking process. The strength of the obtained reactive dye coloured paper is slightly enhanced and the colour stability of the paper samples is commensurate to the direct dyes used.

**Table 1.** White water properties of undyed and dyed with Reactive Dyes paper slurries

White water properties	Paper slurry with added Reactive Dyes								
	Without Dye			RD1			RD2		
	Only pulp	Pulp+AKD + Ret	Pulp+Fix + AKD+Ret	0.2%	0.4%	0.6%	0.2%	0.4%	0.6%
T <sub>700</sub> , s	17.3 5	13.25	17.55	13.85	11.36	11.35	13.52	11.85	11.15
Dye concentration, %	-	-	-	1.653 10 <sup>-6</sup>	1.733 10 <sup>-6</sup>	2.347 10 <sup>-6</sup>	1.845 10 <sup>-6</sup>	1.824 10 <sup>-6</sup>	1.806 10 <sup>-6</sup>
Turbidity, NTU	10.0 3	8.38	15.31	10.46	7.89	5.88	12.51	8.03	7.39
Conductivity, μS	123. 3	123.2	129.1	129.7	133.2	136.2	131.5	132.5	134.1
pH	7.49	7.47	7.49	7.11	7.15	7.15	7.2	7.18	7.12

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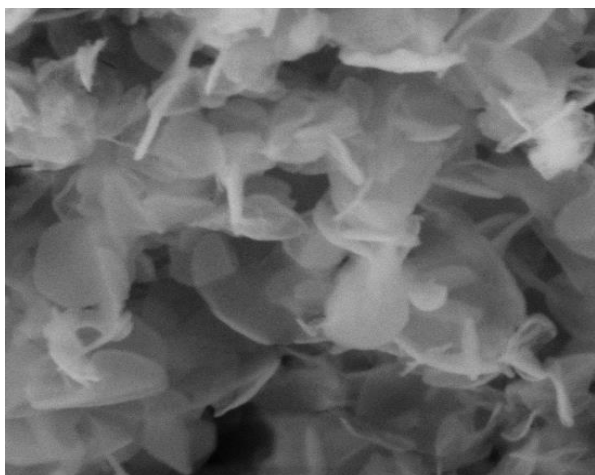


## About the fabrication procedures of layered double hydroxides nanoarchitectonics

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**Fig. 1** Typical SEM image of ZnAlLDH substituted with Cu.

Layered double hydroxides (LDHs) are mesoporous 2D anionic clays that emerged with promising applications in nanotechnology. Their structure derives from the conventional brucite, in which a part of the divalent metal cations ( $Mg^{2+}$ ) is replaced by the trivalent metal cations ( $Al^{3+}$ ) in an octahedral configuration, generating positive brucite-type layers. The cationic layers are held together by interlayer counter anions forming the interlayer gallery together with water molecules. A highly versatile chemical composition of the LDHs can be obtained by tailoring either the nature of cations of the layers and/or the type of inter-layers anions (Carja 2022). The most common method for the synthesis of LDHs is co-precipitation. This work aims on the synthesis conditions of the LDHs during the substitution of  $Me^{2+}$  with  $Me^{3+}$  in the LDH layers. In fact, we synthesized MgAlLDH and ZnAlLDH in which  $Mg^{2+}$  or  $Zn^{2+}$  were partially substituted with  $Cu^{2+}$ ,  $Co^{2+}$  or  $Ni^{2+}$ . Mainly, this study considers the optimization of the synthesis parameters of the LDHs by considering the effect of pH and the aging conditions (e.g.: time and temperature). Data concerning the

metal precursors used and their concentrations are also included in this study. Moreover, we studied how the nanoarchitectonic characteristics of MgAlLDH and ZnAlLDH are tailored by the introduction of  $Cu^{2+}$ ,  $Co^{2+}$  or  $Ni^{2+}$  in the layers (see Fig. 1). Results reveal that the nanoparticle sizes and their interconnection patterns are a function of the degree of the substitution of  $Zn^{2+}$  and  $Mg^{2+}$ . This work might pave the way to fabricate versatile LDHs nanoarchitectonics with specific applications.

### Acknowledgments

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# Modified screen-printed electrodes graphene-based for accurate pesticide residues detection

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Regardless of their advantages, pesticides are considered some of the most harmful environmental pollutants due to their capacity to accumulate and their long-term effects on biological entities. The issue of pesticide traces presence in water, soil, and food products emphasized the need for simple strategies to differentiate low amounts of these compounds (1). Nanomaterials have a strong potential for increasing the competitiveness of new generations of sensors for environmental monitoring and food safety applications through the combination of simple fabrication techniques in the design of nanometric interfaces. Electrochemical sensing methods attract the interest of the research community because they can serve as ideal sensor technology alternatives, with advantages such as rapid response, robustness, high sensitivity and selectivity, low cost, and the potential for real-time monitoring (2).

This work describes the use of a commercial screen-printed carbon electrode modified with graphene-oxide dispersions designed for electrochemical detection of carbendazim. The graphene-modified screen-printed electrode has been tested for the electrochemical quantification of carbendazim in water and real samples (complex matrices). The obtained sensor showed a high detection limit (10nM) and remarkable stability. The cost-effectively developed modified electrode could provide a viable platform for developing improved electrochemical sensors for detecting pesticides without any complex preparation of the real samples (filtration, centrifugation, etc).

## Acknowledgments

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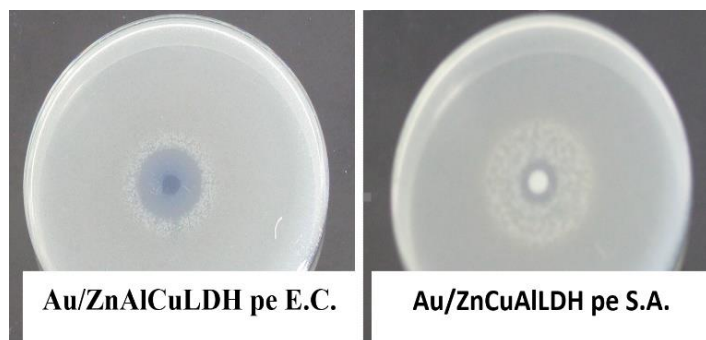


# Hybrid plasmonic nanostructures of Au/Ag nanoparticles and layered double hydroxides: characterization and the inhibition effect against *Staphylococcus Aureus* and *Escherichia Coli*

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Plasmonic nanostructures, such as nanoparticles of Au, Ag, Cu (denoted as MeNP) have emerged as an important class of optically active materials. A question that has emerged recently is whether it is possible to take advantage of the specific properties of plasmonic nanoparticles when these are ensembled with other nano-units such that to device a hybrid plasmonic as an advanced material. In particular, the additional nano-units need to access the wide spectral range from the ultraviolet to the mid-infrared and to have the requisite surface characteristics, temperature dependence, or structural features that are not

intrinsic to or easily accessed by the simple nanoparticles of metals. In this context we describe here a simple procedure (Mikami et al. 2016), to produce hybrid plasmonic nanostructures defined as nanoparticles of Ag or Au on layered double hydroxides (LDH), their physical-chemical characteristics and their antimicrobial activity against *Staphylococcus Aureus* (S.A.) and *Escherichia Coli* (E.C.). Firstly, the morphology, composition and phase structure of MeNP/LDH were characterized by X-ray diffraction (XRD), infrared spectroscopy (FTIR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) while the characteristics of the plasmonic response were studied by Uv-vis spectroscopy. In specific, XRD and TEM results reveal the formation of a specific nanomorphology in which nanoparticles of Au or Ag are highly dispersed on the larger nanoparticles of the LDH. Results point that the LDH composition is an important parameter to modulate the antimicrobial activity against *Staphylococcus aureus* and *Escherichia Coli*. Such that, copper substituted LDH (ZnCuAlLDH) demonstrated the strongest antiviral response.

## Acknowledgments

B.T. acknowledge a doctoral grant for participating at the conference.

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## Modeling and simulation of a continuous glycerol acetylation process

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It is well known that glycerol is nowadays obtained as a byproduct in the synthesis of biodiesel in a mass ratio of 1:10, and, given the recent development of biofuels industry development, its valorization through different processes is emphasized in different published studies. One of the processes that leads to value added chemicals is the esterification of glycerol with acetic acid, with the most important reaction products as triacetin.

As the behavior of the reaction mixture is strongly non-ideal, and the availability of the physical and thermodynamic properties for some of the reaction mixture components scarcely available, the first goal of this work was the evaluation of chemical equilibrium composition. This study was performed is specific operating conditions for acetylation process, with classical UNIFAC group contributions method implemented to consider the non-ideality of the reaction mixture and calculation of the activity coefficients.

The second goal of this study was that, based on published experimental data, to propose a simple power-law kinetic model for glycerol acetylation on Purolite CT-275 ion-exchange resin and to estimate its parameters using non-linear numerical estimation procedures. The quality of the proposed model was tested based on a statistical approach.

The developed kinetic model was further used to develop a conceptual design of a process flowsheet using Aspen Plus process simulator. Due to the presence of acetic acid in a relatively high concentration (at least a molar ratio acetic acid to glycerol of 4), the NRTL-HOC property package was implemented in our study. The results shown that the main product (triacetin) can be obtained with a purity above 94 % (mol) and the proposed flowsheet is feasible from the economical point of view.

# Evaluating the impact of the diamine structure on the performance of some azo-polyimide-based flexible supports for microelectronic applications

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Recently, a special attention has been paid to flexible supports that can be successfully implemented in microelectronics applications. In the category of the materials that are used for these flexible substrates are counted the polymers, especially the polyimides. This class of macromolecular compounds is known for their superior physicochemical properties (Zardetto et al., 2011, Liaw et al., 2012, Wu et al., 2022) that provide noteworthy characteristics to the resulted material. Azo-polyimides represent a particular sort of polyimides containing in their structures an azo-cromophore, which might be included either in the main chain or in the side chain. Such approach provides to the resulting the material a photochromic behavior. In our study, a simple and innovative approach regarding the synthesis method (Sava et al., 2022) was applied to obtain some novel high-performance supramolecular polyimide systems with an improved flexibility. The proposed structural design aims to include azo groups that give the structuration capacity via UV laser irradiation (Stoica et al., 2021, Stoica et al., 2022) and cyano groups that give enhanced dielectric and piezoelectric properties (Tugui et al., 2017). The structures were differentiated by their variable composition, namely by the use of distinct diamines, with or without cyano groups in their configuration. In this context, the impact of the diamine type on the performance of the obtained azo-polyimide-based flexible supports for microelectronic applications is evaluated. Molecular modeling is utilized as a tool to visualize the conformational aspects of the synthesized polymer structures. The morphology of the solid films is inspected by means of atomic force microscopy to verify the UV laser structuring capacity. The dielectric constant of the examined azo-polyimides is theoretically assessed. Piezoelectric characteristics of these polyimides are also discussed as a function of their structural peculiarities.

## Acknowledgments

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## Research on the use of lignin in the production of solid biofuels

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The growing demand for transportation fuels, along with concerns about the harmful effects of greenhouse gas emissions from the burning of fossil fuels, has assured a viable future for the development of alternative fuels from renewable resources, such as lignocellulosic biomass. The efficient utilization of these biomass resources is critically dependent on the in-depth knowledge of their chemical constituents. This, together with the desired fuel properties, helps tailor the chemical and/or enzymatic processes involved in converting biomass to biofuels (Sannigrahi et al., 2010).

Lignin is also being viewed as alternative to the aromatics and polymer industry, apart from the source of biofuels/bioenergy. Despite various physico-chemical and other available abiotic methods, biological methods of lignin depolymerization and its transformation to biofuels or value-added products got significance due to their economic and environmentally benign nature (Radhika et al., 2021).

The major component of lignocellulose materials is cellulose, along with lignin and hemicellulose. Cellulose and hemicellulose are macromolecules from different sugars; whereas lignin is an aromatic polymer synthesized from phenylpropanoid precursors. The composition and percentages of these polymers vary from one plant species to another. Moreover, the composition within a single plant varies with age, stage of growth, and other conditions. Consequently, processes that use enzymes and microorganisms are being developed to explore the potential for their biotechnological applications. Production of ethanol and other alternative fuels from lignocellulosic biomass can reduce urban air pollution, decrease the release of carbon dioxide in the atmosphere, and provide new markets for agricultural wastes. Despite the progress achieved, more effort is needed for lignocellulosic enzymes and/or microorganisms to have significant industrial impact (Perez et al., 2002).

Biorefinery of biomass emphasizes on utilization of all the three components for attaining economic feasibility. Lignin valorisation via biotechnological route is most interesting due to being environmentally sustainable; however, its recalcitrant nature is a major challenge. Microorganisms, mainly, white-rot fungi are known to produce lignin degrading auxiliary enzymes as well as lignin modifying enzymes. These may deconstruct lignin's architecture efficiently to obtain smaller aromatic units or aromatic monomers which can be used as building blocks for various value-added products. Mechanistic understanding, slow rate of reaction and compatibility of all the multienzymes for synergistic action is still a challenge (Singhania et al., 2022).

From the economic and environmental point of views and for reaching a sustainable and clean environment it is recommendable to achieve the concept of circular economy via the valorization of the readily available and low cost or even costless waste resources into value added products. This study valorized rice straw the most available worldwide agricultural lignocellulosic waste via fungal hydrolysis followed by a separate fermentation batch process into bioethanol (110 gallon/ton) with heat value of approximately 25.12 MJ/kg. The spent waste rice straw (SWRS) disposed from the bioethanol process recorded calorific value of approximately 17.62 MJ/kg recommending its applicability as a solid biofuel. Finally, for reaching zero-waste and not causing a new waste management problem, the SWRS discarded from the PPPW treatment process proved to be a new valorized solid biofuel with an efficient calorific value of approximately 38.56 MJ/kg, which can be reused as an energy source for the process itself (Nassar et al., 2022).

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# The influence of environmental factors on the performance of wood coating systems

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Lacquers are coatings sold in large quantities, purchased by consumers and frequently used for the protection and coloring of wooden surfaces. The impregnant has the role of entering the wood fiber, delaying or even stopping the action of microorganisms. Lacquer is the product which, after drying, ensures the formation of a glossy film and a long-lasting protection (Evans et al., 2015; Ozgenc et al. 2021). In this study, the properties of using an impregnant (IAC) and a protective lacquer (LPM) for wood protection were analyzed. They were applied independently on fir wood boards, in one or two layers, kept under laboratory conditions or exposed to external conditions in 4 areas (Iasi – IS; Constanta – CT; Piatra Neamt– PN; Nijmegen, Netherlands –OL) with different climatic characteristics for 6 months, 12 months and 18 months. In order to quantify the thermal stability of the two coating products exposed in different climatic zones, the temperature at which a percentage of 5% of the sample mass is lost was considered. The thermal stability of IAC acrylic impregnant is influenced by both exposure duration and climatic conditions. The most important changes were found in the case of the samples exposed in CT. In the case of the LPM lacquer, for the samples exposed in PN, there is a constant decrease of the thermal stability with the increase of the exposure time. This decrease is stronger when the LPM sample is applied in a single layer. Moderate changes in thermal stability depending on the exposure time are found in the case of the samples exposed in CT and OL. The analysis of the initially measured contact angle for the LPM-treated (protective lacquer, mahogany) boards shows that it is greater than 90° and after 18 months, its value is around 65° regardless of the exposure area. In the case of the IAC sample (acrylic impregnant, chestnut shade) the initial values of the contact angle are greater than 120° and decrease more strongly regardless of the climatic conditions when applied in a single layer. In order to quantify the influence of environmental factors on the composition of the coating products following exposure in different climatic zones, the ratios between the percentages of oxygen and carbon (O/C) and the percentage of nitrogen and carbon (N/C) were calculated – Fig. 1. After exposing the samples for 18 months to the action of environmental factors in the four geographical areas, an increase in the O/C ratio was found, except for the LPM sample applied in a single layer on the fir wood board and exposed for 18 months in the OL area. The N/C ratio values that may be associated with pigment degradation indicate sharp decreases in the ratio (N/C) for LPM samples exposed in the IS area and moderate ones for those exposed in the CT area. In the case of PN and OL exposure areas, the N/C values do not change significantly.

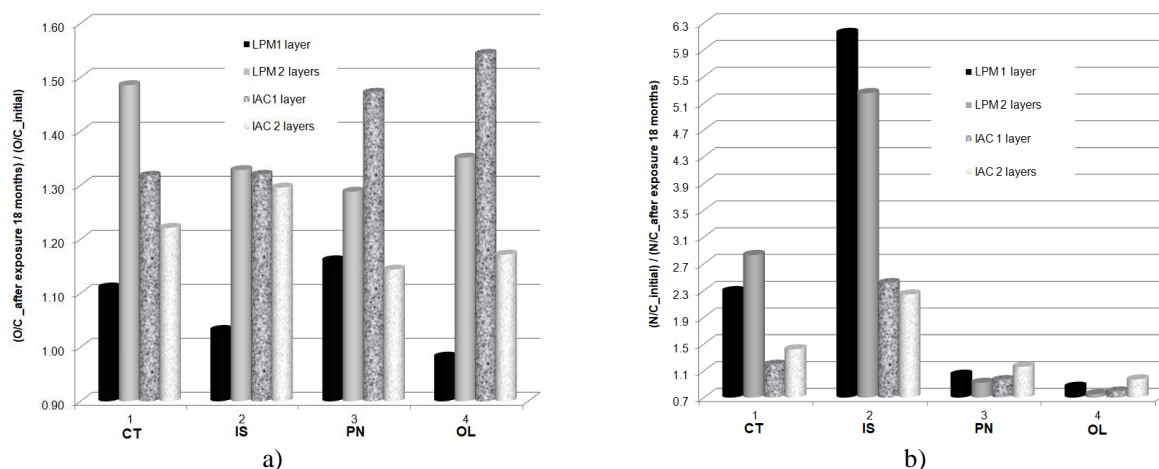


Fig. 1. Change in the O/C (a) and N/C (b) ratios after exposure in the four areas for 18 months

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# Rheological and dielectric properties of eco-composites of hydroxypropyl methylcellulose loaded with a bio-derived filler

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During the past years, an increasing tendency for research of novel materials with friendly impact on the environment was encouraged by companies and scientific communities (Barber et al., 2009). Consequently, chemically modified natural polymers loaded with bio-derived fillers were proved to be efficient alternatives that introduce benefits from economic and environmental point of view (Akter et al., 2022). This work is concerned with achievement of some eco-compatible materials obtained by mixing a cellulose derivative with oat powder. Different amounts of the employed bio-based filler are inserted in the hydroxypropyl methylcellulose solutions in water, which are subjected to magnetic stirring. Optical microscopy is used to examine the homogeneity of the samples. The flow behavior at variable shearing is investigated at room temperature to analyze the effect of the system composition on the sample deformation response. Oscillatory experiments performed on the obtained eco-composite solutions provide information on their viscoelastic properties. The variation of the elastic and viscous moduli with shear frequency helps to evaluate the strength of the interactions occurring in these systems. Also, a theoretical study of the dielectric properties of the filled materials is made. The assessed dielectric constant is slightly dependent on the amount of the incorporated bio-based filler. This investigation provides alternatives to produce eco-compatible materials with adequate performance for applications in electronics, particularly in the design of the biodegradable components for electric energy storage.

## Acknowledgement

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Akter, M., Uddin, M.H., Tania, I.S., *J. Reinf. Plast. Compos.* doi: 10.1177/07316844211070609 (2022).



## Textile wastewater color improvement on a spinning disc reactor

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The spinning disc (SD) technology has been successfully applied to a synthetic textile wastewater to remove its color (discoloration purpose). Preliminary data performed in a regular mixing system using a composite material, i.e. ZnAlLDH type layered double hydroxide, have not provided any significant decrease of the water color content. Thus, ZnAlLDH (4 g/L) was added to the synthetic water containing 50 mg/L Rosso Kemazol that was subsequently fed onto the spinning disc. The SD efficiency was investigated at three different water supplying flowrates 5.76, 6, 7.44 L/h) and four different disc rotational speeds (100, 250, 500 and 800 rpm). The best color removal of 44.39%, 41.14% and respectively of 42.7% were obtained at 6 L/h and 250 rpm, 6 L/h and 500 rpm and respectively, 5.76 L/min and 800 rpm, in only 50 minutes working time period. In case of the lowest color concentration and thus, at the lowest power consumption, a Fenton oxidation was performed for a more advanced color removal of 62.54% within 50 minutes time period. These results indicate that the spinning disc technology correlated with special materials can improve significantly the color index of a textile wastewater.

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# Modeling of excess molar volume for binary and ternary mixtures of benzyl alcohol, n-hexanol and water

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Benzyl alcohol and n-hexanol are part of the emerging pollutants category, which reach surface waters and negatively affect living organisms, as they are included in pharmaceuticals, food, but also in personal care products. The evaluation of interactions between components of mixtures involves the determination of thermodynamic properties, and in the absence of experimental data, precise predictive methods are required (Venkatramana et al, 2014; Agarwal and Sharma, 2021). In this study, the density for binary and ternary mixtures of benzyl alcohol, n-hexanol and water was determined experimentally in a composition range influenced by the miscibility of the components, four temperatures: 293.15, 303.15, 313.15 and 323.15 K and atmospheric pressure (0.1 MPa). The excess molar volume that was correlated with the composition, normalized temperature and refractive index was calculated, which is easily determined experimentally using a small amount of substance. The 108 data sets were mixed, then randomly divided into 93 for the training stage and 15 for the validation stage. To correlate the excess molar volume, neural models were built with one or two layers of hidden neurons. The best performance was obtained with the ANN neuronal model (4:8:4:1). Fig.s 1a and 1b compared the results obtained with this model and the experimental ones for the training and, respectively, validation stage. The standard deviation calculated in the training stage is  $\pm 0.0059$  cm<sup>3</sup>/mol, and in the validation stage  $\pm 0.0070$  cm<sup>3</sup>/mol. The results obtained with neural models were also compared with those provided by the regression algorithms: k-Nearest Neighbor, Random Forest, Support Vector Machines and Linear Regression.

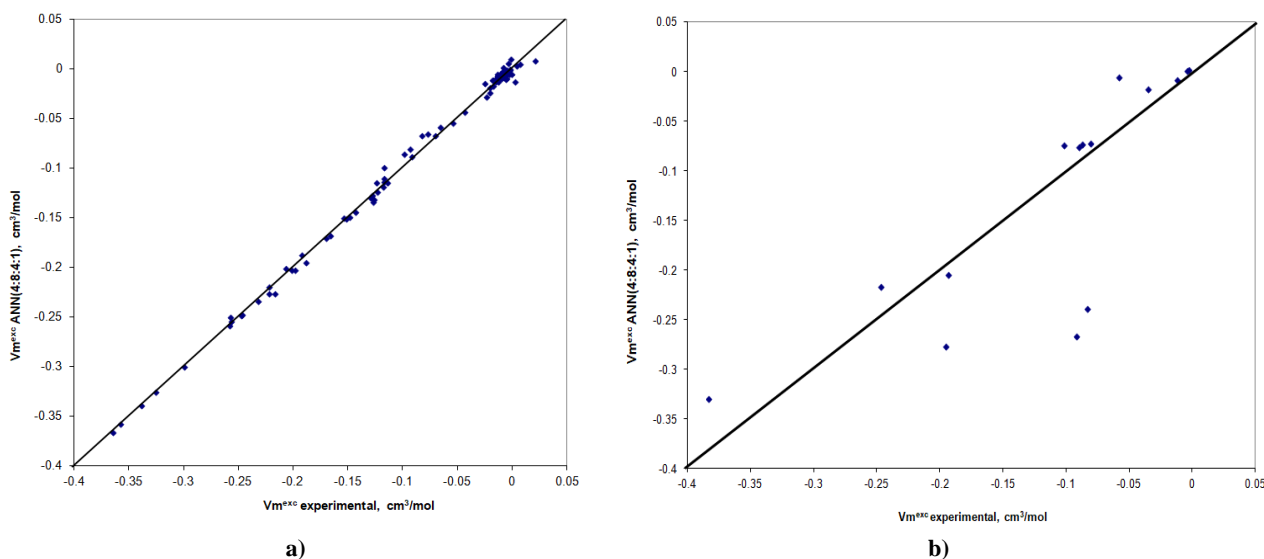


Fig. 1. Checking the RNA model (4:8:4:1) in the training stage a) and in the validation stage b)

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## Shear deformation response and refractive index of hydroxypropyl methylcellulose at variable temperatures

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Polymers arising from natural resources, such as cellulose, have drawn tremendous attention since they possess an interesting balance of properties, while they have the advantage that they do not harm the environment (Kulkarni et al., 2012). Chemically modified natural polymers display improved characteristics in terms of solubility, processability and optical performance (Zhang et al., 2009, Gray and Mu, 2015). This work deals with analysis of solution in water and N,N-dimethylformamide and solid phase properties of hydroxypropyl methylcellulose (HPMC). First, rheological experiments are performed to elucidate the deformation response of the HPMC solutions at a wide range of shear rates. The viscosity at a low shear rate is determined at several temperatures. Based on these data, the processability of the HPMC solutions into solid films is discussed. The solid phase experiments deal with examination of the morphology and the refractive index. Optical microscopy and atomic force microscopy (AFM) are used to discuss the surface features of the HPMC films obtained in these two solvents. The AFM data indicate that the surface roughness is affected by the nature of the solvent. The refractive index of the solid samples is measured at distinct temperatures. Starting from the thermo-optic effect, the volumetric thermal expansion coefficient is further evaluated. Such investigations are helpful for establishing the relation between solution processing and optical performance of transparent HPMC films application in optoelectronic devices.

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## Development of a new type of amphiphilic semiconducting polymer containing aniline and aniline-propanesulfonic acid

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Semiconducting polymers are a large class of polymer materials with increasing importance for organic electronic components. Among these, Polyaniline is one of the most exploited conducting polymers due to the attractive properties, such as ease of synthesizing, high electrical conductivity, on the order of 10 S/cm, thermal and environmental stability, stable redox activity (Chaudhari et al., 1997, Wang et al., 2016). However, the poor processability in solvents and especially in aqueous solvents, poor mechanical properties and low processability are the major drawbacks for the practical use of polyaniline.

In this work we improved the water solubility of polyaniline semiconductor by synthesis of a semiconducting copolymer based on polyaniline and a more polar polyaniline derivative, consisting of propyl sulfone moieties grafted onto the nitrogen atom. Due to different polarity between the two components, an additional property arises, namely amphiphilicity. Varying the ratio between the simple polyaniline and the polar polyaniline derivative components, a homologous series of multifunctional polymers of polyanilines are obtained, which combine both the amphiphilic and semiconducting properties.

The chemical structure of final compounds was determined by FTIR Spectroscopy and UV-Vis Spectroscopy. Interfacial activity of the amphiphilic polymers was investigated by measuring the surface tension with the pendant drop and contour shape analysis method. To further demonstrate the amphiphilic nature of the semiconductive polyaniline copolymers obtained and their interfacial activity, we performed the contact angle measurements. Finally, the electrical conductivity of homologous series was tested by dielectric spectroscopy. The latter technique was employed in two different manners: alternating current (ac) regime and direct current (dc) regime.

### Acknowledgments

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# Behavior of biocompatible alloys in physiological environments

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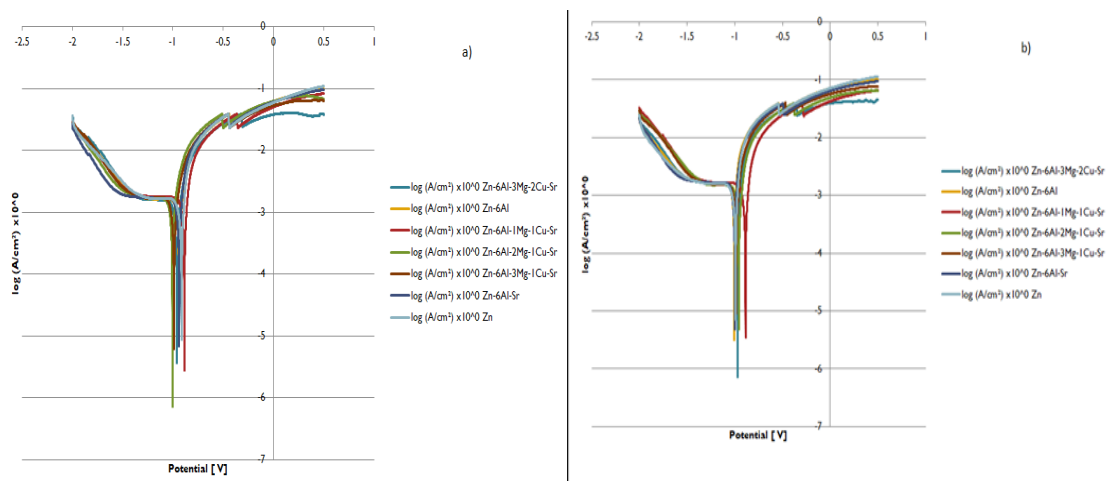
Zinc has been identified as one of the most promising biodegradable metals (Venezuela and Dargusch, 2019).

Zinc seems to address some of the basic problems of Mg and Fe, and it can successfully replace these two biodegradable metals. (Shaoa et al., 2022)

In this study, 7 Zn-based alloys were tested to determine their behavior in NaCl solution, at a solution pH of 6.5, but also in the presence of caffeine. Electrochemical tests took place in electrolytes with different concentrations of caffeine at room temperature.

For each electrochemical test to which the zinc (Zn) alloys were subjected, the following sequence was chosen:

- OCP for 1 hour
- Polarization of dynamic potential, the applied potential being in the range -500-2000 mV. The chosen scan speed was  $5\text{mV s}^{-1}$



**Fig. 1.** Potentiodynamic curves of Zinc-based biocompatible alloys in NaCl + caffeine solution: a) 0.25 mg / L caffeine and b) 0.5 mg / L caffeine

From the polarization curves of the samples immersed in NaCl solution and under the influence of the two caffeine concentrations, a similar behavior is observed for all 7 samples. In the presence of caffeine, the potentiodynamic curves show a peak around -0.5V and -0.3V of the applied potential.

A different behavior from the other samples is represented by the sample with the chemical composition Zn-6Al-3Mg-2Cu-Sr, which has biggest amount of copper, respectively 2.9%. This aspect gives a clear indication of the influence of the type of alloying element on the electrochemical behavior.

The corrosion parameters extracted from the polarization curves ( $E_{\text{cor}}$  and  $j_{\text{cor}}$ ), parameters that were determined by Tafel analysis of the anodic and cathodic branches of the polarization curves, indicate that the presence of caffeine inhibits the corrosion process by decreasing the corrosion current values ( $j_{\text{cor}}$ ). The corrosion potential ( $E_{\text{cor}}$ ) did not change significantly.

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## Copper(II) ions sorption on calcium phosphate adsorbents

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The applications of calcium phosphates depend largely on their properties. Calcium phosphate materials are commonly used in bone reconstruction, mostly in the field of dentistry and orthopaedic surgery (Jeong et al., 2019). In addition to medical applications, calcium phosphates have other implications in various fields, such as: phosphorous fertilizers or food supplements, but also as adsorbents. Among calcium phosphates, the most important representative is hydroxyapatite, with chemical formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . Many scientific studies have shown the adsorbent properties of hydroxyapatite in wastewater treatments (Bernalte et al., 2019; Brazdis et al., 2021). The aim of this study was to obtain a material with the highest hydroxyapatite content using raw sources of calcium and phosphorous, and verify its adsorption capacity of copper(II) ions. The hydroxyapatite powders with crystals smaller than 100 nm were synthesized by a wet precipitation method. The influence of the equilibration conditions on  $\text{Cu}^{2+}$  adsorption from aqueous solutions by uncalcined (HA-uc sample) and calcined (HA-c sample) hydroxyapatite nanopowders was investigated. The effect of some process parameters (solution pH, initial concentration of the adsorbate in solution, adsorbent doses, temperature, contact time) on the removal efficiency of Cu(II) was studied and discussed. The optimum adsorption was found to be at pH = 4.5 and 22 °C, with a  $\text{Cu}^{2+}$  removal rate of about 80.47 % and 90.23 % for the HA-uc and HA-c samples, respectively. The kinetic adsorption data were analyzed by pseudo-first order kinetic, pseudo-second order kinetic and intraparticle diffusion models, and the model with higher correlation coefficient ( $R^2$ ) was chosen. It was found that the pseudo-second order equation was better in describing the adsorption kinetics of  $\text{Cu}^{2+}$  on uncalcined and calcined hydroxyapatite nanopowders. In conclusion, we can say that the hydroxyapatite nanopowder has the potential to be a cost-effective adsorbent for the removal of  $\text{Cu}^{2+}$  ions from aqueous solutions due to the relatively low-cost of the starting materials and the optimized method used.

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## The structure of the soil microbial community and changes in its functionality in response to 2-chlorobiphenyl pollution

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Microorganisms are essential for a healthy soil ecosystem because they have primary functions in biogeochemical cycles and actively participate in the rotation of organic matter as well as in the formation and maintenance of soil structure and fertility. Consequently, changes in the microbial community structure or inhibition of its functions can alter the soil ecosystem. The biphenyl polychlorinated compounds can exert a persistent pressure on the microbial community. In the environment, biphenyl polychlorinated compounds are found as a mixture of chemical derivatives, which can affect both animal and plant organisms and human health. The primary factors affecting the biotransformation of PCBs are dependent on the number and position of chlorine substituents. PCBs have been found to be more resistant to biodegradation if the degree of chlorination is higher. In this study, the effects of 2 - chlorobiphenyl on the soil microbial community were investigated. Two experimental variants were performed, with and without added nutrients, both variants being contaminated with different concentrations (5; 10; 50 mg %) of 2-chlorobiphenyl. The interaction of soil microorganisms - PCB compound was monitored for 21 days, taking samples for analysis every 7 days. The results showed that the presence of 2 - chlorobiphenyl has a toxic effect on soil microorganisms even at a concentration of 5 mg%, reducing the number of individuals by about 50%. The number of microorganisms was reduced by approximately 85-99% at concentrations of 10-50 mg% 2-dichlorobiphenyl. The numerical decrease is both a function of the concentration of the toxic product and a function of the incubation period of the soil samples. Effect of 2 - chlorobiphenyl is more pronounced on fungi and yeasts, their number decreasing by about 50% compared to bacteria.

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# Investigations on the viscosity of L-alanine-based solutions for CO<sub>2</sub> absorption

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Because they are inexpensive and readily available, carbonate salts are frequently utilized for CO<sub>2</sub> absorption. Carbonate salts' delayed reactivity with CO<sub>2</sub> at low temperatures and low partial pressure is their main drawback. It is believed that a number of promoters increase how quickly carbonated salts are absorbed. Due to its resemblance to CO<sub>2</sub> binding by proteins like hemoglobin, carbon dioxide uptake using amino acids is a biomimetic method of CO<sub>2</sub> capture (Majchrowicz et al., 2014). Although more expensive than alkanolamines, amino acid salt solutions are desirable solvents due to their benefits. Amino acid salt solutions differ from amine solutions in that they have lower vapor pressures and are more resistant to oxidative deterioration (Sang Sefidi și Luis, 2019). Amino acids are additionally found in nature and are thought to be environmentally benign. In order to build and implement an efficient and cost-effective method, a carbon dioxide capture absorbent based on 25 % K<sub>2</sub>CO<sub>3</sub> and potassium salt of L-alanine (KAla) was developed, and laboratory tests were conducted to ascertain the absorbent's viscosity values.

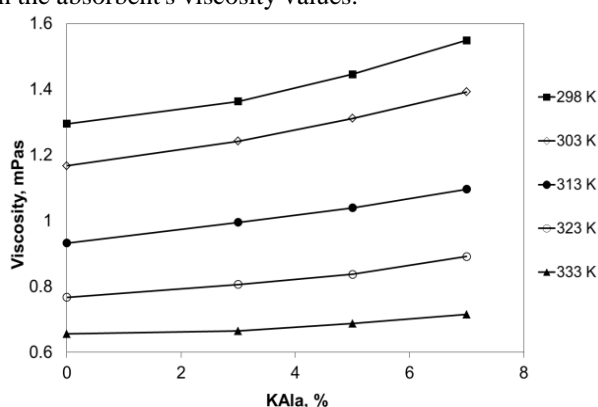


Fig. 1. Variation of viscosity of K<sub>2</sub>CO<sub>3</sub>-KAla based solutions with KAla concentration, at constant temperature

The viscosity was predicted statistically as a function of temperature and the amount of ALA supplied. Regression analysis was the main emphasis of the employed technique, which was carried out using MINITAB 21. The goal was to choose the model that best matches the data and to create the ideal conditions that minimize viscosity. The general statistics of the three procedures used (stepwise (1), forward selection (2), and backward elimination (3)) for the process under consideration are shown in Table 1 for an order 2 model with interactions through order 2 complete cross predictors, and 10-fold cross-validation.

Table 1. Statistics for the obtained models

	S	R-sq	R-sq(adj)	PRESS	R-sq(pred)	AICc	BIC	10-fold S	10-fold R-sq
(1)	0.0084766	99.94%	99.91%	0.0025366	99.83%	-108.28	-117.32	0.0112966	99.83%
(2)	0.0081073	99.95%	99.91%	0.0023666	99.84%	-103.35	-117.84	0.0112262	99.83%
(3)	0.0084766	99.94%	99.91%	0.0025366	99.83%	-108.28	-117.32	0.0112966	99.83%

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# Producing nanofibrillated cellulose-based oleogels for sustainable and ecofriendly lubrication

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Eco-lubricants are being actively demanded by today's industries with the aims of producing in a more sustainable manner and reaching net zero emissions in the near future. A widely-known way of producing more environmentally friendly lubricating greases is to replace the traditional mineral oils with renewable raw materials such as vegetable oils (Almasi, 2021). Even so, the greatest challenge that industries and research centers are facing today is the identification of suited substitutes for the hazardous chemicals traditionally used as thickening agents.

In this context, a prospective novel technique used to prepare totally sustainable lubricating greases formulated with cellulose nanofibers, from elm pulp, and castor oil is reported (Fig. 1). With this aim, a 2, 2, 6, 6 -tetramethylpiperidine - 1-oxyl radical (TEMPO) - oxidized cellulose nanofibril sample and another two cellulose nanofibril samples obtained by PFI mill refining, either bleached or non-bleached, were used. Oleogels were prepared by their dispersion in castor oil, at concentrations up to 2.8 wt.%. The nanofibers were initially supplied as hydrogels with a solid content near to 2 wt.%, which is required to keep their adequate use, handling and storage. The greatest challenge was to totally remove the amount of water retained by the nanofibers during their production. For this, a sustainable methanol-based solvent exchange method was developed and optimized. It was demonstrated that the methanol molecule may properly display the water molecule away from the cellulose nanofibrils (Roman et al., 2021). Widespread techniques such as lyophilization or drying seems to provide unsuccessful results mainly because they yield nanofibers aggregation due to their high specific surface area and their ability to interact among them. In this way, by successive methanol washes the water was efficiently displaced away from the cellulose nanofibrils. Then the methanol-wetted nanofibrillated celluloses were directly introduced in base oil. Subsequently, the residual methanol was vacuum-assisted removed. Finally, highly homogeneous and storage-stable oleogels based on elm wood cellulose nanofibers and castor oil were obtained. The nanofibrillated celluloses exhibited a remarkable thickening effect in castor oil. Hydrogen-bonding interactions between the polar hydroxyl (OH) groups in the glucose units of cellulose and those in the ricinoleic fatty acid of castor oil, and among cellulose nanofibers, is the principal factor that led to the formation of a gel-like structure.

This work explores a potential alternative to produce nanocellulose-based eco-lubricating greases, where both the materials used and production method involved are ecologically sound.

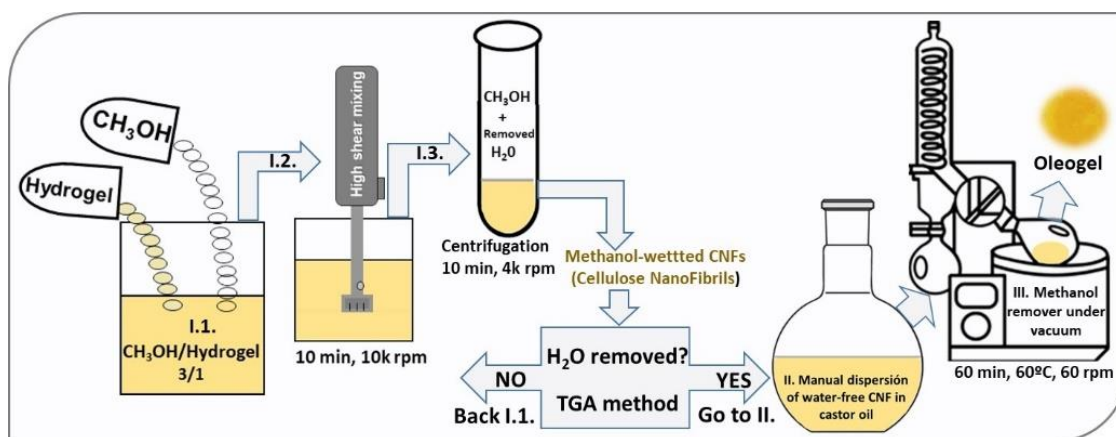


Fig. 1. Schematic illustration of the experimental protocol

## Acknowledgments

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# Copolyimides based on aromatic-aliphatic moieties as materials for energy-storage applications

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Polyimide is a widely-used polymeric material in high performance engineering applications due to its outstanding properties including high mechanical strength, good electrical insulation, high thermal stability, and excellent chemical resistance (Liaw et al, 2012; Ho and Schroeder, 2020; Butnaru et al, 2021). The demand for high energy density capacitors is based on its indispensable importance in various applications, such as hybrid electric vehicles, high energy lasers, electromagnetic railguns, and proposed systems for inertial confinement fusion (Ma et al 2014). In order to be used as reliable power sources, energy-storage devices have to provide stable and persistent electricity output, to maintain adequate performances under various deformations such as bending, twisting and stretching.

Meanwhile, the strive towards polymer film capacitors for high temperature applications is a continuous challenge due to a series of requirement such as good processability, high dielectric permittivity, thermal conductivity and dielectric breakdown strength, as well as self-clearing capability. When an additional criterion of high-power performance is imposed, the materials used in capacitor dielectrics may fall short in achieving the overall properties. The energy density of a capacitor is determined by its dielectric material which stores energy electrostatically through polarization. Polymer-film capacitors are attractive for these applications due to low cost, high dielectric strength, low dielectric loss, and graceful failure (Wang et al, 2010). The current state-of-the-art polymer dielectric film, biaxially oriented polypropylene has a relatively low dielectric constant and suffers from a low upper operating temperature of 85°C due to the increase of electronic conduction at higher temperatures. For a linear dielectric polymer, the energy density is calculated based on the value of dielectric constant and the square of the electric field, which is limited by breakdown strength. Thus, new dielectric materials are required which must possess higher dielectric constants and thermal stability, maintaining in the same time low loss and high breakdown strength. Highly thermostable polymers containing polar units are appropriate to this aim, being attractive for the next generation of dielectrics. Therefore, understanding the structure-property relationship is essential to tailor the targeted dielectric and thermal properties.

Here we focus on a series of high-k copolyimides designed to be used in thin film capacitors for energy storage applications. The polymers were obtained by classical polycondensation reaction between an aromatic dianhydride, an aliphatic diamine and an aromatic diamine incorporating nitrile groups. Beside their structural characterization, an elaborate study is presented with regard to their physico-chemical properties with emphasis on the effect of the position of nitrile group from the structural unit on the overall polyimide behavior.

## Acknowledgments

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## Hybrid plasmonic using layered double hydroxides matrices for activating solar-active photocatalysis

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Heterostructures composed of joined semiconductors and metal plasmonic nanoparticles (MeNP: Au or Cu) display increase solar-light harvesting efficiency that is derived from the synergistic interactions between the components (Carja 2017). The key innovative approach of this work is to use plasmonic energy as input to develop plasmonic MeNP heterostructured with layered matrices of layered double hydroxides (LDH) as novel catalytic systems, able to efficiently-drive the photochemical processes under solar-light irradiation. More precisely, we present here the design, synthesis and properties of Zn/CoLDH and metals nanoparticles (Au/Cu) hybrid structures. The photocatalytic efficiencies of the new photocatalysts are tested to remove toxic organic compounds (e.g: 2-4 nitrophenol) from the aqueous solutions, by using solar-light energy. This work may have a transformative impact on the way we might drive novel optical technologies using light energy for powering the transition to a safe and sustainable society. In conclusion, we established here fast, facile and cost-effective procedures to design efficient plasmonic responsive MeNP/LDH photocatalysts based on noble (Au, Cu) plasmonic nanoparticles and Zn-rich-LDH matrices and their use as efficient systems in solar-active photocatalysis.

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# Polymer composite electrolytes for high-performance lithium batteries

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Polymer electrolytes have received substantial attention in the effort to revive high-energy-density Li-based batteries. In order to increase the capacity of Li-based batteries, researchers have largely focused on new electrode materials: regarding cathodes, Li–air and Li–sulfur batteries represent leading frontier candidates while at anode, Li-metal can replace graphite to increase anode energy density by approximately tenfold. Anyway, electrode advancements require an enabling electrolyte to combat irreversible reactions and dendrite growth during long-term charge/discharge cycling. In order to avoid these issues, solid-state polymer electrolytes should not only provide mechanical stiffness to block dendrites, but also should deliver safer (thermal stability without the leakage, flammability or volatility) operation compared to liquid electrolytes. Ionic liquid gel polymer electrolytes, made by immobilizing Li-salts dissolved in ionic liquids in a polymer matrix or polymerized ionic liquids have received increasing attention due to their potential applications in electrochemical devices. However, because of the trade-off between mechanical properties and ionic conductivity, the preparation of ionic liquid gel polymer electrolytes with both high ionic conductivity and robust mechanical properties remains challenging. In order to achieve high ionic conductivities in these systems, researchers have concentrated in synthesis polymerized ionic liquids with lower glass transition temperatures; unfortunately, the higher ionic conductivity was achieved in detriment of mechanical properties. We have recently developed a class of solid electrolytes, termed polymeric ionic composites (PIC), composed of Li-salt dissolved in ionic liquids (IL) and a rigid-rod polyelectrolyte, poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT). PIC materials, obtained through an ion-exchange process between IL and PBDT aqueous solution, possess an unprecedented combination of high ionic conductivity (>3 S/cm @RT), high thermal stability, low flammability, and widely tunable tensile storage moduli. This PIC material fabrication platform shows promise for safe and high-energy-density energy storage and conversion applications, incorporating the fast transport of ceramic-like conductors with the superior flexibility of polymer. Additionally, the electrochemical performance of a novel highly efficient electrode/electrolyte system based on mesostructured composite anode (Si, Ge, TiO<sub>2</sub>/SBA-15) and single-ion conducting polymer electrolyte will also be discussed.

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## Enhancement of hydrophobicity of xylan hemicellulose by chemical modification with alkyl ketene dimer

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Xylan is a major type of hemicellulose that has attracted many research and development activities for large area of applications such as in biofuels, platform chemicals, and materials. Producing packaging materials is a potential high-value application of the xylan hemicelluloses. Nevertheless, being high hydrophilic, in native state xylan hemicellulose has poor barrier properties when it is used in packaging applications. To improve the strength and performance for packaging and coating applications, xylan has often been modified with hydrophobic moieties. The esterification is among the most frequently used method for chemical modification of xylan and there are many publications on acetylated xylan. Recent research reports the reaction of alkyl ketene dimer (AKD) with different types of polysaccharides, e.g., microcrystalline and microfibrillated cellulose [1-3], bacterial and nanocellulose [4-6], carboxymethyl and hydroxyethyl cellulose [7,8], starch [9], and cashew gum [10]. In this context it is of high interest to study the reaction of xylan hemicellulose with a ketene dimer, also.

In this paper was analysed the effect of alkyl ketene dimer on the improving of xylan hydrophobicity in coatings for packaging papers and edible films. The coatings with xylan hemicellulose and different amounts of AKD (0,2%, 0,5%, 1%, 1,5%) were applied on paper surface in a single layer using Mayer rod laboratory system. The samples of coated papers were dried for 10 min in air at laboratory temperature and in oven at 60°C. To complete the reaction of AKD with xylan hemicellulose, the coated paper samples were hot pressed at 110 -120°C after oven drying. The obtained results emphasized that the improvement effect is significant for the oil and water absorption as well as for water vapour barrier properties at 1.0% quantity of AKD in coating formulation. A slightly increased for the mechanical properties was registered, also. To strengthen these results and to settling the optimum parameters of xylan-AKD reaction, the continuous films of xylan with 1.0% and 1,5% AKD were prepared and dried at 60°C, 80°C and 110°C. To enhance the flexibility of films, glycerol was used as plasticizer. The films were evaluated regarding the water barrier properties (water absorption and solubility) and functional groups. The FT-IR analyses highlighted the presence of keto esters functional groups with effect on the improving of barrier properties of films and coated papers. In summary, these improved properties of the resulting AKD-modified xylan hemicellulose expand the applications of hemicelluloses biopolymers in the food packaging area.

### Acknowledgments

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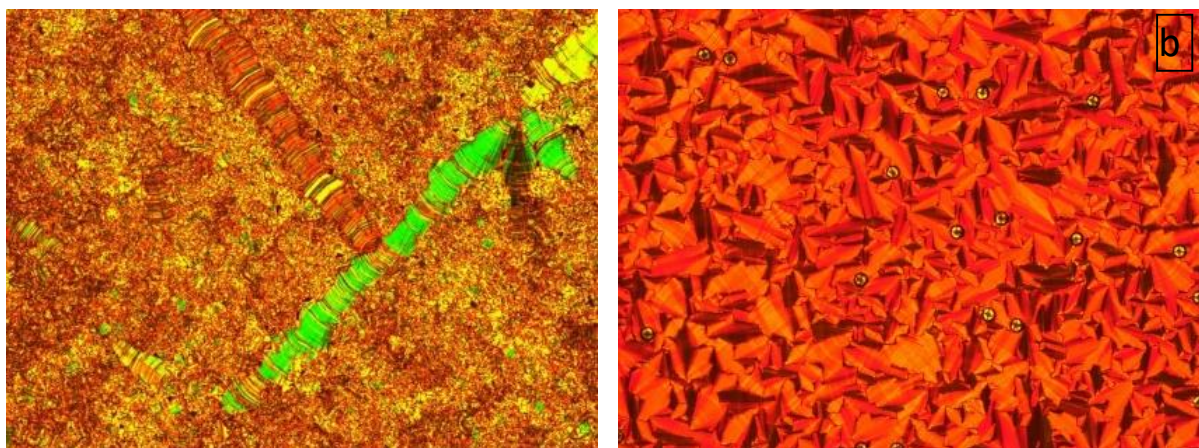
## New ferroelectric materials with fluoro-substituted bent shape molecules

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Since the discovery of chirality and polar order in bent core mesogens with achiral molecules, bent-core liquid crystals have become exciting materials of interest for materials science. Indeed, their importance lies not only in understanding the fundamental principles of self-assembly in soft matter, but also in practical applications such as nonlinear optics (Etxebarria et al., 2008), sensors (Iglesias et al., 2012) and fast-switching electro-optic devices (Nagaraj et al., 2010). However, the desired electro-optical properties are closely related to the structure of the bent core molecules. To obtain ferroelectric materials with high spontaneous polarization, we synthesized some resorcinol derivatives with the following structural characteristics: multiple conjugated double bonds as azo, imino or ester polar linking groups and fluoro-substituted benzene cores, to increase the molecular dipole moment and temperature range of mesophase domains. The structure of the intermediate compounds and Schiff Base derivatives was confirmed by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra. The liquid-crystalline properties were investigated by Differential Scanning Calorimetry (DSC) and Polarized Optical Microscopy (POM), while the electro-optical measurements were carried out in commercial planar cells (instec), in triangular AC and DC electric field. The synthesized compounds exhibited outstanding electro-optical properties as switching between ferroelectric polar order and antiferroelectric order with and without triangular wave field, a characteristic behavior for B2 phase. A high polarizability of 500–600 nC/cm<sup>2</sup> has been measured for these new materials, making them suitable materials for electro caloric applications or ferroelectric devices.



**Fig. 1.** POM photomicrographs for compound NCF12 in commercial planar cells (instec), 20 $\mu$ m thickness at a) without electric field, antiferroelectric polar order b) 5V triangular wave field 60Hz, ferroelectric polar order.

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# Unique physicochemical properties of gold nanoparticles/layered double hydroxides heterostructures facilitating the controlled release of nanogold

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Nanosized gold has size-dependent optical and photothermal properties that are of high interest for applications in targeted cancer detection and thermo-therapy. The stability and controlled delivery of gold nanoparticles are key-variables in tailoring nanogold controlled release for biomedical applications.

We present here nanoparticles of gold heterostructured with hydrotalcite-like anionic clay matrices (Au/LDHs) as new nanoarchitectures able to incorporate, storage and controlled release nanoparticles of gold. Layered double hydroxides (LDH) are a class of 2-D layered materials. They have attracted great attention in many technological important fields, such as nanomedicine and nanotechnology, due to their interesting properties in anion exchangeability, adsorption flexibility and biocompatibility (Grosu 2022). The fabrication of Au/LDH heterostructures are based on the formation of nanoparticles of gold directly on the matrix of the LDH during the structural reconstruction process of the layered clay matrix. Powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscopy (TEM) and UV-Vis spectrometry (UV-Vis) measurements were used to investigate the structure, morphology and size-dependent optical features of the gold-clay assemblies. Results show that the plasmonic characteristics and nanogold controlled release is a function of the composition and characteristics of the LDH. The results presented herein provide an attractive strategy to control the release of nanogold from the biocompatible matrices of the LDH for future applications in nanomedicine.

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## Preparation and characterization of alginate/LDH nanocomposite and investigation of its adsorption performance for phosphate ions

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Although phosphorus is an essential nutrient in aquatic environments, an excessive concentration of this nutrient in water is the cause of eutrophication in lakes and reservoirs. In the present study, LDH based on magnesium and aluminum nanomaterial and alginate/LDH nanocomposite were prepared by coprecipitation method and characterized by transmission electron microscope, Fourier transform infrared spectrometer, and x-ray diffraction. Effects of different factors, including initial solution pH, agitation time, temperature and adsorbate concentration, on adsorption capacity of alginate/LDH for phosphate ions were also investigated.

The result shows that the alginate/LDH nanocomposite has a higher adsorption capacity and reaches equilibrium in a short time in comparison with raw LDH. Therefore, the nanocomposite can be effectively used as an adsorbent for the removal of phosphate ions from wastewaters.

# Cyto- and hemocompatible nanoparticles based chitosan grafted poly (ethylene glycol) methyl ether acrylate as a novel drug delivery system

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Chitosan (CS) crosslinking has been widely investigated, however, the chemical reactions leading to the formation of nanoparticles (NPs) pose problems due to various physical/chemical interactions which lead to the limitation of CS processability. This study employs the chemical modification of CS through Michael's addition of poly (ethylene glycol) methyl ether acrylate (PEGA) to the CS amine groups [1] to further prepare nanoparticle-based modified CS. Thus, modified CS was subjected to a double crosslinking reaction, ionic and covalent, in a water/oil emulsion [2]. The studied process parameters are polymer concentration, stirring speed, and quantity of ionic crosslinker (Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>), (table 1). The NPs were structurally, and morphologically (Fig. 1) characterized through FT-IR spectroscopy, SEM, light scattering granulometry, and zeta potential, showing that modified CS allows better control of dimensional properties and morphology as compared with neat CS. Swelling properties were studied in acidic and neutral pH conditions, showing that pH-dependent behavior was maintained after grafting and double crosslinking. The applicability of NPs were further tested for drug loading and *in vitro* delivery of levofloxacin (LEV), showing excellent capacity. NPs were found to be cyto- and hemocompatible demonstrating their potential for effective use as a controlled release system for different biomedical applications.

Table 1. NPs—preparation parameters and size measurements.

Sample Code	Polymer Solution Conc., %	Molar Ratio NH <sub>2</sub> / Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub>	Speed, Rpm	Water Phase, ml	The Organic Phase, mL	Surfactants Conc., %	Ionic Crosslinking Time, min	Yields %	Average Diameter (LD), μm	Potential Zeta (mV)
A1	0.5	1:05	5000	50	200	2	60	32	Aggregates	-
A2	0.5	1:1	5000	50	200	2	60	41	Aggregates	-
A3	0.5	1:2	5000	50	200	2	20	36	Aggregates	-
A4	0.5	1:2	5000	50	200	2	40	44	Aggregates	-
A5	0.5	1:2	5000	50	200	2	60	79	3.548	15.4 ± 0.2
A6	0.5	1:2	9000	50	200	2	60	80	3.263	15.2 ± 0.1
A7	0.5	1:2	12000	50	200	2	60	76	0.708	14.9 ± 0.2
A8	0.5	1:2	15000	50	200	2	60	78	0.562	14.8 ± 0.2
A9	0.35	1:2	15000	50	200	2	60	56	0.089	11.9 ± 0.2
A10	0.5	1:3	15000	50	200	2	60	59	0.141	15.5 ± 0.1
A11	0.75	1:2	15000	50	200	2	60	51	0.730	15.8 ± 0.1

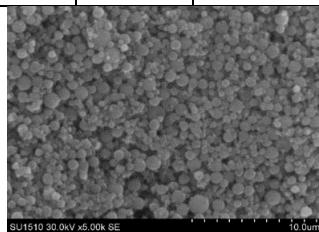


Fig. 1. Micrographs SEM of NPs (sample A9, magnification graphical bar length:10 μm)

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# Comparison between oxygen and steam gasification agents for liquid waste valorization process

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Plasma gasification of the used and mixed lubricating oils has a great potential for green fuel production (Agavriiloaie and Harja, 2022; Gaber et al., 2019). The specific conditions and the energy efficiency, however, must be carefully calculated for a better understanding of the process and a good technological process design. Different oxidizing agents can be used for two different of syngas utilization – fuel or raw material for chemical synthesis. This paper studies the partial oxidation of n-pentadecane, the main chemical compound from used oils, with different oxidizing agents, O<sub>2</sub>, steam, at various temperatures and debits. For the assessment of the process evolution, the H<sub>2</sub>:CO ratio, measured in the resulting gas, was compared. Fig. 1 presents the process diagram for pentadecane gasification at 900°C and 3 atm, that was used for process simulation.

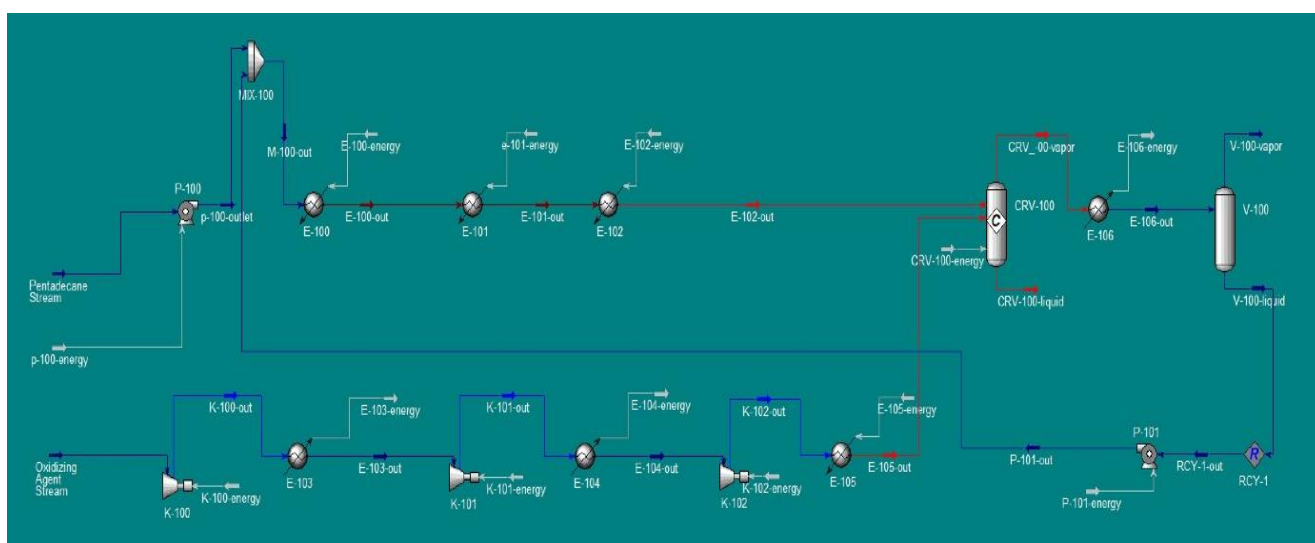


Fig. 1. Process design for waste oil gasification

The results showed that temperature and the steam/oxygen debit in the system have direct influence over the H<sub>2</sub>:CO ratio, in the gasification of waste oil. The ratio is greater in 900-1200 °C temperature range, in accord with literature (Raza et al., 2021). On the other hand, was observed that the steam present in the system has to be adjusted in the process for a maximized syngas (H<sub>2</sub>+CO) production and minimized CO<sub>2</sub> content in the reaction products. The obtained results permit establishing of temperature, type of oxidizing agent and its debit for obtaining the imposed H<sub>2</sub>:CO ratio.

## Acknowledgments

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## Removal of tetracycline from waste water using zinc-based photocatalytic materials

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Although tetracycline-based antibiotics come from the first generations of antibiotics, they are part of the essential medicines and are used both for human and veterinary treatment (as medicine or as additives in animal feeding). They are considered to have low toxicity, but they are also very widespread. The low cost and their versatile properties make them among the most widely used drugs, leading to the release of significant amounts into the environment with harmful effects on marine or terrestrial fauna (by promoting the development of antibiotic-resistant genes and bacteria). TCs are ubiquitously detected in wastewater and the aquatic environment because they are not completely metabolized in organisms, are difficult to degrade, have high hydrophilicity and low volatility. The demand for tetracycline (Chlortetracycline) is expanding. Currently, there are several methods for removing TC from wastewater, based on adsorption, photolysis, photocatalysis or bioremediation processes. In this study, the photocatalytic properties were evaluated for a series of zinc-based materials (ZnS, ZnO, ZnO-ZnS mixture, at different pH values and for different doses of photocatalytic material: 25mg/L, 40mg/L and 60mg/L).

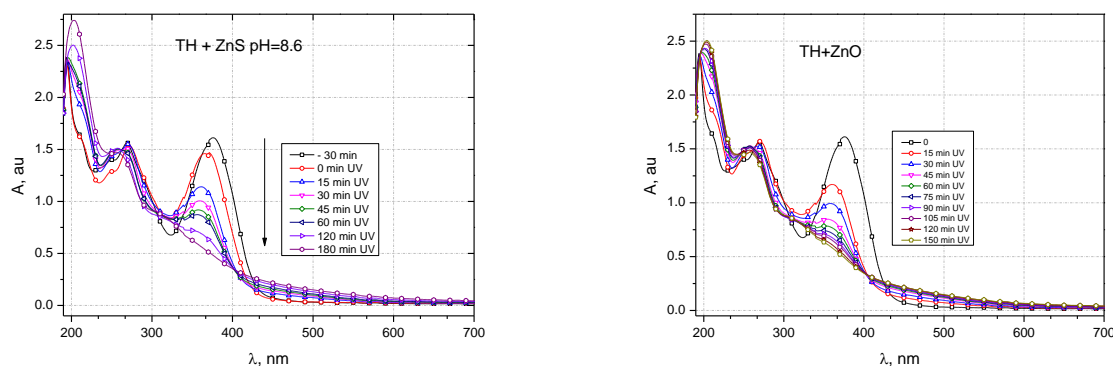


Fig. 1. UV-Vis in time evolution spectra for TH +ZnS and TH+ZnO

The photocatalytic materials were synthesized and characterized in the laboratory. By varying the reaction conditions (irradiation time, nature and concentration of the catalyst) to obtain an optimal degradation time, and analysing the obtained results, it is concluded that zinc-based materials can be successfully used to degrade this type of antibiotics.

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# Synthesis and photodegradation activities of mixed oxides under UV-A irradiation for water treatment applications

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In the recent years, water pollution with pharmaceutical compounds has become a major concern among scientists due to their harmful effect on the aquatic system (Sescu et al., 2020). Conventional wastewater treatments are not always effective to completely remove this type of pollutants. Therefore, there is an increasing need to develop new and eco-friendly technologies for water purification. In this respect, advanced oxidation processes, especially heterogeneous photocatalysis, have been applied as an alternative method. Photocatalysis is a simple and harmless process based on the use of a semiconductor material capable of generating highly reactive species, such as hydroxyl radicals, when irradiated with UV light.

In this work, the coprecipitation method was considered for the synthesis of zinc and lanthanum mixed oxides in alkaline medium. The metal precursor solution was obtained by dissolving zinc nitrate and lanthanum acetate to obtain a 0.5 mol/L metals concentration. Afterwards, the mixture was then added dropwise in a beaker, under magnetic stirring, at a flow rate of 10 mL/min while a solution of NaOH (1M) was slowly added in order to maintain the pH value at 10. After the complete addition of the reactants, the mixture was kept under stirring for 30 min followed by heating (100°C) on an oil bath and then vigorously stirred (750 rpm) for 24h. The mixture was cooled at room temperature and centrifuged for 10 min at 4000 rpm, washed with distilled water and then dried at 60°C. The product was split in half and calcined at 400°C for 4h. The as obtained samples were characterized by BET, SEM, UV-DR and IR spectroscopy. Their photocatalytic activity was tested in the degradation of clofibric acid (CA), a common pharmaceutical product used as a blood lipid regulator (Janani et al., 2022). The residual concentration of CA was determined by HPLC analysis and its mineralization was evaluated by TOC measurements. Preliminary tests have shown that for the calcined sample (Zn4La\_400), a degradation yield of 97% was obtained, while the uncalcined sample removed only 80% of the pollutant. Further tests have shown that after 60 min of irradiation in the presence of Zn4La\_400, the CA is completely removed at an initial pollutant concentration of 3 mg/L. On the contrary, over 80% degradation is achieved after 180 min of reaction for an initial concentration of 50 mg/L. Additionally, the photocatalyst performance was also evaluated by its reusability.

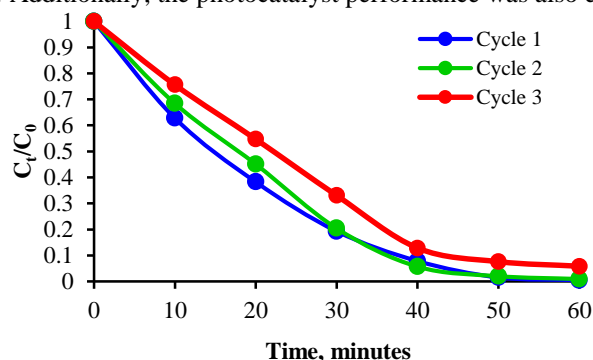


Fig. 1. Recycling performance of Zn4La\_400 against CA removal

As shown in Fig. 1, the performance of the photocatalyst remains remarkable after three cycles of photocatalytic tests. In the first two cycles, CA is completely removed after 60 min, while in the third cycle only a 6% loss of activity was observed.

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## Advanced recovery of valuable metals from e-Waste

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Both positive and negative effects of industrial growth have been noted. However, some of these flaws have been addressed by individuals. Recycling can thus significantly lessen the negative effects of pollution, provided that it is considered an alternative to "conventional" waste disposal that results in material savings and lower greenhouse gas emissions. Recycling also reduces the amount of energy required to produce new materials and objects from waste (Apostolescu et al., 2022).

The point of the research is to recover precious metals from electrical and electronic waste and to do so by obtaining new substances or other products. Although it is already possible to recover valuable metals, this research is focused on using thiosulphate to recover copper from electrical and electronic waste. Thiosulfate leaching is an attractive approach, greener substitute for cyanide leaching in the recovery of copper. To prevent thiosulphate decomposition in the presence of oxygen as an oxidizing agent, it is often carried out in alkaline conditions. After the copper has been collected, it will be poured into a copper sulphate solution to allow for further recovery.

The hydrometallurgical method has traditionally been used to extract valuable metals from mineral ores. These procedures have been used to recover metals from solid E-waste by selectively dissolving the desired metals using acid or caustic leaching. The targeted metal and a few contaminants are then concentrated using solvent extraction, adsorption, or ion exchange techniques after the solution has been further purified (Cui and Zhang 2008). Finally, the solid metals from the E-waste are recovered in whole via electrorefining or electrochemical reduction operations (Ashiq et al., 2019).

For the recovery of metals from WEEE at all concentrations, hydrometallurgy is a potential method.

The entire process is indicated in Fig. 1, which includes the steps of leaching, solvent extraction, ion exchange, adsorption, and electrodeposition.

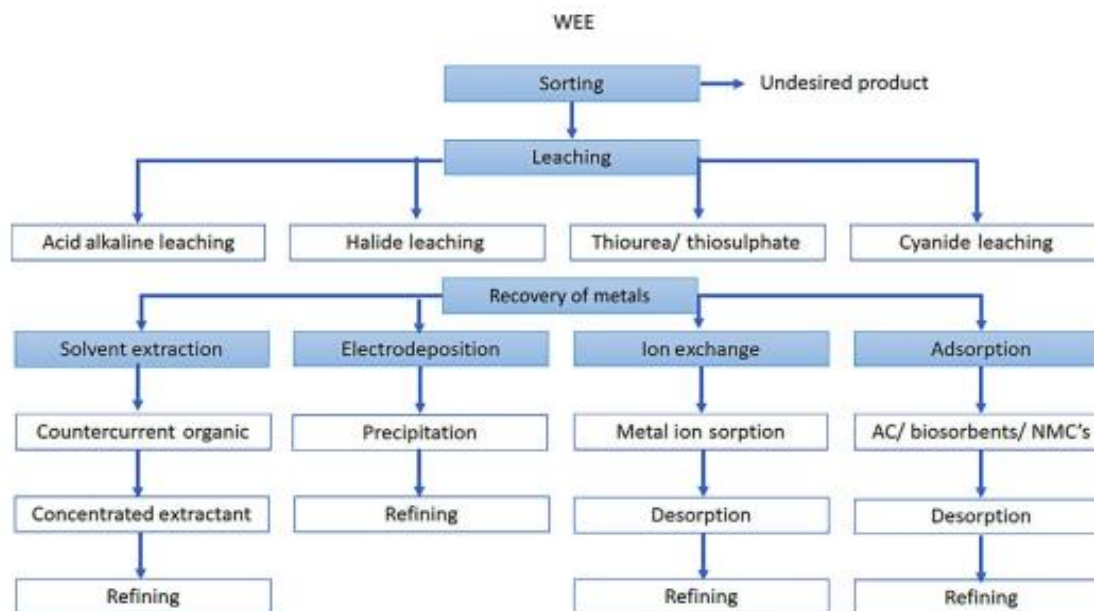


Fig. 1. Scheme of E-waste recovery (Ashiq et al., 2019)

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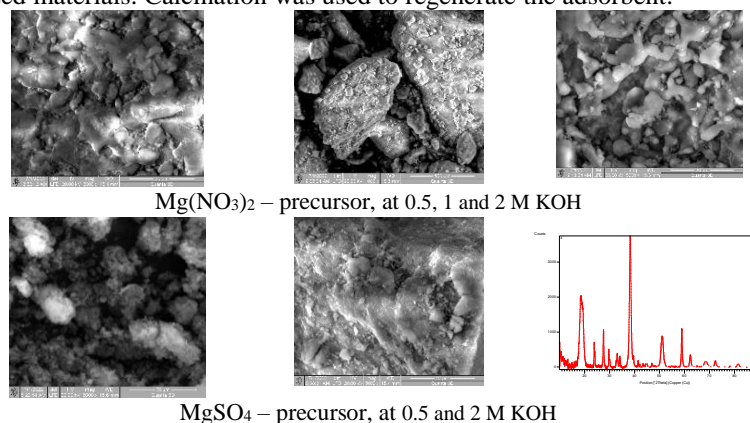
# Synthesis of magnesium hydroxide adsorbent for Congo Red dye adsorption

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The increased usage of organic compounds (dyes or drugs) in pharmaceuticals, cosmetics, personal care products, textiles, printing, plastics, and other sectors causes serious environmental problems when they are released as effluents. As a result, developing ways for removing colors from polluted waters is crucial (Sescu et al. 2020). Some of the most often used procedures are photocatalysis, adsorption, and coagulation (Lutic et al., 2022). Adsorption is the most achievable strategy for polluted waters treatment, because of its effortlessness and cheap operating costs, high efficiency, low energy consumption, etc. As a result, enhancing the adsorption process demands the development of efficient adsorbents (Dalvand et al., 2020). The removal of organic compounds has been researched using activated carbon, clays, zeolites, metal oxides, and hydroxides; though, some of these adsorbents have drawbacks such as limited adsorption capacity, high cost, or ineffective reprocessing. Since of their numerous uses as adsorbents and/or catalysts, metal oxides have been extensively researched (Cui et al., 2022), from this magnesium oxide is the most interesting of the group because it's cheap, stable, non-toxic, and ecologically friendly. Magnesium adsorbents have drawn a lot of interest for removing organic compounds due to their large surface area, low cost, low human and environmental toxicity, etc. The use of magnesium hydroxide was studied in this study; it is possible to synthesize more types of Mg(OH)<sub>2</sub> function of precursors and/or synthesis conditions. Magnesium hydroxide was made by chemical precipitation from 0.1 M solutions of magnesium nitrate and magnesium sulphate, as well as potassium hydroxide concentrations of 0.5, 1, 1.5, and 2 M. SEM, XRD, EDAX, particle size distribution, were used to examine the characteristics of materials as a function of molarity and alkali excess. Magnesium hydroxide has different morphologies and particle sizes, function of synthesis conditions (Fig. 1). Mg(OH)<sub>2</sub> nanoparticles are used to remove organic molecules such as Congo red (CR). At 20 °C, the adsorption removal of the synthesized sample might be as high as 94.5%. Congo Red sorption followed the Langmuir adsorption model on the as-synthesized materials. Calcination was used to regenerate the adsorbent.



**Fig. 1.** Synthesized materials morphology and XRD

## Acknowledgments

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# Gas separation membranes obtained from hexafluoroisopropylidene-containing polyimide blends

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Aromatic polyimides are among the most attractive materials for gas separation membranes owing to their excellent balance of thermal, mechanical, chemical and electrical properties (Liaw et al, 2012). The main drawback for their application at large scale arises from the low permeability, although they possess high selectivity for most gas pairs of industrial interest, thus limiting their application in small and medium scale gas separation operations (Sulub-Sulub et al, 2018). The challenges associated with the use of membranes in gas separation processes relates to the limitation of membrane separation performance in terms of the trade-off between gas permeability and selectivity of most polymeric membranes, poor membrane stability and short lifetime when exposed to a gas stream that incorporates acid gases impurities, besides an unsatisfactory resistance to plasticization. Through blending, materials may exhibit new characteristics, different from the pristine materials. A method to improve plasticization resistance may consist in blending membranes which have an easy plasticization feature with anti-plasticized membrane materials. Moreover, blending one relatively cheap polymer component with another one which is more expensive can reduce the capital cost. Addressing the above advantages, blending can be exploited to tailor the performance of the original single membrane (Zhang et al, 2019). Facilitated transport of a specific gas can be accomplished by tuning the blend compositions and the subsequent morphologies which are formed by blending. Usually, a phase-separated blend is necessary for a better transport of species, while miscible blends are more appropriate for increasing the gas selectivity. During the mixing process of immiscible blends, a polymer free volume expansion takes place which provides increased gas permeation rates. Conversely, a miscible polymer blend displays significant negative volume change upon mixing that leads to a significant decrease in gas permeation rates and consequently, an increase in gas selectivities (Mannan et al, 2013; Robeson, 2010).

When bulky hexafluoroisopropylidene groups are incorporated into the structural unit of imide-based macromolecules, the close packing of the polymer chains is prevented by reducing the interchain interactions, while the free volume increases, thereby improving the gas permeability. Therefore, polyimides derived from 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride are known as high gas permeable polymers (Alaslai et al, 2016).

Here we present our attempt to obtain gas separation membranes from blends of a polyimide containing hexafluoroisopropylidene groups. The miscibility of the two components in the blends was demonstrated by different techniques like DSC, XRD, and SEM. The physico-chemical properties of the membranes along with the gas transport properties are reported.

## Acknowledgments

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## The tires waste used as alternative fuel in Portland cement plants

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The tire waste may be used to replace coal in Portland cement plants, which gives them a strategic advantage by decreasing production costs and pollutant gas emissions (Castañón et al., 2021). The main goal of this study is to determine the effect of the tire waste utilization over clinker kiln technical parameters, energy efficiency, and stability, as well as the effect of tire waste incineration on clinker process and pollutant emission (CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, and heavy metals) at the industrial scale. Measurements were realized at the industrial scale in the different operating regime of the raw mill. Researches have confirmed a solution not only economically advantageous but and environmentally acceptable. The energy consumption for the manufacture of a ton of clinker was 3.3 GJ, while the costs reduced was with 30-40% of the total cost. The burning temperature warrant the total transformation of pollutant that can be exist tire waste (Kishan et al., 2021; Mentés et al., 2022). The use of tire waste as an alternative fuel is a waste management strategy, which has positive effects on the environment and traditional fuel consumption. The outcomes achieved allow other cement factories to pursue this sustainable approach. The cost of tire waste capitalization is low, and the impact on clinker quality and environment is insignificant. More studies are required to determine the impact over final costs, design of kilns, alternative fuel quality, caloric value, etc. The presented method has several advantages, including saving raw materials and methane gas, reducing CO<sub>2</sub> emissions, recovering energy content, and reducing this large amount of trash.

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## The quality of materials obtained by the waste glass capitalization

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In the last decade more materials used different types of wastes, from these and windows waste glasses (Siddika et al., 2021). The effect of windows waste glass over the properties of composite materials was studied. The composites were characterized by: density, consistency, porosity, water absorption and mechanical properties, in order to establishing the impact of waste glass (WG) dosage. In this study the river aggregate was replaced with WG in various proportions. The glass waste was purchased from the Piatra Neamt factory. The waste was selected, crushed and sieved to become comparable with natural aggregates. The prepared samples were used for obtaining the C16/20 concrete using 2, 4, and 10 wt. WG percent. The experiments were realized in a concrete station laboratory, all results were compared with imposed values by standards. The densities were inferior than the witness sample (Without waste glass), reaching from 2335 to 2380 kg/m<sup>3</sup>. The conclusions show that adding glass has a relatively negative impact over its properties, in accord with literature (Dong et al., 2021). By adding of WG, the mixture became non-homogenous, with asperities on the sample surface. The samples containing 10% WG obtained the lowest value. The results indicate that adding waste to concrete has a negative effect on its properties, yet the percentage strength loss was only up to 14% for concrete with 10% WG and 7% for concrete with 4% WG. The foiled WG had lower values when compared to waste from double glazing. Although the final readings were within the limits of Romanian regulations, the experiment's compressive strength was reduced by the addition of WG aggregate. This study shown that WG aggregate may be used to replace natural aggregate. Losses in features were negligible for the WG percent utilized. Significant economic and environmental advantages came from using window glass debris as a portion of the coarse aggregate. Prior to the usage of WG in industrial applications, more studies are required.

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# The characterization of wastes used for obtaining geopolymeric materials

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In the last decade, the capitalization of wastes is highlighted with obtaining of valuable materials, in the frame of “zero waste” concept. The goal of this study is to characterize wastes for incorporation into waste-incorporated geopolymers and to identify obstacles to their industrial use. More researches have been realized into geopolymers during the last period, indicating the potential of the alternative materials to substitute Portland cement (Mohajerani et al. 2019). In this topic an important attention is according for obtaining geopolymers – concrete or mortar, as materials with low carbon dioxide footprint. In the word are generated large quantities of industrial wastes as fly ash, slag, bottom ash, residual sand, red mud, demolition wastes, etc. (Podolsky et al., 2021). The wastes from thermal power plants consisting in ashes (fly ash, - from electro filters, bottom ash and wastes generated by desulfurization system), these have a major human and environmental impacts (cretescu et al. 2018). The literature reported different applications of these wastes including adding as such or modification for obtaining new building materials (Harja et al., 2022). The waste with alumino-silicates has been recognized as one of the potential precursors for geopolymeric materials production, materials with good workability, high durability and improved mechanical properties. The ash is not a standard by-product world-wide, the chemical and physical properties varying according to the source. Thus, increasing researches are being carried out to understand the reaction mechanism of geopolymer material. The wastes used in this study are fly ash (class F and class C), slag and residual sand. Different materials were fabricated according to an experimental design matrix. The wastes are investigated using chemical and microstructural analysis (XRD, SEM, EDX, TGA, etc.), in order to understand the occurred modifications in geopolymerization processes. The investigations were complemented with testing of two geopolymeric materials. The most interest in this research study was the geopolymerization process, which will determine the properties of the produced material.

Future studies should pay particular attention to the different properties of the waste materials, using mix designs that emphasize readily accessible waste materials from the local area, usable with minimal processing.

## Acknowledgments

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# Sorption capacity of silicone-based membranes with functionalized silsesquioxanes. Characterization and perspectives for environmental applications

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A series of three silsesquioxanes were obtained by acid hydrolysis of three organo-trialkoxysilane (3-aminopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, and 3-cyanopropyltriethoxysilane) which conducted to the formation of cubic silsesquioxanes 1, 2 and 3, respectively, containing either the original organic function (SH) (silsesquioxane 2, SH\_SS), a derivatized one (NH<sub>3</sub>Cl) (silsesquioxane 1, A\_SS) or completely chloro derivative (silsesquioxane 3, Cl\_SS). The structures were investigated through X-ray single crystal diffraction, spectral (FTIR and NMR) techniques and elemental analysis.

Each silsesquioxane compound was incorporated into a polymeric matrix of low molecular weight polydimethylsiloxane. After the incorporation of the silsesquioxanes, the matrix crosslinking was performed resulting in free-standing films. The composite films were investigated by dynamic vapour sorption (DVS) analysis, scanning electron microscopy (SEM), stress-strain measurements and dielectric spectroscopy. Thermal behavior was studied by thermogravimetric analysis and differential scanning calorimetry. The presence of the siloxane moiety in the materials, improves due to its surface energy effect the compatibility between the silsesquioxanes and the silicone matrix, thus ensuring good mechanical properties. Depending on the silsesquioxane type, an increasing of the dielectric constant value up to 4.5 as compared with the value for the silicone matrix was obtained. The biological compatibility was also tested for the three composite films. Investigations on hybrid membranes surface, based on the water vapor sorption data, have demonstrated that on their surface exist nano-sized pores. The values of water vapors sorption capacities increase in the following order: P\_Cl\_SS < P\_SH\_SS < P\_A\_SS. Consequently, according to our results, for obtaining a good membrane with superior characteristics for environmental applications it is necessary to ensure a high pore density and a high permeability of the free-standing film membrane.

## Acknowledgments

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**BOOK OF ABSTRACTS**

**Section 2 Biotechnology and Bio-industries**

## Sustainable algae processing by real-time analysis of its products

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Algae bioprocessing is widely seen as a sustainable strategy aligned with UN Development Goals, COP23 and many other world forums on climate change and sustainability. Algae are biocatalysts, biomass raw materials and microbial factories commercially exploited to produce biooil, food and health care molecules, like omega 3, to cite a few. EPA and DHA are essential omega 3 fatty acids being part of a multimillion pounds nutritional industry. Currently, most omega 3 are extracted from oily fish. However, fish farming is seen as unsustainable and thus manufacturers are turning to microalgae for omega 3 production from light and nutrients. Microalgae bioprocessing is relatively easy but still has drawbacks like manual monitoring, variability of omega 3 content between batches and more. Successful production of desirable amounts and quality of omega 3 is only assessed at the end of experiments or trials, after a great deal of time, cost and effort. Thus, at industrial scale, real-time automatic monitoring of omega 3 production inside microalgae along time is desirable, and it would propel algae bioprocessing into a new XXI century biotechnology. Recent studies provide hopes on how to overcome such limitation. However, approaches to select real-time monitoring strategies for industrial omega 3 production in microalgae remains far from clear. In this work, clarity is provided through a scouting technicoeconomic assessment, with emphasis on EPA. Several analytical techniques used in real-time monitoring of microalgae metabolites and similar fatty cells were compared. For instance, Fourier-transform infrared spectroscopy, nuclear magnetic resonance, cell cytometry, mass spectrometry, differential scanning calorimetry and fluorescence spectroscopy. Seven analytical techniques have been compared with Raman spectroscopy chosen as the most viable option to monitor omega-3 production in micro-algae. This preliminary information could one day enable 1) the selection of the most appropriate strategy for real-time monitoring of industrial omega 3 production in microalgae, 2) pioneering studies on automatic control, digitalization of microalgae bioprocessing, 3) process integration and 4) sustainable manufacturing of omega 3 with a more environmentally friendly alternative to fish-derived omega 3 in a circular bioeconomy with net zero carbon emissions.

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# Towards a green, flexible and sustainable continuous manufacturing of pharmaceuticals

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The state of the art in pharmaceutical industry traditionally relies on batch processes. During the batch manufacturing process, quality check samples are taken to separate laboratories to conduct in-process-control measurements before moving the material to the next transformation [1]. For drug products, ensuring consistent quality is of utmost importance for producer and end-user (patient) alike. The great advantage of continuous processes is that the raw materials and the product are continuously fed into and discharged from the equipment, allowing an on-the-go adaptation of parameters to maintain specs in a changing context of operation environment, hence eliminating the idle time between the different technological steps [2]. Furthermore, continuous manufacturing (CM) of pharmaceuticals is also one of the goals within the new roadmap for sustainable and green medicine production (Fig. 1). The environmental impact of drugs manufacturing is higher than in other chemical industry. There are studies

which reveal that CM has advantages such as: process safety and performance improvements; economic and ecological advantages; shorter supply chains and minimal production times [1,3]. Therefore, a shift paradigm towards green chemistry has also an important role as it is evident that the enemy of sustainability is waste and by making the transition to CM this will result is a less wasteful production process. Hence, green chemistry provides new opportunities for the drug manufacturers for innovative industrial operations. This paper focuses on the development of simulation platform which will provide the research community with a versatile tool to explore the advantages of CM.

## Benchmark simulation model for continuous pharmaceutical manufacturing (BSM4PM)

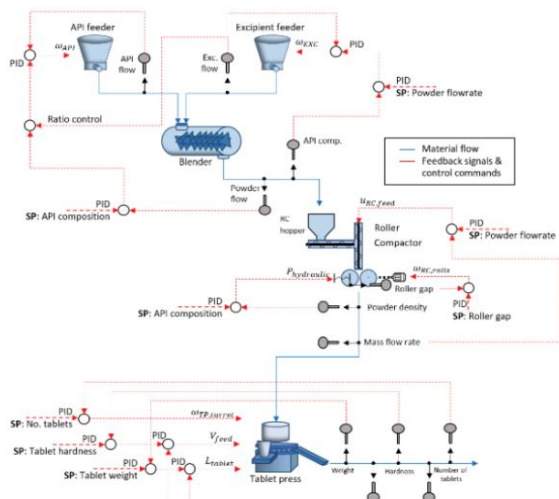


Figure 2 Overview of the process units to be implemented in Matlab/Simulink benchmark platform

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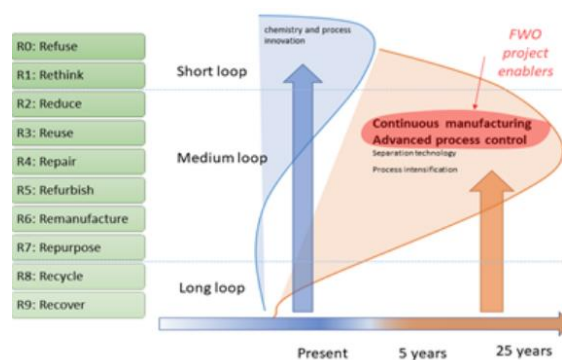


Figure 1 Pharmaceutical sustainability objectives to fulfil the

A schematic representation of the process units implement in the benchmark simulator is given in Fig. 1. A detailed description of the benchmark simulator can be found in [3]. The most common processes characterizing the manufacturing process of tablets are: direct compaction, dry granulation wet granulation, extrusion, granule lubrication, tablet pressing, coating, splitting, etc. A model library to describe the dynamics of the different process units in a tableting manufacturing line was developed. The library is still under development and later versions will feature process models derived and combined with data driven models for the process and for disturbances occurring during the continuous manufacturing process execution. To explore the challenges posed by transition to Industry 4.0 and RAMI 4.0 framework, there is need to look at the interconnectivity of horizontal (production line) and vertical (operations to management planning) axes.

# Preparation by electrospinning and characterization of different food-grade microstructures containing polyphenols and vitamins

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Electrospinning is a new tool for the food and packaging industry and has gained large interest due to its ability to form different microstructures (fibres, films and particles) and to protect the food or food constituents from oxidation, moisture and light (Coelho et al., 2021). In the present work, electrospinning was used to produce different microstructures from an edible polysaccharide: zein, a prolamin protein extracted from the corn. These microstructures can be used to carry bioactive compounds such as polyphenols and vitamins, which are well known for their health benefits: anti-oxidative, anti-bacterial, anti-mutagenic, anti-inflammatory, anti-viral and anti-cancer properties. The incorporation of polyphenols (epigallocatechin gallate (EGCG)) and vitamins (Vitamin E) in the microstructures was studied.

The operational conditions of the electrospinning equipment were optimized. The food-grade microstructures were characterized in terms of morphological properties, namely by scanning electron microscopy (SEM) (Fig. 1). Their release profiles were simulated and evaluated using different kinetic models, namely: Korsmeyer-Peppas, Weibull and Baker-Lonsdale. Different microstructures and different release behaviors were obtained depending on the formulation used.

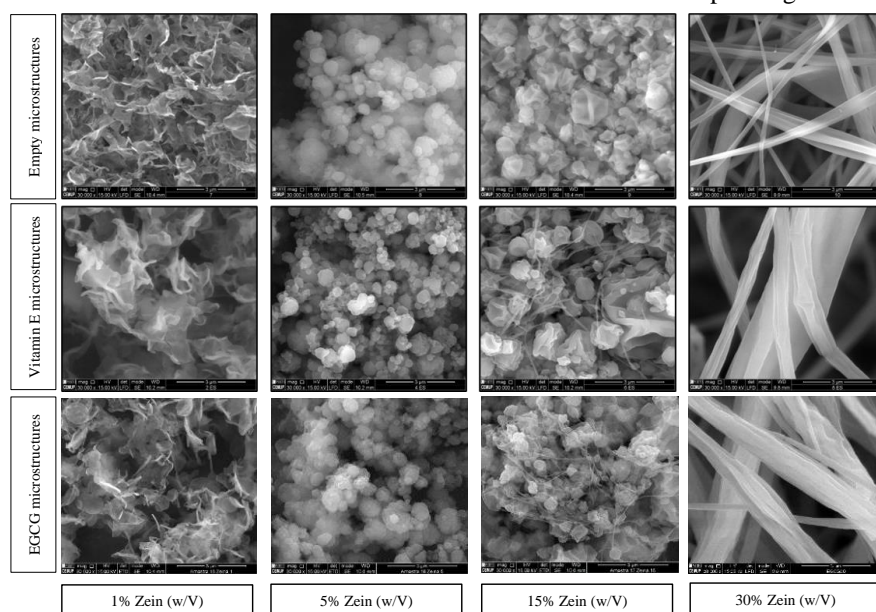


Fig. 1. SEM Images of the microstructures produced by electrospinning. Magnification 30000 x.

In conclusion, the microstructures prepared present promising characteristics for food and nutraceutical applications. This research is significant for the development of food products with unique textures and functionalities.

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# CHARACTERIZATION OF ESSENTIAL OILS AND AROMATIC COMPOUNDS WITH POSSIBILITY OF USE IN FOOD PRODUCTION

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Many plant species synthesize and accumulate extractable organic substances in sufficient quantities, used industrially as raw materials for various commercial applications. Aromatic plants biosynthesize volatile organic compounds and odoriferous substances that can be extracted by various technical processes, in the form of essential oils, extracts, oleoresins, etc., used profitably in industries such as pharmaceuticals, food, cosmetics, perfumery, detergents, flavors, beverages, etc.

Conventional extraction technologies are characterized by several disadvantages and are usually energy consuming. Rising energy costs and greener trends in this subject (ie reducing carbon dioxide - CO<sub>2</sub> emissions) have led to a focus on alternative technologies that are cost-effective, sustainable and able to produce products with the same or often improved features.

Considering the organoleptic properties and the considerable antimicrobial / antioxidant activity of the natural essential oils, two main directions of use were chosen:

- Preservative use - highlighting the antimicrobial, antioxidant properties of some mixtures of essential oils;
- Use in order to produce flavoring preparations for various meat products.

Studies have been carried out on obtaining mixtures of natural essential oils with the best preservative and flavoring properties for finished food products, based on which a mix of essential oils was chosen consisting of: thyme oil (*thymus vulgaris* L.): 35%; oregano oil (*origanum vulgare* L.): 40%; rosemary oil (*rosmarinus officinalis* L.): 20%; coriander oil (*coriandrum sativum* L.): 3%; eucalyptus oil (*eucalyptus globulus* L.): 2%.

The main physico-chemical parameters for the characterization of natural essential oils, which we also measured for the products used, are: density (g / ml., Measured at 20 °C), refractive index (nD at 20 °C) and rotary power (°). These parameters were measured for each essential oil.

The mixture of essential oils was tested on crops of Enterobacteria, Molds, Yeast

Given that essential oils are chemically and structurally complex, it is therefore possible that there are different mechanisms by which they exert their antimicrobial properties. However, essential oils are generally hydrophobic and are therefore likely to penetrate the cell membranes of microbes and the cell membranes of eukaryotic organisms (Burt, 2004).

The hydrophobic nature of EO's may also explain why they tend to be less effective against gram-negative bacteria whose outer cell membrane, which is composed of lipopolysaccharides, is a barrier to the molecules of active compounds in essential oils due to its hydrophilic character.

In general, aromatic compounds in essential oils have in their molecular structure double bonds, conjugated double bonds and OH-phenolic groups. These structural features allow double-bonded molecular structures to function as antioxidants. Thymol, carvacrol, and eugenol appear to be the most powerful antioxidants. In addition to the potential direct health benefits of the antioxidant activity of essential oils, there is also the preservative aspect of food protection by inhibiting lipid oxidation.

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## Development and characterization of fortified cultured buttermilk with vegetable ingredients

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Acidic dairy products are known worldwide for their health benefits and pleasurable sensory properties. Buttermilk is a fermented dairy product that is obtained as a by-product of butter production. In the present study, the milk used in the manufacture of whipped milk was fortified with apple peel powder and baobab powder in various percentages in order to improve the physicochemical and sensory characteristics of the product. Apple peel and baobab powders have the ability to improve the quality and acceptability of products such as buttermilk due to their high dietary fiber content.

Buttermilk was obtained in the laboratory, using: cow's milk from a private farm with a content of 3.5% fat, 3% protein, 4.5% lactose. The mesophilic starter culture used was from Hansen. The processing of buttermilk was done following the traditional technological scheme. 4 samples were prepared: Control sample (milk, starter culture) PL1 (milk, starter culture, 2 g baobab powder, 5 g dried apple peels), PL2 (milk, starter culture, 3 g baobab powder, 3 g dried apple peels), PL3 (milk, starter culture, 5 g baobab powder, 2 g dried apple peels).

The sensory evaluation was done for 15 attributes related to appearance, taste, smell, consistency and aroma. (Desai, Shepard, & Drake, 2013) (Swi & Florowska, 2002) (ISO 8589:2007, 2014) (ISO 13299:2016, 2014) The evaluation team consisted of 5 members who gave scores from 1 to 5 for each sample (1 = no sensation, 5 = very strong sensation).

To determine the parameters related to the quality of yogurt samples, the following methods of analysis were used: Titratable acidity, lactose content - polarimetric method II, syneresis and water activity. (Tița, 2002), (Barkallah, și alții, 2017) Physicochemical determinations were performed on 3 different days over a 20-day storage period.

Statistical analysis was performed using Minitab Statistical Software, version 16.0 at a significance level at  $p < 0.05$ . Measurements were made in triplicate for each sample and the results were expressed as mean  $\pm$  standard deviation. Principal Component Analysis (PCA) was used to reduce the number of dependent variables and to identify similarities and differences between the sensory attributes of buttermilk samples.

All the buttermilk samples with addition of baobab powder and apple peel powder obtained better values compared to the control sample in terms of sensory analysis, especially in terms of attributes related to consistency, but also attributes related to general acceptability. The sour taste is well highlighted in all samples, the addition of powders does not change the taste very much.

Normal values for titratable acidity and lactose content were obtained throughout storage. Better values were obtained for the samples with the addition of vegetable powders in terms of water activity and syneresis. The best values were obtained for the PL3 sample.

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# Studies on the possibility of using by-products from the wine industry and their introduction into the manufacturing process of food and pharmaceutical products using technologies environmentally friendly

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The wine industry has experienced lately a remarkable development, given that the technology and biotechnology have also taken an unprecedented boom. There are more and more offers on the market of yeasts, bacteria or enzymes, indispensable products in modern wine technologies. But an interesting and current segment is the study and valorification of wine by-products. The specialized literature estimates the amount of wine by-products from their valorification technology at approximately 25% of the value of the annual grape harvest. Each technological operation during the winemaking of the grapes or the conditioning of the wine produces by-products whose properties vary according to many ecological, technological and biological factors (the state of maturity, the variety from which the grapes come, climatic and soil conditions).

Phenolic compounds constitute a diverse group of secondary metabolites, which are present in both, in grapes and wine. The phenolic content and the composition of processed grape products (wine) are strongly influenced by the technological practice to which the grapes are exposed. During the handling and maturation of grapes several chemical changes may occur with the appearance of new compounds and/or the disappearance of others, subsequent modification of the ratios of the total content of phenolic compounds, as well as their qualitative and quantitative profile. An important factor in the recovery of valuable compounds from wine by-products is the evolution and the chemical and biochemical profile of grapes. Their evolution, the accumulation of valuable compounds depends on a number of factors such as climate, soil, vineyard exhibition, etc. Grape pomace, seeds, skins and waste from wine production also contain many bioactive compounds that differ from those found in grapes and wines. Important studies lead to the determination of the special qualities of wines and wine by-products, which have bioactive capacities against food poisoning caused by microorganisms. The objectives assumed in this paper are:

- qualitative and quantitative analysis of valuable substances from wine by-products
- physico-chemical characterization of valuable substances from wine by-products
- optimization of procedures for extraction of valuable substances from wine by-products
- obtaining and characterizing products from wine by-products

The studies also present aspects of antioxidant and immunostimulating activity as well as the adverse effects associated with wine consumption. Informations and studies are needed to optimize the use of wines and by-products to help improve microbial food safety and prevent or treat a range of health problems. In order to obtain higher yields of valuable substances (tartaric acid, tannin, oil, alcohol, fodder flour) it is very important that the grape pomace to be fresh, fermented and processed during the winemaking season. If this process cannot be done immediately, storage cannot exceed the end of February of the following year and a number of conditions must be met to avoid their degradation. Grape seed extract is known as a powerful antioxidant that protects the body from premature aging, disease and decay. Grape seeds contain mainly phenols, such as oligomeric proanthocyanidins (proanthocyanidins). Scientific studies have shown that the antioxidant power of proanthocyanidins is 20 times higher than that of vitamin E and 50 times higher than that of vitamin C.

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# ***Saccharomyces pastorianus* residual biomass/calcium alginate system acts as an efficient biosorbent to remove pharmaceuticals from aqueous matrices in different operational conditions**

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Recent advancements in pharmacological science have transformed both human and veterinary medicine. Pharmaceutical usage has grown along with considerable changes in medication prescribing practices. Thus, it is possible to estimate that hundreds of tons of pharmacologically active substances are used annually to treat and prevent illness (Felis et al., 2020; Carvalho et al., 2016). The prevalence of drugs in the aquatic environment, directly reflects the extent of their use worldwide and represents a potential risk for human health and living organisms that inhabit in this environment (Barbosa et al., 2016).

From the numerous techniques have been used for the removal of pharmaceuticals from aqueous matrices, the biosorption process is the most promising option if the viable biosorbent can be found. Research on biosorption methods is currently concentrating on the creation of increasingly complex systems employing biocomposite materials with novel characteristics (Rusu et al., 2021; Rusu et al., 2022).

Biosorptive removal of the antibacterial drug, Ethacridine lactate (EL), from aqueous matrices was performed using *Saccharomyces pastorianus* residual biomass immobilized in calcium alginate as biosorbent. The aim of this study was to determine the effect of agitation speed on biosorption process.

The morphology and surface functionalities of synthesized biocomposite materials were acquired by scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) analysis, both before and after biosorption.

The response surface methodology (RSM) based on a Box-Behnken design (BBD), were used to optimize EL biosorption conditions. The two responses (removal efficiency, R % and biosorption capacity q mg/g) were maximized as a function of three factors: initial concentration of EL solution, contact time and agitation speed. The highest values for R% (93.34) and q (25.41 mg/g) were obtained in following operational conditions: EL initial concentration=53.42 mg/L; contact time=120 minute; agitation speed=198.94 rpm.

For the purpose of validating the biosorption kinetic behavior of ethacridine lactate by this type of biosorbent, a variety of widely used nonlinear kinetic models, including pseudo-first-order, pseudo-second-order, Elovich, Weber-Morris and Avrami, were employed for this. The experimental data of EL removal were best fitted by pseudo-first-order and Avrami models, in both cases the obtained correlation coefficients values are over 0.99.

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## ZnMgY experimental alloy: Case of study for possible medical applications

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Zinc biodegradable alloys present an increased interest in the last few years in the medical field among Mg and Fe-based materials. Knowing that the Mg element has an effective strengthening effect on Zn, we analyzed the effect of the third element, Y on ZnMg alloy with expected results in mechanical properties improvement. Ternary ZnMgY samples were obtained through induction melting in Argon atmosphere from high purity (Zn, Mg, and Y) materials and MgY (70/30 wt%) master alloys with different percentages of Y and keeping the same percentage of Mg (3 wt%). [1] All the experiments were made after lamination state. pH determination and mass variation after immersion in Dulbecco solution was determined with dual time of 1-3-7 days [2]. Materials were characterized using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), linear and cyclic potentiometry and immersion tests [3-4]. All samples present generalized corrosion after immersion and electro-corrosion experiments in Dulbecco solution. The experimental results show an increase in microhardness and indentation Young Modulus following the addition of Y and participate in formation of YZn<sub>12</sub> intermetallic phase elements. In this article, preliminary results obtained on a new alloy (ZnMgY) were analyzed compared with pure Zn and Zn<sub>3</sub>Mg materials. Zn alloys are, nowadays, appreciate as a promising material for medical biodegradable applications since their corrosion rate is between magnesium (too big corrosion rate - degradation) and iron (small corrosion rate - degradation), besides other benefic biological reactions of Zn.

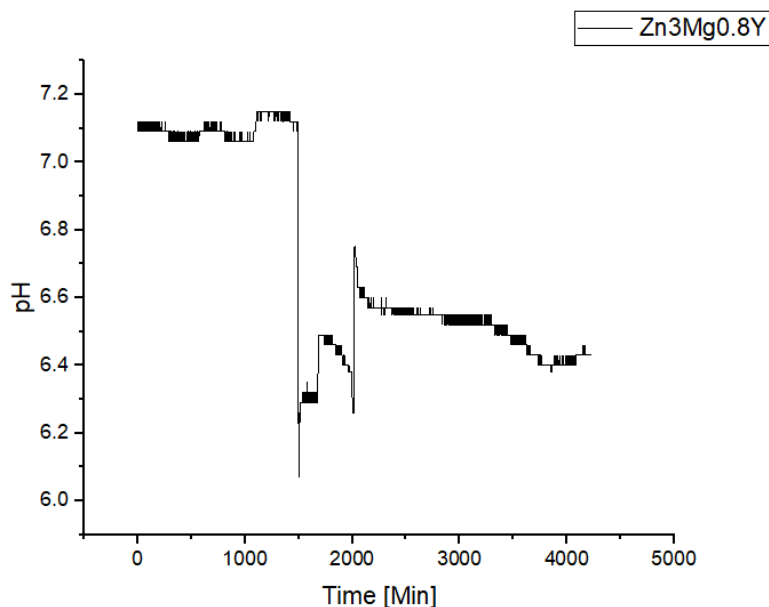


Fig. 1. pH determination of ZnMgY alloy after 3 days immersion in Dulbecco buffer solution

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# Fe-Mn-based alloys investigated as possible biodegradable materials

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Degradable biomaterials are intended for those implants that only require their temporary presence to heal the diseased tissue. The medical applications for which their use would be considered relate to certain specific cases, such as in cardiovascular, orthopedic and pediatric specialties. In most scientific papers, the topic of biodegradable metals is treated from the perspective of material development, improvement of properties, study of degradation rates and mechanisms and in vivo implantation of the material. There is still not enough data and research leading to the transformation of biodegradable metals into implant or prototype. A critical aspect that these materials must possess is a compromise between degradation and mechanical integrity during implantation. Ideally, a suitable degradation rate should be maintained concurrently with the optimal mechanical integrity of the implant during healing, so that later degradation progresses while mechanical integrity decreases. It is de droit that during decay, the uniform corrosion mechanism should start from the surface to the interior to maintain mechanical integrity. Three major classes of biodegradable alloys for temporary implants are being studied in the scientific world, namely, Fe, Mg or Zn-based alloys, each with pluses and minuses correlated with corrosion and mechanical properties (Nayak et al., 2020).

In this paper, we studied FeMn-based alloys as potential biodegradable materials, presenting results on the corrosion behavior manifested by in vitro experiments. The pH variation values for Dulbecco's physiological solution, in which small samples were immersed for different times, were acquired and processed. The surface of the samples was studied initially, after the formation of the corrosion layer and after removal of the compounds in an ultrasonic bath, using optical microscopy and scanning electron microscopy (SEM). Using energy dispersive spectroscopy (EDS), initial and post-immersion chemical analysis of the samples with the formation of salts, chlorides and carbonates and the cleaning of some of them by ultrasound of the surface was performed. Degradation rates of the study alloys were calculated from the biofluid immersion tests at time intervals of 1, 3, 7 days and 14 days relative to mass loss. Electro-corrosion tests were performed in Dulbecco's working solution at room temperature, which was used as the electrolyte. Tafel diagrams helped us acquire the corrosion process parameters and the linear and cyclic polarization curves were interpreted. The in vitro study of Fe-Mn-based alloys provided results that may indicate good preliminary biodegradability properties, but the study needs to be continued for further research.

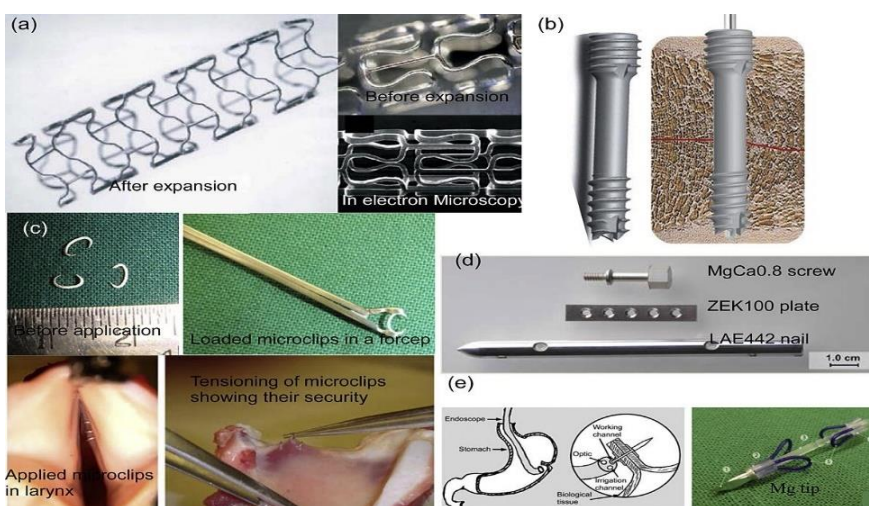


Fig. 1. Applications of biodegradable implants (Chen et al., 2014)

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## Modeling the survival rate of *Leptinotarsa decemlineata* Say pests by the use of spontaneous flora extracts

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In recent decades, agricultural research started to aim at partially or completely replacing synthetic pesticides with sustainable alternatives, also known as biopesticides. Biopesticides can be obtained from various sources such as: microbial biopesticides, biochemical biopesticides and plant protection agents. These are the main categories of biopesticides that have a share of 5% of the global pesticide market, and of these, the most used are microbial biopesticides (Pathma et al., 2021). Due to the adopted legislation in some developed countries, the reduction of the synthetic pesticides use in agriculture is urgently needed, especially due to their restrictions, regulated by a number of state institutions. Although the use of biopesticides is an alternative with major advantages, they also have a number of drawbacks, which makes the partial or total substitution of synthetic pesticides with alternative products more difficult than expected. However, some countries adopted the substitution policy of these synthetic pesticides, agriculture registering 10% increases in the use of biopesticides (Damalas and Koutroubas, 2018). The use of these extracts obtained by environmentally friendly extraction methods has a number of advantages compared to synthetic pesticide alternatives such as: they are biodegradable, harmless to non-target and specific organisms in action, and have potential mechanisms to counteract pest resistance (Mishra et al., 2020).

Given the global trend of finding alternative solutions to control crop pests, this paper aims to (i) provide data on obtaining raw extracts from the spontaneous flora with potential pest control of *Leptinotarsa decemlineata* Say, using *Origanum vulgare* and *Artemisia absinthium* species, and (ii) identify the 50% lethality of the pests by modeling the survival rate obtained by the 2 extracts. The treatments obtained from the spontaneous flora of Romania, represented by *Origanum vulgare* and *Artemisia absinthium*, were obtained by using the ultrasonic assisted extraction method (UAE) and a combined method between UAE and maceration (M), for an extraction time of 30 min, at a temperature of 60° C, and an S / L ratio of 1/10 for both plant species and both extraction methods. After extraction, the biopesticide products were stored and in airtight containers with a spray device at the refrigeration temperature until the time of administration. The mode of administration was performed in by direct spraying (DS) per plant and indirect administration (IS), by spraying on an absorbent disk located in the middle of the growth cage with a capacity of 10L. First order kinetic model was applied to survival rate data considering both extraction methods. We observed that the highest correlation coefficients,  $R^2$ , were obtained for indirect application using both plant extracts ( $R^2 > 0.9$ ). In this way we were able to estimate the 50% lethality of *Leptinotarsa decemlineata* Say by *Origanum vulgare* extracts obtained by UAE method in 138.62 h and by UAE+M method in 99.02 h. On the other side, 50% lethality was attained by *Artemisia absinthium* extracts obtained by both extraction methods in 231.04 h. *Artemisia absinthium* extracts gave the best results, by direct application and using UAE+M method, showing 50% lethality of *Leptinotarsa decemlineata* Say in 138.62 h. Our results demonstrated that extracts obtained from *Origanum vulgare* and *Artemisia absinthium* were able to predict 5 times higher responses in terms of lethality of *Leptinotarsa decemlineata* Say compared to control.

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# Microencapsulated residual *Saccharomyces pastorianus* as biosorbent for dye retention

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In biotechnology, microorganisms are important sources for a wide variety of intracellular and extracellular compounds such as: organic acids, amino acids, antibiotics (Blaga et al., 2021). In these biosynthesis processes, the residual microbial biomass is an inevitable waste, generated mainly in the separation stage. These microbial by-products (bacteria, yeasts or filamentous fungi) can be used as a potential alternative to existing technologies for the recovery of pollutants from industrial flows, due to their ability to retain, through various mechanisms, pollutants from wastewater by biosorption (Torres, 2020).

An important alternative to current wastewater treatment processes is biosorption - a cost-effective, simple, reversible, passive accumulation process by which inactive biosorbent binds (by ion exchange, precipitation, absorption, adsorption and complexation) certain ions or molecules in solutions. aqueous.

The biosorbents include various microbial cells - bacteria or fungi, due to the presence, in the cell wall and plasma membrane, of several functional groups (amino, carbonyl, carboxylic, phosphoryl, hydroxyl, phosphate or sulfate) that are able to interact with pollutants (Torres, 2020; Redha, 2020). Residual biomass can be used in free or immobilized form, the latter offering several advantages such as: easy separation, increased operational stability, multiple uses, incorporable in columns with fixed and fluidized layer, higher productivity. Different polymers (chitosan and alginate) can be used for immobilization to obtain cheap, non-toxic biosorbents with reactive functional groups (Torres, 2020; Redha, 2020).

The use of microencapsulation (in natural polymers such as chitosan and alginate) to immobilize biomass have some advantages: improved stability, extended shelf life (storage time) and a wide variety of particle shapes and sizes according to the desired purpose (Blaga et al., 2021).

In this context, the aim of the paper is to investigate the biosorbent properties of the residual microbial biomass of *Saccharomyces pastorianus* (*S. pastorianus*), a hybrid interspecies between *Saccharomyces cerevisiae* and *Saccharomyces eubayanus* to retain textile dyes from aqueous media (Methylene Blue and Orange 16). *Saccharomyces pastorianus* yeasts are by-products in the biosynthetic processes underlying the production of fermented alcoholic beverages (wine and beer, respectively) and as a result large amounts of residual yeast are available. We used biomass in immobilized form by encapsulation with the help of Buchi microencapsulator.

The evaluation of the biosorptive capacity of the obtained biosorbents involved the study of the effect of some physical parameters on the biosorption process of the selected dyes: temperature, pH solution, amount of biosorbent, dye concentration and phases contact time.

The obtained results confirm that the studied residual microbial biomass immobilized in chitosan can be considered as a good biosorbent and it can be used in the treatment of wastewater containing small quantities of organic dyes.

## Acknowledgments

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## Cosmetic formulations for combating cutaneous oxidative stress based on plant bioresources

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In line with a modern approach to skin health and beauty, a performant formula for dermato-cosmetic products is expected to include an antioxidant ingredient. Nowadays lifestyle encompasses numerous factors which increase the skin oxidative stress, thus rendering the antioxidant activity of the formulation essential.

The objective of this study was to formulate a dermatocosmetic O/W emulsions containing a synergistic biologically active complex based on a plant-derived meroterpene phenol, bakuchiol (BAK) [1- (4-hydroxyphenyl) -3,7- dimethyl-3-vinyl-1,6-octadiene] and a peptide as a n-prolyl palmitoyl tripeptide-56 acetate (TPA). Bakuchiol is an active substance found in the species *Psoralea corylifolia* which exhibits antioxidant and antibacterial activity and it is an alternative to retinoids. The n-prolyl palmitoyl tripeptide-56 acetate is a small peptide that has been reported to stimulate the production of elastin, fibronectin, glycosaminoglycan and collagens.

O/W emulsions were prepared using an emulsifier (methyl glucose sesquistearate) obtained from the esterification of stearic acid and glucose from vegetable sources. This emulsifier of vegetable origin allows formulation of an extensive range of textures, ranging from milky to thick creams, and with a more or less rich feel. The emulsions obtained are very fine and particularly appreciated by dry skin and mature skin. As a dispersed phase, we use a mix of vegetable oil and as a continuous phase *Rosa damascena* hydrosol.

A preliminary assessment of the stability of the emulsions was performed by means of optical microscopy. This technique was used to observe the distribution and dimensions of droplets. The optical microscopy showed that the formulated emulsions were nonfloculated, the droplets were homogeneously distributed in the image with a relatively small size. DPPH and ABTS assays were used to evaluate the antioxidant activity of the active complex (BAK /TPA) and of emulsions containing this biologically active complex. As a quality condition, the susceptibility to microbiological contamination of the obtained emulsions was also tested. The results confirmed that the proportions of the biologically active complex used for preparing emulsions with BAK and TPA showed good antioxidant activity and are suitable for topical use due to their antioxidant effect and to the potential utilization in antiaging therapy.

## The potential of *Acmella oleracea* in dermato-cosmetic products

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*Acmella oleracea*, a member of the *Asteraceae* family, has impressive applications in the food industry and a solid scientific foundation in diverse research reports. It offers a wide range of functional activities that may result in new pharmaceutical applications.

*Acmella Oleracea* is considered an important medicinal plant due to various pharmacological activities of all its parts, flowers, leaves and roots. Among the numerous active principles of *Acmella Oleracea*, spilanthol is the most abundant one and has been proven as a significant antiseptic, anaesthetic, analgesic and antioxidant agent, essential to modern, efficient dermato-cosmetic formulas for a wide range of skin pathologies with increasing impact. The other bioactive compounds of the plant potentiate specific activities, such as the antioxidant effect, which recommends *Acmella Oleracea* for in-depth further studies.

For this purpose, we aimed to obtain hydroalcoholic extracts and their qualitative and quantitative characterization in order to subsequently introduce them into dermatocosmetic preparations.

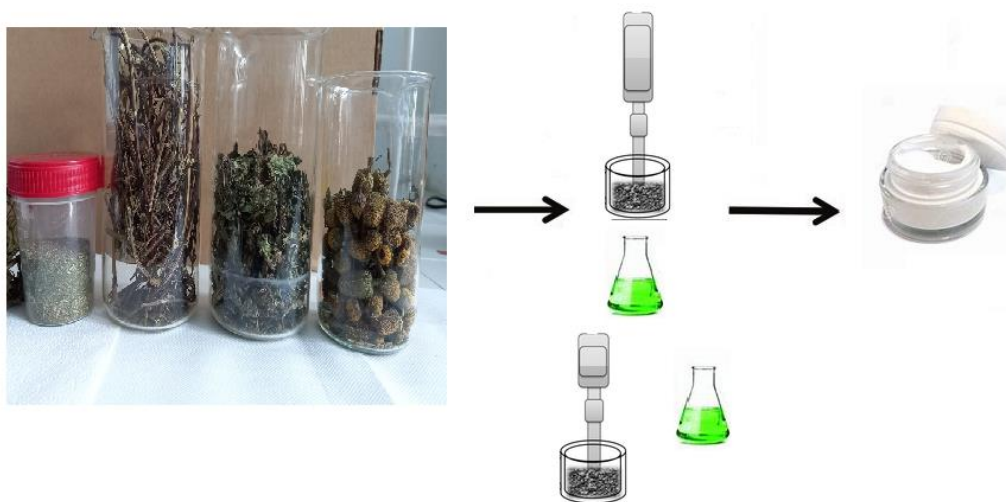


Fig. 1. Extraction methods used for *Acmella oleracea*

As solid-liquid extraction methods we applied maceration at room temperature (M), ultrasound-assisted extraction (UAE) and ultrasound-assisted extraction combined with maceration (UAE-M), as it can be seen in Fig. 1. As an extractant we used 96% ethyl alcohol in the form of a hydro alcoholic solution of different concentrations. The efficiency of these methods was monitored according to three parameters: solid-liquid ratio (1:15; 1:20; 1:30), extractant concentration (30%, 50% and 70%) and extraction time (chosen according to the studied extraction method). Quantitative characterization was done by determining the concentration of flavonoids and total polyphenols and antioxidant activity.

The results allowed us to select the extract with the best efficiency and the highest content of active compounds for introduction into preparations of dermatocosmetic interest.

# Lignocellulosic crop residues – characterization as raw materials for bio-based production chain

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Lignocellulosic crop residues (LCR) represent a large biomass category generated by agricultural harvesting activities. Generally, LCR are represented by plant parts of little economic value and regarded as crop wastes and may include cereal straws, corn, rapeseed and sunflower stalks. Cereal straws and corn stover are ubiquitous in the temperate climate zone due to their large amount and availability (Giannoccaro et al., 2017; Jain et al., 2022).

LCR are made up mostly by biopolymers (polysaccharides and lignin) resulted from biosynthesis process. This is giving LCR the character of carbon sequestering and of renewability (Klemm et al., 1998). The main polysaccharides, making up about 60-70% of the chemical composition, are cellulose and hemicelluloses. Cellulose, which comprises interlinked an-hydro-glucose units is the most abundant natural polymer with countless applications (Habibi et al., 2010). LCR's hemicelluloses are mostly of xylan backbone type, branched with short carbohydrate chains constituted of different sugar anhydro-units (arabinose, uronic acids, galactose) interlinking cellulose micro-fibrils (Ren and Sun, 2010, Kopetz, 2013). Lignin is a cross linked amorphous aromatic polymer originated in condensation of three phenyl-propanic: p-coumaryl, coniferyl alcohol, and sinapyl alcohol. Lignin and hemicelluloses constitute the amorphous matrix binding together cellulose fibers (Berlin and Ba-lakshin, 2014). Besides cellulose, hemicelluloses and lignin, a number of minor constituents such as: tannins and polyphenols, lipids, terpenes and esters also exist as secondary components in LCR. An average Fig. of the proportions of main components of LCR shows: cellulose 32-42%; hemicelluloses: 22-31%, lignin 15-25%; organic solvent and hot water extractives 6-17%, ash 2-10% (Yogalakshmi et al., 2022; Li et al., 2017; Puițel et al., 2021).

The main objectives of the current work are to emphasize the potential of LCR by revealing the important chemical components contents cellulose, hemicelluloses, lignin, and ash and preliminary results of laboratory trials on the extraction of hemicelluloses and their chemical structure elucidation.

## Acknowledgments

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# The influence of stress response in anaerobic fermentation processes of *Saccharomyces cerevisiae*

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In the context of the increased need to obtain products through sustainable processes, from environmentally friendly and renewable resources, the researchers' attention was directed to fermentation processes. Fermentation processes are the oldest and largest applications of microbial technology. In these processes, a variety of microorganisms such as yeasts, bacteria, or fungi produce enzymes that catalyze chemical reactions to break down the substrate and convert it into chemicals and by-products (Balaman, 2018).

The complexity and optimization of fermentation processes comes from knowing how each factor involved in the process influences the speed of enzymatic transformations. The fundamental characteristic of the fermentation process consists in the fact that the modification of a parameter entails the modification of all other parameters, and the negative influence on the process performance is profound. Among the factors that are involved in the fermentation processes, the most important are the composition of the biomass, temperature, pH-value, rH-value, and dissolved oxygen in the medium. Additionally, the presence of inhibitors cannot be avoided, as they occur as a result of biomass degradation and metabolic reactions. The process of transforming the substrate into a useful product is accompanied by four main types of inhibitions: competitive inhibition, non-competitive inhibition, substrate inhibition, and product inhibition (Oniscu and Cascaval, 2002).

Due to the fact that the performance of the fermentation process depends on the ability of microorganisms to transform the substrate into the desired product, it is of the utmost importance to investigate the factors that can lead to favorable changes in these metabolic reactions. Thus, the research carried out aimed at investigating the analysis and modification of the culture medium composition used for the obtaining of bioethanol by *Saccharomyces cerevisiae* cells fermentation in anaerobic conditions.

The studies have showed that changes of the membrane lipid composition by chemical supplementation or modifying the fermentation broth composition (salt nature and concentration) were able to confer yeast cells increased tolerance to heat, ethanol or oxidative stresses. Found in the cell plasma membrane, ergosterol ensures the yeast's structural integrity (which is responsible for membrane fluidity and permeability). The level of this sterol is of great importance, as it also ensures resistance to ethanol.

## Acknowledgments

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## Changes of synovial fluid rheological parameters in knee joint degenerative disease

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Knee Osteoarthritis (KOA) is one of the most common public health problems that cannot be cured and ultimately leads to disability. Current management is largely limited to the treatment of symptoms (Hamood et al, 2021). Joint degradation in KOA is a slow, step-by-step process of the articular cartilage, and the synovial fluid which has a lubricating, trophic, and mechanical shock-absorbing role loses its non-Newtonian properties and becomes a Newtonian fluid (Boutefnouchet et al, 2017). Matrix metalloproteinases and proinflammatory cytokines are involved in the degradation process of synovial fluid, which cleaves the hyaluronic acid chain making the synovial fluid mechanically ineffective. To avoid the late stages of KOA leading to knee replacement, viscoelastic products are used to restore the rheological properties of the synovial fluid and return it to its original state (Altman et al. 2016). We hypothesized that synovial fluids assessed after viscosupplementation would have different rheological properties, as physiotherapy influences the inflammatory processes in KOA (Onu et al., 2022)

We conducted a single-center observational study to compare the combined effect of physiotherapy and intra-articular hyaluronic acid injections versus intra-articular injections in patients with moderate KOA. Twelve patients entered this study divided into two groups, the pilot group received hyaluronic acid (3 Mda) viscosupplementation, and physiotherapy ( $n=7$ ), and the control group ( $n=5$ ) received injections only. Patients in the control group underwent 10 consecutive days of physiotherapy including TENS currents, LASER biostimulation, ultrasound, exercise, and cryotherapy. Synovial fluid samples were taken from all patients immediately after viscosupplementation of the knee joint and at 6 weeks to assess rheological behavior.

For rheological evaluation, a rotational parallel plate rheometer, heated to 37 degrees Celsius was used in which synovial fluid was subjected to a series of flow and oscillatory tests to determine viscosity and elasticity modulus at different shear rates. The Kinexus Pro+ rotational rheometer and rSpace for Kinexus software were used for the following tests: Three Step Shear Rate - Thixotropy Test at 0.5, 10 and 40 share rate; Viscometry single rate 0.5, 2, 10 and 40 share rates; Oscillation Frequency sweep strain controlled with G' G'' cross over analysis at 0.5 and 2.5 Hz; Frequency Sweep - Measure Viscoelastic Response at 0.5 and 2.5 Hz.

The results of this study show that combined physiotherapy and hyaluronic acid viscosupplementation therapy can play a key role in the non-surgical treatment of KOA, effectively controlling pain, and stiffness and improving patients' quality of life (Onu et al., 2022). The pilot group that underwent combination therapy showed fewer rheological changes in synovial fluid than the other group, in which degradation is more evident. Although the small number of rheologically assessed patients does not allow us to generalize the results, but we can state that the synovial fluid from the pilot group better maintained its rheological properties over 6 weeks.

### Acknowledgments

Informed consent was obtained from all subjects that were involved in the study. The authors declare no conflict of interest.

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## Studies on itaconic acid separation from fermentation broth

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In the context of sustainable development, many important chemical substances are suitable to be replaced by natural ones by means of biobased processes. Therefore, itaconic acid represents one of the promising substances, an organic acid with a wide range of applications and has a significant advantage of being produced by fermentation processes. The biotechnological production of itaconic acid is represented by fungi fermentation of *Aspergillus itaconicus*, *A. terreus*, *Pseudozyma antarctica*, *Ustilago maydis* but also yeasts were tested *Candida sp.*, *Rhodotorula sp.* *A. terreus* fermentation from glucose substrate is the most frequently used commercial producer of itaconic acid with a maximum concentration in the fermentation broth of 129 g/l (Hevekerl et al., 2014). After fermentation, the development of an economically viable downstream process represents the most important step in biobased itaconic acid production. A promising method for itaconic acid separation is represented by reactive extraction with improved results in the recovery of organic acids (Kaur and Elst, 2014).

This work investigates the possibility of reactive extraction of itaconic acid with tri-n-octylamine (TOA) dissolved in different solvents, with and without addition of 1-octanol as a phase modifier. Because the solvent polarity controls the extraction efficiency, the extraction mechanisms and influencing factors have been analyzed in direct correlation with the polarity of the considered solvents (dichloromethane and n-heptane). To improve the efficiency of extraction, a second solvent immiscible with aqueous phase can be added in the organic phase, 1-octanol, leading to the increase of solvent polarity. As shown in Fig. 1, with the reduction of solvent polarity, from dichloromethane to n-heptane, and with increasing amine concentration over 200 g/l, the extraction efficiency for itaconic acid is higher in system with 1-octanol compared with system without phase modifier. Therefore, the extraction degree of 93% was reached at 120 g/l concentration of TOA dissolved in dichloromethane with 1-octanol.

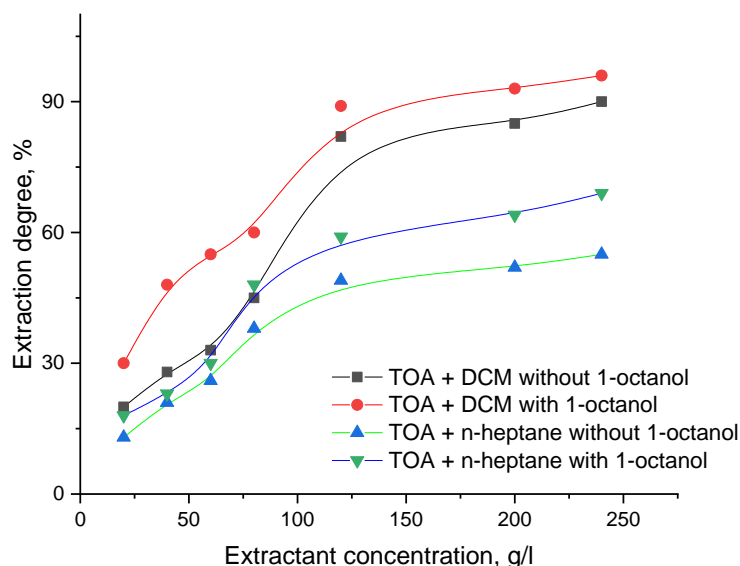


Fig. 1. Influence of extractant concentration on efficiency of itaconic acid reactive extraction at pH=3

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## Separation of cinamic and p-metoxicinamic acids by synergic extraction

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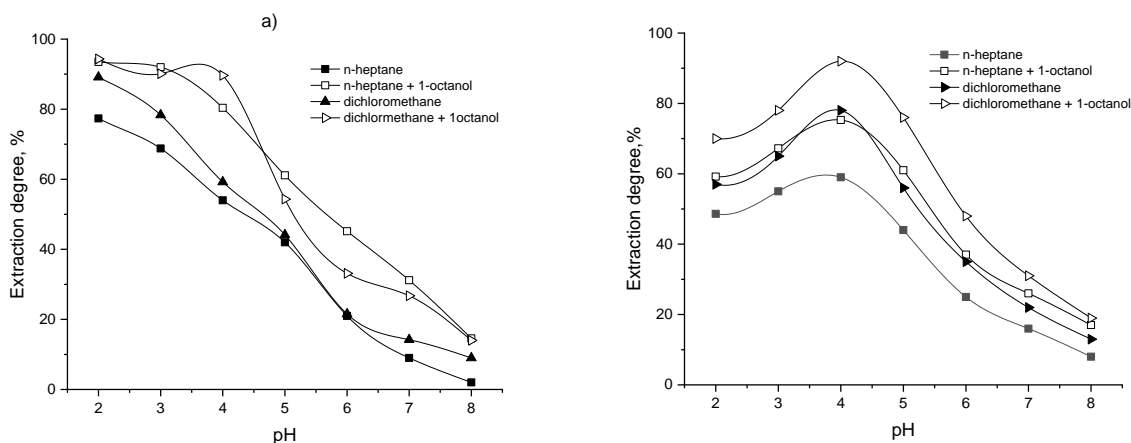
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Cinnamic acid, also called phenylacrylic acid, is a natural compound derived from phenylalanine, naturally existing in plants. Cinnamic acid as such, or its derivatives, p-hydroxycinnamic and p-methoxycinnamic acids, are used in various pharmaceutical preparations, having antibacterial and antifungal activity (Kumar et al., 2008). Cinnamic acid can be obtained, along with p-hydroxy- and p-methoxycinnamic acids, by extraction from vegetable raw materials, by chemical synthesis or biosynthesis. Liquid-liquid extraction is an important separation technique and is usually applied in biotechnology as a first step in the recovery of carboxylic acids, as well as primary and secondary metabolites.

This work investigates the possibility of reactive extraction of cinnamic and methoxy cinnamic acids with tri-octylamine dissolved in different solvents, with and without addition of 1-octanol as a phase modifier. Because the solvent polarity controls the extraction efficiency, the extraction mechanisms and influencing factors have been analyzed in direct correlation with the polarity of the considered solvents (dichloromethane and n-heptane).

The effect of the pH change on the extraction efficiency depends, however, on the chemical structure of the solute, as well as on the type of extraction, physical or reactive. Fig. 1.a) shows the influence of the pH of the aqueous phase on the efficiency of cinnamic acid separation by reactive extraction with and without phase modifier using two different solvents. From the graphic representation it can be seen that by using dichloromethane as a solvent, the efficiency of extraction is higher compared to the results obtained by using n-heptane. It can also be observed that at the value of pH = 2 the highest degree of extraction was obtained both in the case of dichloromethane and in the case of n-heptane. From Fig. 1.b) it can be seen that in the case of physical extraction with n-heptane, the shift of the pH value towards the neutral range causes a reduction in the yield of p-methoxycinnamic acid extraction, due to the dissociation of this acid. Although the methoxy group in the structure of p-methoxycinnamic acid is a hydrophobic group, in the range of pH = 2-4 the efficiency of physical extraction of this acid is much lower than that of cinnamic acid, becoming superior only for pH values higher than 4.



**Fig. 1.** Influence of initial aqueous phase pH on reactive extraction efficiency of a) cinnamic acid and b) methoxycinnamic acid with and without phase modifier

For all studied systems, the addition of 2-octanol into the solvent phase led to the improvement of extraction efficiency, the most important effect being recorded for cinnamic acid and for the solvent with the lowest polarity (n-heptane) the extraction degree being  $\eta = 93.5\%$  compared to  $77\%$  without 2-octanol. Also, according to the analyzed data, the extraction system that provides the highest extraction degree ( $92\%$ ) for the separation of p-methoxycinnamic acid by synergic reactive extraction consists of dichloromethane,  $10\%$  2-octanol and  $20\text{ g/l}$  tri-octylamine and a phase aqueous pH of 4.

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# Separation of biosynthetic products by pertraction using ionic liquids

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Pertraction is a process that uses a semi-permeable organic solvent layer between two aqueous phases (feed phase and the stripping), that allows the selective transport of a solute between the aqueous phases. This method combines in one equipment an extraction and stripping process. There are three main types of liquid membrane: emulsioned – ELM, supported – SLM and bulk – BLM, with the following mechanism:

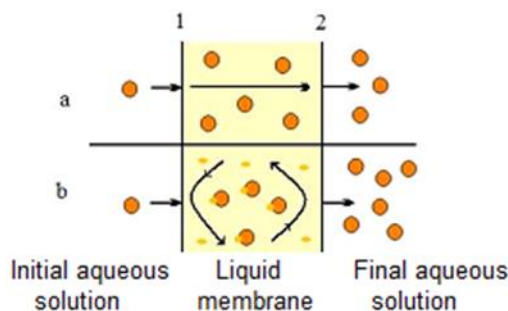


Fig. 1. Schematic representation of liquid membrane separation process

Liquid membranes are homogeneous membranes, in which the biosynthetic product is dissolved at the contact interface between the feed phase and the liquid membrane and releasing it at the interface between the membrane and the stripping phase, based on the concentration gradient between interfaces. Several carboxylic acids have been separated using pertraction with ionic liquids (Table 1).

Table 1. Carboxylic acid pertraction with ionic liquids

Carboxylic acid	Ionic liquid	Type of membrane	Obs
lactic acid	(triethyl- (tetradecyl) phosphonium bis 2,4,4-trimethylphosphinate, Cyphos IL-104	SLM	global mass transfer coefficient to increase by 50 to 70%.
	tetramethylammonium acetate [TMAm][Ac]	ELM	94.50% lactic acid separation
	tri-n-octylmethylammonium chloride, [TOMAC]	ELM	90% extraction efficiency
levulinic acid	1-Hexyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide [HMIM][Tf2N]	BLM	98.63% and 90.92 stripping efficiency
succinic acid	1-butyl-1-methylpyrrolidinium bis(trifluoromethyl sulfonyl)imide	SLM	$1.5 \cdot 10^{-6}$ m/s membrane permeability
acetic acid	1-Butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide [BMIM][Tf2N]	BLM	92.38% extraction efficiency and 80.55% stripping efficiency

All membrane types were used for carboxylic acids separation using either only ionic liquid or a mixture of ionic liquids. Compared with conventional solvents it can be concluded that ionic liquids are important alternatives to be considered for further improvement of carboxylic acid separation process.

## Acknowledgments

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**BOOK OF ABSTRACTS**

**Section 3 Environment and Sustainability**

## Application of membrane separation and adsorption for nutrient recovery from dairy waste waters

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Among the current environmental challenges facing humanity is the protection of water in quantity and quality. The objective of reduce to zero the generation of waste in productive activities by applying the concept of circular economy has led to the emergence of proposals for the production of biomaterials capable of contributing to environmental protection and that do not imply huge investments of money.

As a good example of these proposals, biochar had to be mentioned which is a material with excellent adsorbent properties, with low production costs and that is made with any type of organic matter such as agricultural waste. In this work a nanoparticle-modified ultrafiltration membrane was used as a pre-treatment method prior to ammonium adsorption.

As adsorbent for ammonium removal alkaline modified biochar produced from banana leaves were used. The characterization of biochar and the research about kinetics and isotherm models obtained after batch experiments. The general results obtained after the combination of membrane filtration and adsorption are promising and reflect a satisfactory ammonium removal percentage, and these results prove that biochar would be a good adsorbent for nutrient recovery from wastewaters.

## Investigation of filtration properties of dairy wastewater

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The food industry, such as the dairy industry generates the large volume of wastewater due to the high water consumption during technological operations, washing and cleaning. Dairy wastewater has high biochemical and chemical oxygen demand, high in organic matter mainly due to carbohydrates, proteins and fats from milk. It also contains minerals, phosphates, ammonia, cleaning chemicals and detergents so it requires proper care. Many different methods such as biological and physico-chemical methods are used to treat dairy wastewater efficiently but they have their disadvantages (high operating costs, high space requirements, operational difficulties). Membrane technologies are promising methods to treat dairy wastewaters. The main disadvantage of membrane filtration in dairy wastewater treatment is membrane fouling, which causes flux decline, decreased membrane life-time, and increased operational cost.

One way to reduce the fouling is to increase the surface shear rate of the membrane. The method for increasing shear rate is to change flow properties (stirring and using 3D printed spacers). 3D printing technology is an emerging and promising technology to create an object through a layer-by-layer fabrication method. 3D printing technology and membrane module design, it could potentially address the membrane fouling problem through the optimization of spacers to increase mass transfer and reduce the concentration polarization at the membrane surface. 3D printing technology could possibly revolutionize the current design of membrane modules and potentially reduce the energy consumption and chemical usage in the wastewater treatment.

Ultrafiltration (UF) experiments were performed model dairy wastewater with different transmembrane pressures (0.2, 0.3 and 0.4 MPa) and stirring velocities (200, 300 and 400 rpm). Polyethersulfone (PES) UF membranes with molecular weight cut-off (MWCO) of 50 kDa and polylactic acid (PLA) 3D printed spacer configurations were used. The permeate flux values, resistances and membrane rejection were examined and the effect of spacer was observed.

### Acknowledgments

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# Numerical modeling and logical scheme for managing the environmental impact of a large combustion plant

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The present paper presents the results of a computational simulation of coal reburning in any powdered coal boiler from a large combustion plant (LCP). The numerical modeling was developed in order to analyze the environmental impact of varying the main work parameters (which will be presented below), with the aim to minimize this impact.

More specifically, the nitrogen oxides emissions reduction, as well as the carbon loss, were analyzed under different circumstances, so that this study allowed us to notice which ones are the best values for the work parameters of each powdered coal boiler of the LCP, by following a simple logical scheme that we shall propose within this paper.

The main zones of the boiler are: at the bottom – the primary combustion zone (where main coal is fired, together with primary and secondary air, through the main ports), in the middle – the reburning zone (where reburn coal is added, together with reburn air, through the reburning nozzles, in order to create oxygen-deficient conditions for reducing the nitrogen oxide produced in the primary combustion zone) and at the top – the burnout zone, in which overfire air (OFA) is added to complete the combustion, through the OFA ports. Each of these three zones has a stoichiometric air ratio (SR<sub>1</sub>, SR<sub>2</sub> and SR<sub>3</sub>), determined by the different air flows. Numerical modeling of the coal reburning was conducted with Computational Fluid Dynamics (CFD), by using CHEMKIN-CFD 4.1 software tool. The global nitrogen oxides reduction rate can be expressed as:

$$\frac{d[NO]}{dt} = -k[CH][NO] - k'[CH_2][NO] - k''[CH_3][NO] \quad (1)$$

The amount of NO that is produced during combustion may be characterized by a stationary state transport equation:

$$\frac{\partial}{\partial x_i}(\rho u_i Y_{NO}) = \frac{\partial}{\partial x_i}(\rho D \frac{\partial Y_{NO}}{\partial x_i}) + S_{reburning,NO} \quad (2)$$

in which  $x_i$  represents the coordinate in general index-notation (m),  $u_i$  – the time-averaged velocity component (m/s),  $\rho$  – the density (kg/m<sup>3</sup>),  $D$  – the diffusion coefficient,  $Y_{NO}$  – the mass fraction of NO in gas phase, whereas  $S_{reburning,NO}$  indicates the source term for NO associated with the reburning reactions:

$$S_{reburning,NO} = M_{NO} \frac{d[NO]}{dt} = -M_{HCN} \frac{d[HCN]}{dt} = -S_{reburning,HCN} \quad (3)$$

Let us denote by  $L$  the reburning zone length (distance between the OFA ports and the reburning nozzles), by  $h$  the reburning nozzles height (the distance between the reburning nozzles and the main ports), and let  $D_i$  be the inner diameter of the boiler. The first two important work parameters may be now defined: the relative reburning zone length,  $L_r = L/D_i$ , and the relative height of reburning nozzles,  $h_r = h/D_i$ . The reburning zone stoichiometric ratio, SR<sub>2</sub> (total air supplied reported to the total stoichiometric air requirements), is the third studied work parameter. The fourth work parameter to be specified is the amount of reburn fuel (ARF). Finally, the fifth parameter involved in this discussion is the the mean diameter,  $\bar{d}$ , referred to as „coal particles’ size” or „fineness”.

Two essential indicators of reburning performance will be investigated within this numerical model. One is the NO<sub>x</sub> emission reduction, denoted as NOR(%) and the other one is the carbon loss (loss on ignition), denoted as CL(%).

$$NOR = \frac{(NO_x)_{initial} - (NO_x)_{final}}{(NO_x)_{initial}} \cdot 100. (\%) \quad (4)$$

$$CL = \frac{m_{initial} - m_{final}}{m_{initial}} \cdot 100. (\%) \quad (5)$$

where  $(NO_x)_{initial}$  and  $(NO_x)_{final}$  are the nitrogen oxides emissions without and with reburning, respectively, whereas  $m_{initial}$  and  $m_{final}$  are the ash sample mass that will be investigated, before and after reburning. As these two indicators are the most relevant for reburning performance, and consequently for the environmental impact management of the LCP, it is obviously essential to propose a logical scheme for investigating the way that each of the five work parameter should be optimally chosen, so as to provide a high nitrogen oxides reduction, keeping a low carbon loss.

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## Enhancing the use of rotating biological contactors for medium-size communities

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By default, Rotating Biological Contactors (RBC) are used for small-size communities (Meena et al., 2021), i.e. less than 2500 population equivalent, but there are places where they were built for larger communities. An example is Agnita, a Romanian town with near 10000 inhabitants. Because of this number, for the time being, according to European and Romanian norms, there should be no requirements in what the removal of nitrogen and phosphorus concern, but the Local Water Authority has decided that not only organic matter and total suspended solids should be removed to comply with the maximum admitted concentrations, but N and P too.

Because RBCs are aerobic reactors, creating an environment for denitrification is almost impossible, so other solutions must be chosen. The one we have applied, based on our previous expertise at WWTP Medias (Gaspar et al., 2022), is the use of FeCl<sub>3</sub> 40%, with continuous dripping.

The good results after one year of application of this method are comparable with those of Waquas et al. (2021) or Cvetkovic et al. (2014).

We have also defined the elimination power of FeCl<sub>3</sub>, as defined by Gaspar et al. (2022), an example of its variation being presented in Fig. 1.

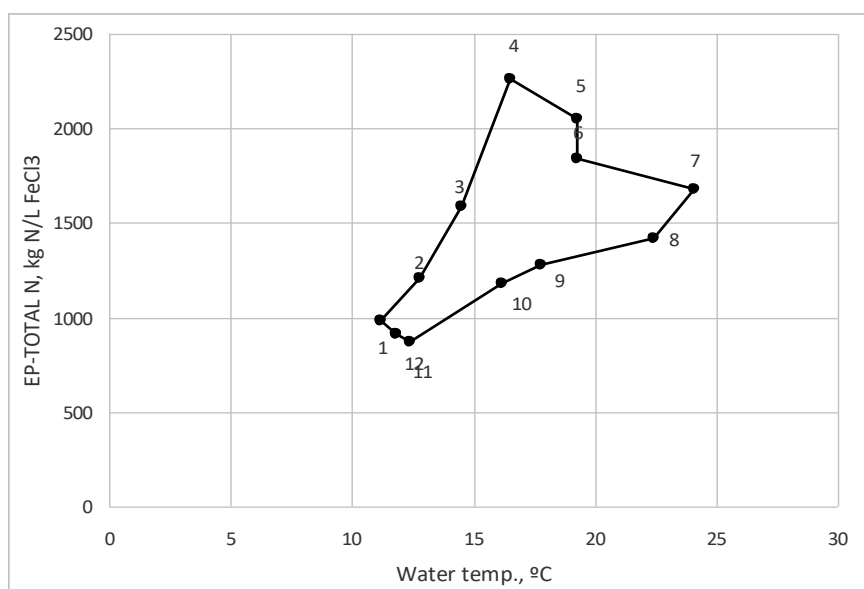


Fig. 1. Elimination capability of FeCl<sub>3</sub> for total nitrogen

The preliminary results enable us to continue the use of FeCl<sub>3</sub> in this RBC, for reducing BOD, COD, TSS and especially total nitrogen and phosphorus.

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# Sheep wool waste – environmental impact and valorisation possibilities

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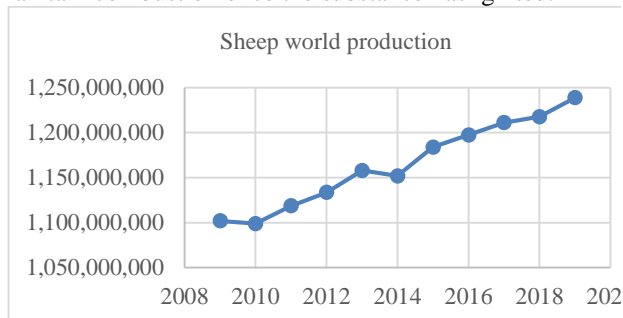
Sheep wool is an organic, long-lasting, widely available, and renewable material. Sheep's wool is 95% pure keratin; the remaining 5% is made up of hydrocarbons and other materials. Over 20 different kinds of amino acids may be found in wool fibre, which is a fibrous, keratinous protein. Depending on the breed of sheep, the wool fibre's diameter ranges from 11.5 to 47 $\mu$ m, and in sheep wool, 40% of the amino acids are hydrophilic and 60% are hydrophobic.

All more than 20 types of amino acids are side chain representations, except for one chain, having the formula,  $^+\text{NH}_3\text{-CHR-CO}_2^-$ . When the amino group of one molecule condenses with the carboxylic group of the second molecule to form an amide (or peptide) bond, a dipeptide is formed, with the formula,  $^+\text{NH}_3\text{-CHR-CO-NH-CHR-CO}_2^-$ . Condensation with another amino acid forms a tripeptide, and the process continues to form a polypeptide chain.

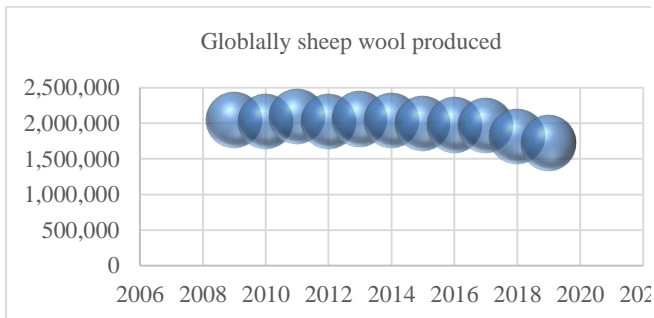
**Table 1.** Parameters of wool fibre (N. A.G. Johnson, 2003)

Parameter	Value
Crystallinity (%)	47.8
Moisture regain (%)	13 – 18
Specific gravity (g/cm <sup>3</sup> )	1.28 – 1.32
The temperature that wool fibres are thermally stable up to (°C)	150
Limit oxygen index (LOI) (%)	25
Thermal conductivity (mWm <sup>-1</sup> K <sup>-1</sup> ) at 0% moisture regain	194
Thermal conductivity (mWm <sup>-1</sup> K <sup>-1</sup> ) at 30% moisture regain	290

Wool is the most burn-resistant of all the regularly used textile fibres. It burns quickly, spreads slowly, and is difficult to ignite. Wool will be among the last materials to ignite in a fire because of its high ignition temperature. A high limit oxygen index (LOI) suggests a material that is challenging to ignite since it gauges the oxygen concentration needed to maintain combustion once the substance has ignited.



**Fig. 1.** Sheep world production



**Fig. 2.** Globally sheep wool produced

Huge quantities of useless wool are discharged, burned, or simply left on the ground due to weak laws, which pollute the environment. Due to the enormous volumes that have been gathered and the challenges in developing solutions for its effective treatment, wool waste is one of the main solid wastes that is causing rising concern. This work will highlight the structure and properties of the sheep wool, its impact on the environment if left as waste, and the possibility to be valorised taking into account its keratin-rich structure and the property of burn resistance.

## Acknowledgments

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# Using Python multi-paradigm programming language in monitoring the concentration of the main toxic metals within suspended particles – case study: Craiova, May 2022

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As the modern society nowadays considers air pollution with suspended particles (which contain toxic metals as Pb, Ni, As and Cd) as a priority environmental policy, the present paper aims to present the results of a case study performed during May 2022 in Craiova (one of the major Romanian cities) consisting in determining the concentrations of these metals within TSP (total suspended particles) and PM<sub>10</sub> (suspended particles having the diameter less than 10 microns) and then comparing the experimental results – processed by statistical means – with the values provided by the local Environmental Protection Agency during the investigation period.

The experimental part consisted in: taking samples (in two determined points of the city) represented by daily changed filters (20 samples for PM<sub>10</sub> and 24 for TSP), mineralization of these filters and spectrophotometric analysis of the heavy metals from the solutions obtained after mineralization, using the AAS technique (with specialized software).

The values obtained by our application were displayed as arrays, in order to use Python multi-paradigm programming language to determine the main statistical parameters, as to monitor pollution with toxic metals within PM<sub>10</sub>/TSP.

As an example, we now present the results obtained for nickel. The arrays obtained for this metal are given below:

Ni\_TSP = np.array([13.8, 14.5, 13.8, 14.1, 13.7, 13.6, 13.8, 14.3, 14.1, 13.6, 13.9, 13.5, 13.8, 14.2, 14.0, 13.9, 13.6, 13.7, 13.5, 13.9, 13.4, 13.4, 13.0, 13.3])

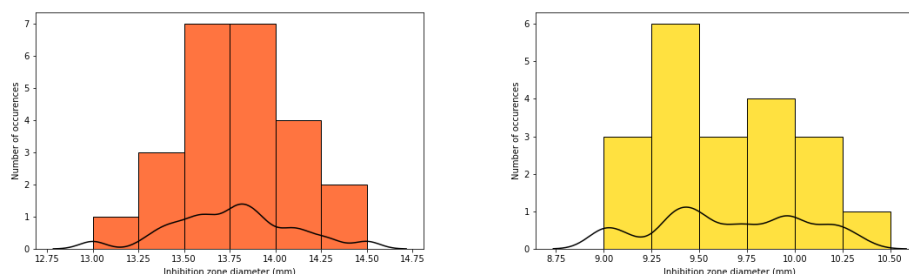
Ni\_PM10 = np.array([9.9, 9.3, 9.4, 9.4, 9.7, 10.2, 10.4, 9.9, 9.2, 9.2, 10.2, 9.2, 9.3, 9.4, 9.7, 9.9, 9.4, 10.0, 9.7, 9.9])

For each array reported above, we used Python multi-paradigm programming language to determine the following six statistical parameters, which are the most representative in order to minimize the experimental errors.

**Table 1.** Statistical parameters determined by using Python for the arrays containing the concentrations of nickel in TSP/PM<sub>10</sub>

Statistical parameter	Ni_TSP	Ni_PM10
mean	13.77	9.67
median (the second quartile)	13.8	9.7
standard deviation	0.34	0.37
empirical standard deviation rule interval	[13.09, 14.45]	[8.93, 10.41]
variance	0.12	0.14
confidence interval	[13.65, 13.89]	[9.53, 9.81]

The Fig. shown below presents the situations referred to (provided curve represents the kernel density estimate).



**Fig. 1.** Plots afferent to the arrays containing the concentrations of nickel within TSP (left) and PM<sub>10</sub> (right)

In our examples, it shows that the concentrations of nickel, whose lower and higher assessment thresholds are 10 and 14 ng/m<sup>3</sup> respectively, appeared to be between these two thresholds for TSP and lower than them both for PM<sub>10</sub>.

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# Response of *Medicago sativa* plant to zinc pollution and the opportunity of its use in phytoremediation

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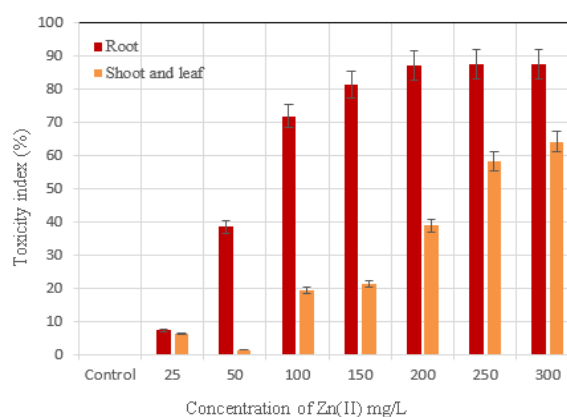
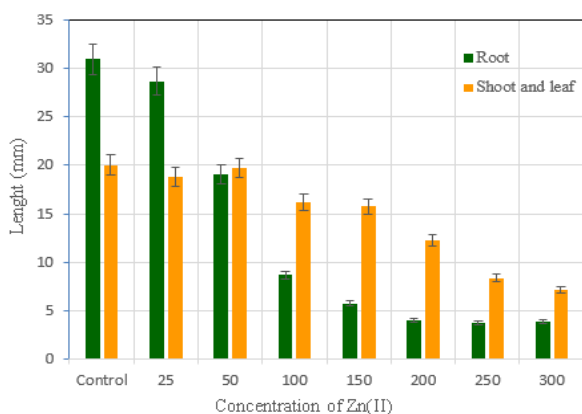
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One of the great problems of the 21st century is the accelerated spread of pollution, which has emerged as a consequence of industrial unsustainable development. The implications of widespread pollution produce imbalances in both the aquatic, terrestrial and air environments. Given these considerations, both flora and fauna can be contaminated with various pollutants, and ultimately human health can be endangered.

Zinc is an essential metal element for plants, but it can become toxic in high concentrations, so exposing plants to high concentrations of zinc can lead to alteration of plant components, chlorosis or inhibition of their growth (Yahaghi et al., 2019). Given this, the purpose of the paper is to examine the effects of zinc on *Medicago sativa* (alfalfa), in the range of concentrations 25-300 mg/L Zn(II), by performing phytotoxicity tests, in laboratory conditions.

Our research has shown that the development of *Medicago sativa* was inhibited by high concentrations of Zn(II) (Fig.1), the toxicity of the metal being about 10% for the concentration of 25 mg Zn(II) /L, and about 90% for the concentration of 300 mg Zn(II) /L (Fig. 2). The phytotoxicity tests confirmed the possibility of using *Medicago sativa* in phytoremediation, through the visible and quantified effects, appeared after the contamination.



**Fig. 1.** Influence of Zn(II) on the length of the root, shoot and leaf of *Medicago sativa*

**Fig. 2.** Toxicity index on the length of the root, shoot and leaf of *Medicago sativa*

Future experiments will be the subject of a study regarding the development of this species in vegetation vessels containing contaminated soil for a detailed view on the use of this plant for the phytoremediation of soils polluted with Zn(II).

## Acknowledgments

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## Comparative sustainability assessment of using inactive vs. active microbial biomass for Cd(II) ions uptake from wastewaters

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Heavy metals remain to this day one of the most impactful category of pollutants. Their increasing presence in the environment correlated with industrial development and bioaccumulation in living organisms has determined significant negative effects. Although conventional sorbents can remove metal ions from wastewaters, their performance at low concentrations is not as high as that of biosorbents based on microbial biomass. Moreover, according to scientific literature, conventional sorptive materials are expensive to produce. In spite of the thoroughly analyzed efficiency of microorganisms in metal uptake at laboratory level, this type of biomass is not yet applied at large scale for wastewater treatment. In order to fulfill this milestone, it is important to carry out sustainability assessments as well. Their number is extremely low though (Filote et al., 2021). Therefore, the current work aims to compare and quantify the environmental impacts of Cd(II) removal from wastewaters using two microorganism species, *Arthrobacter viscosus* and *Trichoderma viride*, in both active and inactive form. Environmental impact quantification was performed by applying the Life Cycle Assessment (LCA) methodology according to international standards (ISO 14040, 2006 and ISO 14044, 2006) with the fulfillment of all mandatory stages: goal and scope definition, inventory analysis, impact assessment and interpretation. The environmental impact assessment was carried out in GaBi software, considering Recipe2016 method. The data were analyzed based on the established functional unit of 1 L of treated wastewater using inactive or active selected microorganism, given an initial concentration of 25 mg/L Cd(II). The environmental impact determined considering Recipe method showed the highest total environmental impact for the biosorption of Cd(II) by *T. viride* (91.5 pers. equiv.), while the lowest was obtained in case of bioaccumulation of Cd(II) using *A. viscosus* (7.27 pers. equiv.). In terms of impacts per category, the highest value was identified for the impact category Ionizing radiation (IR) for all scenarios with the exception of the bioaccumulation process using *A. viscosus*, in which case the highest impact was determined for Climate Change Terrestrial Ecosystems (CCTE) and Climate Change Freshwater Ecosystems (CCFE) impact categories. Electricity had the highest contribution to the total environmental impact among the used resources. Also, among the processes included in the analyzed scenarios, the highest value for electricity consumption was identified in case of the biomass preparation phase for Cd(II) uptake by *Arthrobacter viscosus* through biosorption and bioaccumulation, respectively. Thus, considering the overall results it can be concluded that the best scenario in terms of environmental impact for Cd(II) uptake is the scenario that considers the bioaccumulation process using *A. viscosus* as biosorbent. The current study successfully contributes to the scale-up of more eco-friendly and cost-effective wastewater treatment methods for the removal of heavy metals such as Cd(II) and to the development of the bioeconomy.

### Acknowledgments

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## Studies on the behavior of *Amaranthus retroflexus* L. growing on agricultural soil polluted with nickel ions

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Various anthropogenic activities (mining, electronic, pesticides and fertilizers, burning fossil fuels, waste disposal) lead to the release of nickel into soil. The presence of nickel in soil in high concentrations can further affect the soil fertility, the growth and development of plants, and finally its bioaccumulation through the food chain may induce negative effects on human health. The use of plants for removal of heavy metals became a feasible solution, especially due to lower costs involved compared to physico-chemical methods. Several plants possess the ability to tolerate and to remove nickel ions from soil. *Amaranthus retroflexus* L. (redroot pigweed) is one of the most widespread plant in the world with a high adaptability under different environmental conditions, being a fast-growing plant that can growth until 3 m height providing a tall aerial biomass which gives it efficient capacities for bioaccumulation of pollutants (Wang et al., 2018). Literature studies reported the redroot pigweed as a suitable plant for phytoremediation of soils polluted with nickel, cadmium, chromium, copper and other heavy metals (Khoramnejadian and Saed, 2015). In this context, we tested the tolerance of *Amaranthus retroflexus* L. in the presence of nickel ions in soil at different concentrations (10 mg/kg-500 mg/kg). The experiments were carried out in triplicate, in pots (height 13 cm, inner diameter 14.5 cm) containing 1000 grams of soil (ratio 2:1, agricultural soil : sandy soil). The plants were grown during 12th of August until 21th of September 2021 in greenhouse conditions. After 39 days, the roots and shoots length and biomass content were measured. The results showed that the highest concentration (500 mg/kg) was toxic since the seeds of redroot pigweed did not germinated. But in the range of concentrations between 10 mg/kg-300 mg/kg, the growth of plants was not significantly affected by nickel ions presence in soil, while in case of shoots a slightly decrease was observed where the tolerance index was between 87%-91%.

In conclusion, *Amaranthus retroflexus* L., can develop a good tolerance to nickel ions in the range of metal concentrations between 10 mg Ni<sup>2+</sup>/kg soil - 300 mg Ni<sup>2+</sup>/kg soil, and may be successfully applied in phytoremediation of moderated nickel polluted soil.

### Acknowledgments

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# Heavy metals toxicity on the development of *Sinapis alba* (white mustard): Preliminary studies for establishing its phytoremediation potential

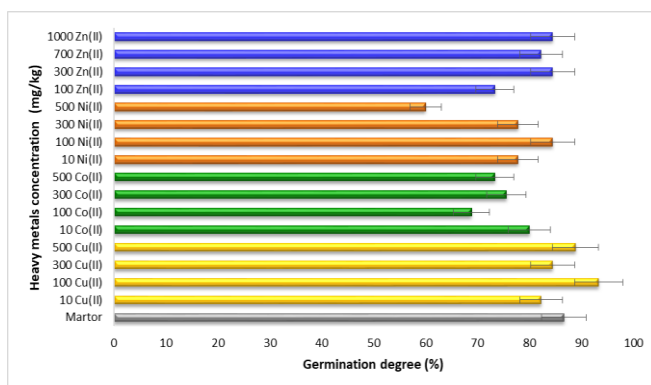
G.-M. Fînaru Chelaru<sup>1</sup>, P. Cozma<sup>1\*</sup>, M. Minuț<sup>1</sup>, I.-C. Vasilachi<sup>1</sup>, M. Paiu<sup>1</sup>,  
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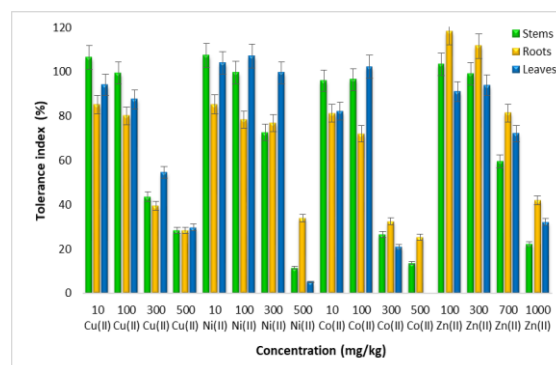
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Heavy metals are natural components of the earth's crust and essential elements, some of which are considered trace elements for maintaining the metabolism of the human body (eg. copper, selenium and zinc). However, at concentrations exceeding natural values, heavy metals are known to be toxic and / or carcinogenic. Among the bioremediation processes applied for the decontamination of polluted sites with heavy metals, phytoremediation is one of the economically and ecologically feasible alternatives applied to date. Phytoremediation is a bioremediation technology that uses plants to reduce the amount, toxicity and mobility of pollutants in the soil through various mechanisms. Thus, some plants developed effective strategies and mechanisms for survival in heavily polluted site, being widely used in phytoremediation/phytomining of polluted soils. In this regard, our work tested the ability of *Sinapis alba* (white mustard) to tolerate and grow in soil polluted with Cu(II), Co(II), Ni(II) and Zn(II) ions in different concentrations (10, 100, 300, 500, 700, 1000 mg/kg soil). The plants were grown in pots containing 1000 grams of urban soil collected from Iasi city area. Ten seeds / plant species / pots were sown at a depth of about 2-3 cm in the soil. After sowing, 5 seedlings per pot (the most vigorous) were preserved. The experiments were performed in greenhouse conditions for 41 days. A thermal regime of 25-30°C during the day and 15-20°C during the night was ensured. Our results showed that Cu(II) and Zn(II) in high concentrations (100-1000 mg/kg soil) induce positive effects on the germination of mustard seeds (Fig. 1). Obvious effects of stress on the germination degree of mustard seeds occurred for Co(II) and Ni(II) at concentrations of 300-500 mg/kg. At higher concentrations (Cu(II) and Co(II): 300-500 mg /kg; Ni (II): 500 mg/kg and Zn (II): 1000 mg /kg), all these metals negatively affect the plant development in terms of roots, stems and leaves length and the effects become more and more visible as the concentration of metals increases (Fig. 2). In conclusions, it can be said that *Sinapis alba* can be effectively used for phytoremediation of soil polluted with heavy metals at moderate concentrations.



**Fig. 1.** Effects of heavy metals ions on white mustard seeds germination degree (error bars represent the percentage error)



**Fig. 2.** Effects of heavy metals ions on the relative increase in length of the roots, leaves and stems of white mustard (error bars represent the percentage error)

## Acknowledgments

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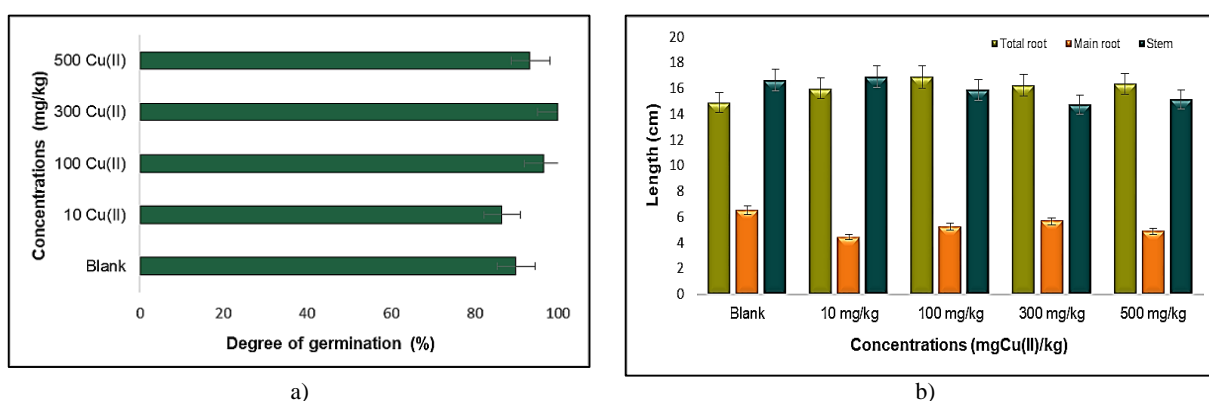
## A study of the use of alfalfa (*Medicago sativa* L.) for the phytoremediation of soil polluted with copper

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Soil contamination with heavy metals is a growing environmental problem, with serious threats to the environment and living organisms. Phytoremediation is a sustainable, widely used technology that offers safe ecological solutions. The use of green plants as hyperaccumulating agents for heavy metals has proven to be advantageous in terms of feasibility, cost and is environmentally friendly. For an efficient applicability of phytoremediation, the selection of plants with a high tolerance to metal ions, a high bioaccumulation factor and a rapid growth is necessary. Therefore, this paper has the main objective of investigating the tolerance of alfalfa plant at different concentrations of copper. For this purpose, a greenhouse experiment was performed in pots, in the concentration range of 10-500 mgCu(II)/kg, to analyze the rate of phytotoxicity of Cu(II) ions in the soil on seed germination, degree growth and development of plant components, as well as color changes and their deformation, but also the biomass yield, over an experimental period of 8 weeks. The experiment found that the seed germination rate was over 87%, alfalfa being insignificantly affected by the presence of Cu(II) ions, and the growth of plant components indicates a relatively weak negative effect on stem growth with increasing soil concentration. In the case of roots, a slightly higher growth was found in the selected interval, compared to the control sample, despite the fact that the root system is the first organ to come into contact with metal ions (Fig. 1).



**Fig. 1.** Effects of Cu(II) ions on: a) the degree of seed germination b) the growth and development of the alfalfa plant components

Due to its acceptable tolerance to Cu(II) toxicity, alfalfa (*Medicago sativa* L.) can be considered a bioaccumulator for this metal. Biomass can be processed as a secondary source of raw materials for Cu(II) extraction by chemical and thermal methods.

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# Measurement of key compositional parameters in three type of biomass wastes in order to define the appropriate feedstock for thermochemical conversion

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Biomass wastes are considered as feedstocks for the production of bio-based chemicals or fuels through thermochemical conversion. When the ultimate goal of conversion is the obtain of porous carbon rich materials, two processes have to be considered: hydrothermal carbonization (HTC) and pyrolysis. HTC uses heat to convert wet biomass to hydrochar. Some of HTC advantages including no requirement for pre-drying, low carbonization temperature (180–350°C) and air pollution avoided by the dissolution process. Pyrolysis is a thermochemical decomposition of organic material in the absence of oxygen and can be operated as conventional/slow pyrolysis, fast pyrolysis and ultra-fast/flash pyrolysis with temperatures starting from 400 °C to 1000 °C and residence time between 0.5 sec to 30 min. The distribution and quality of the products (bio-oil and biochar) depend on effective control of process parameters.

A good match of appropriate feedstocks and conversion process is crucial for a well-functioning thermochemical system (Robbins et al., 2012). However, the choice of suitable biomass type for thermochemical conversion has received little attention. The paradigm within which biologists analyze biomass is different than that of engineers discussing feedstocks for thermochemical processes (Tanger et al., 2013). But an overlap between paradigms and a good knowledge of key compositional parameters of feedstocks might result in reduced pre-and processing costs as well as maximized yields.

This paper focuses on a comprehensive characterization of three type of biomass wastes with a large availability in the central-east part of Europe: spruce bark (a woody primary and secondary residue from forestry and wood processing), vine shoots and steams (a woody biomass resulted as waste from vineyards) and wheat straws (agricultural waste harvest from arable and permanent cropland). Chemical (proximate and ultimate analysis), biochemical, trace elements, and thermal analyses were conducted. Furthermore, Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) are undertook to point out the structural characteristics of the feedstocks. Additionally, this assess provides an overview of the available quantities which are annually renewable.

The data were corelated with the conversion degree and/or yield in solid phase in order to highlight a better and an easier path for choosing the appropriate feedstock for thermochemical conversion conducted for the obtain of carbonaceous materials. We suggest that the lignin level have an important impact on thermochemical conversion as well as a reduce ash and moisture (only for pyrolysis). Also, the ultimate analysis and associated properties might be more feasible than biochemical analysis. Moreover, the pretreatments (grinding and grindability of the feedstock) impacted the properties of carbonaceous final products (biochar and hydrochar) and consequently their further application as carriers for bacterial immobilization, plant growth promoter, soil amendment, adsorbent substrate for pollutant removal and precursors for high porous materials used for alternative energy storage.

Expanding the knowledge on feedstocks traits will play a critical role in the thermochemical conversion of biomass.

## Acknowledgements

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## Preliminary study on the effect of cobalt and nickel ions on the growth and development of *Brassica napus* (rapeseed)

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The study of heavy metal contaminated soil pollution is highly topical and has become a serious worldwide concern. The release of toxic heavy metals such as cobalt (Co) and nickel (Ni) in high concentrations into the environment has become a major pollution problem affecting soil quality, posing a threat to ecosystems and ultimately to human health. Phytoremediation is a plant-based approach that involves using plants to extract and remove elemental pollutants or to reduce their bioavailability in soil. This method is recommended as successful in remediating soils polluted with toxic heavy metals in a cost-effective manner. Thus, certain categories of plants have demonstrated an extraordinary ability to tolerate and remove heavy metal pollutants from the affected environmental components. In this context, the fundamental objective of this work is to evaluate the growth and behaviour of *Brassica napus L.* (rapeseed) in the presence of cobalt and nickel ions in soil. In the experimental program, rapeseed was exposed to synthetic contamination with Co(II) and Ni(II) solutions using polypropylene pots containing 15 g of soil and 10 mL of metal solution in the concentration range of 50-1000 mg/kg soil. The experiments were carried out under laboratory conditions for 20 days.

The toxicity of cobalt and nickel ions on the growth and development of rapeseed was assessed by taking into account phenological observations and determinations based on different growth indicators: seed germination rate, elongation rate (tolerance index) of the root system and aerial part of the plant. The results showed a higher growth rate of root length when Ni(II)-contaminated solutions were applied compared to Co(II) solutions. It was observed that, at concentrations of 1000 mg/kg soil for both metals, the tolerance index (Er%) for rapeseed plant components (roots, stems, leaves) showed relatively similar values with no significant effects on the plant. It was found that roots of the rapeseed plant displayed a higher tolerance to nickel compared to cobalt, while stems were more tolerant to cobalt ions.

In conclusion, we can consider *Brassica napus L.* a plant with potential for phytoremediation of soils polluted with cobalt and nickel ions at moderate soil concentrations.

### Acknowledgments

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## Food waste management: evaluation of the environmental, economic and social performances of some recovery alternatives

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Food waste loss is, without a doubt a serious problem nowadays, which arises, both during food production and processing, but also in terms of retail and consumption. Population contributes to food waste generation by buying food, which eventually ends up being discarded, either because it is spoiled, or because it is beyond its expiration date.

Climate change is compounded by pressure on food security, and some regions feel more stressed than others since droughts, fires or floods directly hamper the production capacity for food. Unfortunately, climate change often affects countries that are more vulnerable and may not have the means to adapt. In this context, food waste generation is a consequence of the inefficient and unsustainable use of natural resources and energy in production processes and other human activities, most often resulting in economic losses.

The purpose of this paper is to identify the most viable economic and environmental criteria required in food waste management resulting from the application of Cost-Benefit Analysis (CBA) and Life Cycle Assessment (LCA) to assess the environmental, economic and social sustainability of some food waste management scenarios. In the paper, two management scenarios are considered, for which economic and environmental criteria are analyzed: (i) recovery of food waste in the form of compost used as soil amendments; (ii) combined processing of food waste for both compost and energy. A number of basic principles are used to highlight the set of economic and environmental criteria, which reflect how to build a problem.

Both methodologies, CBA and LCA highlighted a series of environmental benefits, but also some economic and social performances, compared to the situation of unrecovered waste, because food waste is no longer stored, but is transformed into by-products and energy. The results of the study can help us in a better understanding the harmonization of circular economy with the priorities of sustainable development, and the measure the overall environmental benefits and impacts in energy and compost production from food waste.

### Acknowledgements

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## The assessment of Pesticide Contamination Index in soil

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Soil is the most complex and diverse ecosystem in the world and represents a basic natural resource which support human live. However, soil is a finite resource, and the pressure generated by human population growth, changing consumption models, demand for biofuel, limited land resources creating unprecedented pressure on soils, through the intensification of agricultural production by increasing of crop yield per unit of agricultural land.

For increasing the crops yield around 2.7 million tonnes of active ingredients are produced and applied annually worldwide. Moreover, it is estimated that only 0.1% of the pesticides applied for crops protection reaches the target pest and the main flux of chemical remains in the environment, with important consequences to soil, water and air. According to data reported by FAO in order to achieve global food security, food production must increase by 70% until 2050. It is well known that the maintaining the productivity in the ecosystems depends on their physicochemical and biological characteristics.

In this general context, these study is focused on the determination of *Pesticide Soil Contamination Index* (PSCI) using as model a representative organochlorine pesticide - pentachlorophenol (PCP). Pesticide contamination index is a tool developed to guide farmers in the application and appropriate dosage of organic pesticides, which has been developed at the EU and China level for increasing agricultural productivity and improving soil quality. PCP is considered one of the most recalcitrant chemicals present in the environment, due to its stable aromatic structure and chlorine atoms. For this purpose, has been used data obtained in experimental studies, the adsorption parameters and the Groundwater Ubiquity Score (GUS) index of PCP were determined for three different classes of soil, the results are presented in Table 1. PSCI index has been calculated on the base of specific indicators the *Indicator on Pesticide Persistency and Movement in soil* (PPMsoil) and the *Indicator on Soil Environmental Exposure to Pesticides* (EEPsoil).

**Table 1.** Pesticide contamination index (PCI)

<i>Pesticide</i>	<i>Soil type</i>	<i>Soil half-life (days)</i>	<i>Sorption coefficient (soil K<sub>oc</sub>)</i>	<i>GUS</i>	<i>Pesticide persistence and movement (PPM)</i>	<i>Environmental Exposure to Pesticides (EEP)</i>	<i>Pesticide Contamination Index (PCI)</i>
Pentachlorophenol	Cernisoil	2	1.14	1.1	Good	Good	Good
Pentachlorophenol	Protisoil	12	0.546	4.6	Bad	Bad	Bad
Pentachlorophenol	Andosoil	11	0.013	5.9	Bad	Bad	Bad

The results showed that for the same dose of pesticide applied onto soils with different chemical and mineral characteristics and using values of *GUS* score determined experimentally, very large differences appear. It is found that for soils with higher uptake capacity and low leaching score, the Pesticide Contamination Index has been classified “good”, while for soils with *K<sub>oc</sub>* values lower than 0.5 the PCI is classified “bad”, being associated with the worst scenario. The effects of soil contamination with PCP depend mainly on soil properties, as these have higher impact on the mobility/movement, uptake, bioavailability, half life time and dose of contaminants. Restricted limits must be established on the dosage and use on agricultural land of different classes of pesticides in correlation with soil types.

In conclusion, at global level there is an urgent need to raise awareness and to promote sustainable use of limited soil and land resources, using sustainable management solutions and developing new and complex tools to lead in decision-making in agricultural systems and to reduce the pressure exerted on soils.

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## Application of hydrogel based on tricarboxi-cellulose in vinyl alcohol matrix for Methylene Blue dye removal from aqueous solutions

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Adsorption techniques remain appreciated and selected methods for removing chemical pollutants from different environmental components. But the challenge is to find new types of adsorbents that meet the current requirements, respectively to have high efficiency of recovery, obtaining through economic processes, recyclability and reusability, chemical and physical properties that ensure adaptation to different adsorption systems, minimum impact on the environment after exhaustion. In this context, attention is increasingly focused on renewable resources.

Being a renewable resource, cellulose still remains a serious candidate for obtaining various types of biomaterials with adsorption properties, due to their physical, mechanical and chemical characteristics which are dependent on the technological process used for their synthesis, thus being able to be modeled according to the needs/requirements.

A category of surface water pollutants is represented by the organic dyes resulting from both the textile industry and the chemical synthesis industry. The dangerous action of dyes on the aquatic environment can also be the result of the toxic effect due to the accumulation in time in fish or other aquatic life, the decomposition of pollutants into carcinogenic or mutagenic compounds and the poor biodegradability in aerobic conditions. Due to their synthetic nature and mainly aromatic structure, most dyes are non-biodegradable (refractory), having carcinogenic action or causing allergies, dermatitis, skin irritation or various mutations.

As a material with sorptive properties we selected for the study a hydrogel obtained by introducing tricarboxi-cellulose as a key component, in the polyvinyl alcohol matrix, called Ox25C.

As a dye we selected the cationic dye Methylene Blue. We studied its sorption present in aqueous solutions, in static regime and we followed the influence of some physico-chemical parameters, such as the amount of adsorbent, contact time, initial concentration of dye, pH and temperature. The behavior of the adsorbent was studied by analyzing SEM images and FTIR spectra. The sorption balance has been studied on the basis of isotherm models of Freundlich, Langmuir and Dubinin – Radushkevich.

The obtained results prove that the studied sorbent based on cellulose and polyvinyl acid (Ox25C hydrogel) can be considered as an adsorbent, with medium adsorption capacity for cationic dyes removal from aqueous medium. They also encourage the research extension in the direction of the adsorption equilibrium study in order to obtain useful information for extending the process at a large scale, and also to study the adsorption of other organic pollutants (such as drug) or inorganic species, such as metallic ions.

## Application of two residual biomass types as biosorbent for removal of textile dyes and heavy metals from aqueous effluents

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In the present times, water remains a permanent concern of the modern society and its good quality a key issue of the integrated water management system in region where the diminishing of natural water quantity and quality became a significant problem.

To save fresh water and reuse/recycling of the treated wastewater onsite of the company emplacement became an almost required target. For the reuse/recycle of treated wastewater in a productive activity or direct discharge in an aqueous receptor, specific qualitative and quantitative standard norms are taken into consideration in association with the imposed legal requirements/measures stipulated in the company compliance plan.

An important wastewater treatment step is actually based on adsorption/biosorption, and thus the application of two types of residual biomass, i.e. pine sawdust and residual algae-based material as specific biosorbent for organic dyes and heavy metals removal from aqueous effluents, was considered and the experimental findings discussed considering the type of process mechanism, its kinetic and thermodynamic aspects in association with the biosorption performance.

Therefore, the influence of several process operating variables as pH, residual biomass concentration, initial pollutant concentration, temperature, contact time, type of pollutant, type of biosorbent and its activation form (free or immobilized form) were discussed and the biosorption efficiency comparatively underlined for selection of alternatives considering the very good biosorption efficiency with minimal costs.

The experimental data underlined that the abovementioned two residual biomass-based biosorbents are considered as efficient in static operating systems, for aqueous effluents with moderate concentrations of pollutants (organic dyes and heavy metals).

## Investigation on *Spirulina platensis* development under heavy metal ions exposure

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Pollution of the aqueous streams with toxic and persistent compounds such as heavy metal ions is an important environmental issue, as it can affect the human health and the aquatic life. Particularly, microalgae are common microorganisms of the aquatic ecosystems that could be directly influenced by the heavy metal pollution. In this study, a microalgae model (*Spirulina platensis*) was grown in a Zarrouk culture supplied with nickel acetate (as a heavy metal source model), in order to determine the development of the microalgae under different heavy metal concentrations. Batch experiments in Erlenmeyer flasks were performed and the response of the microalgae to the heavy metal presence was observed by the determination of several development indicators such as the biomass production, the protein content and the settling index.

The variation of these indicators was more or less affected by the investigated nickel concentrations. Extending the study to the investigation of *S. platensis* response to the presence and of other heavy metal ions could provide key elements in defining the tolerance and inhibition levels of such microalgae in contaminated environments, which are important for the maintaining of an adequate aquatic ecosystem equilibrium or developing alternative options for heavy metal uptake from contaminated streams.

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# Adsorption of methylene blue (MB) and basic red 9 (BR9) in binary solutions using rice husk: factorial design analysis

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Dyes wastewater from the textile industry is highly toxic and carcinogenic (Sharma et al., 2018). They decrease the environmental quality and relate to various diseases in animals and humans (Khan and Malik, 2018). Wastewater treatment technologies are needed to reduce pollutants from dye wastewater. Adsorption is an excellent method for removing dyes from wastewater because of the simple design and lower processing cost (Cai et al., 2019). Today, research about material from agricultural waste for wastewater treatment is still under development; one of the potential resources is rice husk. Rice husk could become a material for wastewater treatment that is low-cost, efficient, and environmentally friendly. This study was performed to investigate the adsorption of methylene blue and basic red 9 in binary solutions using various rice husks.

The batch adsorption method was used to determine the equilibrium time and effect of initial concentration on MB and BR9 adsorption by Hungarian Rice Husk (HRH) and Indonesian Rice Husk (IRH). For this purpose, 250 mL of dye binary solutions 30 mg/L was stirred at 100 rpm with 500 mg dose, pH values 7, and at a constant temperature of 25 °C. To identify the most important factors affecting the removal of MB and BR9 by HRH and IRH, 23 factorial designs (three factors each, at two levels) with the Minitab 21 software was used. The initial concentration of dye binary solutions (30 mg/L), contact time (60 min), and stirring speed (100 rpm) were kept constant, and the three factors of the adsorbent type, pH, adsorbent dose were varied at two levels, as shown in Table 1.

**Table 1.** Levels of parameters used in the factorial design for binary solutions

Parameter	Coded symbol	Low level (-1)	High level (+1)
Adsorbent type	A	IRH	HRH
pH	B	3	7
Dose	C	250	500

Factors that influence the adsorbed percentage of these dyes onto the two types of rice husk were evaluated by using factorial plots: main effect, interaction effect, Pareto, and normal probability plots. The result shows, interaction between Adsorbent type\*pH\*Dose effects have insignificant for both dyes. Thus, it can be discarded. At the same time, all MB and BR9 effects were significant except for interaction between Adsorbent type\*Dose effect in BR9. In addition, the model presented an adjusted square correlation coefficient R<sup>2</sup> (adj) of 99.89% for MB and 99.70% for BR9. The dyes removal efficiency could be expressed, after discarding Adsorbent type\*pH\*Dose effects using the following equations:  
 %MB = 66,624 - 1,221 Adsorbent Type + 1,291 pH - 0,01868 Dose + 0,3958 Adsorbent Type\*pH + 0,001580 Adsorbent Type\*Dose + 0,008030 pH\*Dose

%BR9 = 68,248 - 0,992 Adsorbent Type + 0,366 pH - 0,02273 Dose + 0,5327 Adsorbent Type\*pH + 0,009418 pH\*Dose  
 This function describes how the experimental variables, and their interactions influence the adsorption of the dyes.

Finally, Adsorption was an effective process for treating dyes, and HRH provides a high removal percentage compared to IRH. For both dyes, the interaction between Adsorbent type\*pH\*Dose was insignificant, and another parameter was significant for MB and BR9 except for interaction between Adsorbent type\*Dose in BR9.

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# Chitosan and thiourea-chitosan ultra-lightweight macroporous hydrogels as efficient sorbents for removal of Ag(I) and Pb(II) ions

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Recently, novel adsorbents based on chitosan and its derivatives received a lot of attention as alternatives for heavy metal removal from contaminated wastewaters (Dinu et al, 2022; Ghiorghita et al, 2020; Dragan and Dinu 2020; Desbrières and Guibal, 2018). Considering the perpetual search for more and more efficient materials, we designed ultra-lightweight chitosan (CS) and thiourea-chitosan (CSTU) hydrogels by formaldehyde-mediated cross-linking/grafting (Fig. 1A, B) using cryogelation coupled with freeze-drying technique. Optimization of hydrogels properties was performed by changing the composition (concentration of CS solution, absence/presence of thiourea and  $-\text{NH}_2:\text{CH}_2\text{O}$  molar ratio) of feed reaction mixture. The assessment of structural, textural/morphological and mechanical features was accomplished by FTIR, BET, SEM, EDX and uniaxial compression analyses. SEM micrographs revealed a highly macroporous architecture of interconnected pores, while the compressive stress-strain investigations indicated an outstanding elasticity and toughness for the CS-based hydrogels. The sorption performance of CS and CSTU hydrogels towards Ag(I) (Fig. 1C) and Pb(II) ions (Fig. 1D) was studied with respect to the initial solution pH, contact time, equilibrium concentration, and presence of competitive contaminants in aqueous medium. The experimental results, along with the accessible preparation and low cost of the input chemicals, support the application of the prepared hydrogels as promising adsorbents for removal of different heavy metal ions from wastewaters.

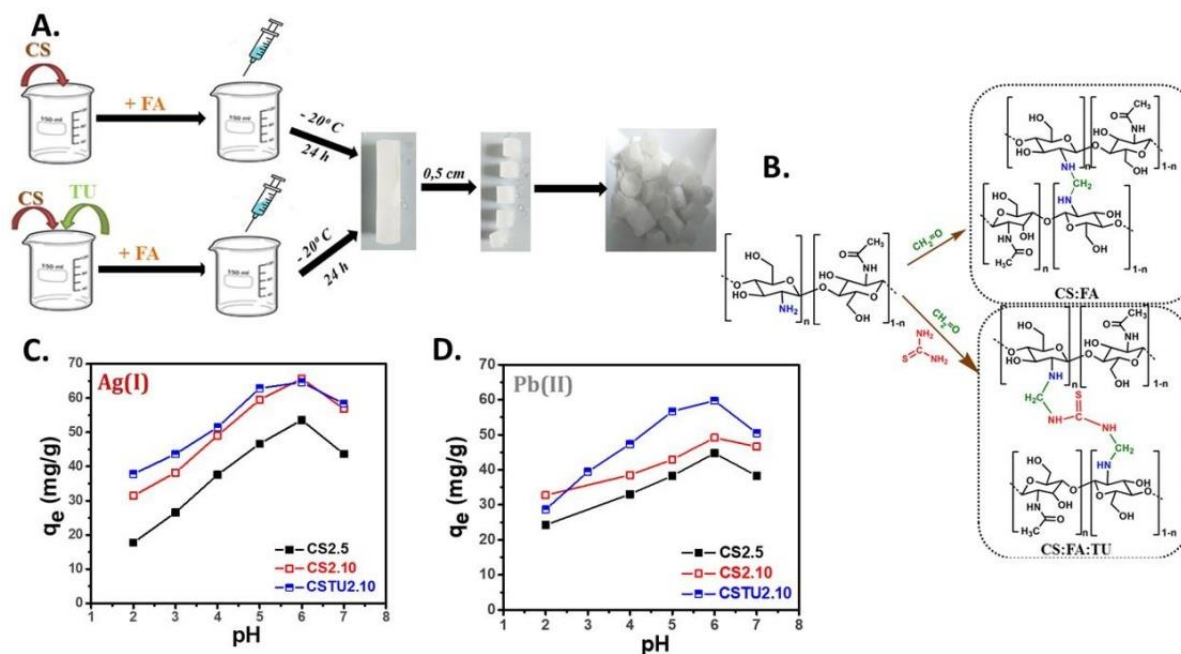


Fig. 2. Schematic illustration with the preparation method (A) and with the reactions (B) for the formaldehyde cross-linked CS and CSTU hydrogels. Influence of pH on Ag(I) (C) and Pb(II) (D) sorption by CS and CSTU hydrogels

## Acknowledgments

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# Identification and examination of phenol biodegradation pathways of *Acinetobacter towneri* isolated from landfill leachate Cekend, Harghita country

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Phenol can be released into the environment by several anthropogenic activities such as the associated industrial effluents. Wastewaters containing phenol and phenol derivatives can pose a risk to human health, water resources and can have negative impacts on the ecosystems concerned. It is toxic to the human body and affects many biochemical functions. The presence of phenolic compounds in our environment is a cause for concern, given their toxicity and their high resistance to biodegradation (Pradeep et al., 2015). However, many soil microorganisms (bacteria, fungi) are able to use various aromatic compounds, including phenol and its derivatives as carbon and energy source (Panigrahya et al., 2022). Under aerobic conditions, the biodegradation of phenol produces catechol by the phenol-hydroxylase enzyme. The catechol is further broken down by intradiol or extradiol dioxygenase enzymes as catalysts (Hasan and Jabeen, 2015). The aim of our work was to investigate the phenol degradation capacity of a bacterial strain isolated from leachate treating bioreactor of the Cekend landfill (Harghita country, Romania) and to characterize the enzymatic biodegradation. In a first step, we identified the CFII-101 strain, which showed the highest similarity to *Acinetobacter towneri* species. Then, we tested the phenol cleavage capacity of our strain in phenolic carbon source containing minimal medium in the presence of the resazurin indicator. We find that, at hour 6 from the start, the absorbance of the resazurin indicator started to decrease, while the absorbance of resorufin started to increase. *Acinetobacter towneri* CFII-101 strain can degrade 100 mg/L initial phenol concentration in maximum 6 hours.

In the enzyme activity assay, *Acinetobacter towneri* CFII-101 strain was found to lack catechol-1,2-dioxygenase (cat 1,2) activity, but has a catechol-2,3-dioxygenase (cat 2,3) activity, so biodegradation occurs via meta-pathway. The optimal pH for cat 2,3 enzyme activity was further determined in three buffers at 3-3 different pH values. Cat 2,3 enzyme showed the highest activity at pH = 9.0 in Tris buffer. During the optimal temperature determination, we found that the cat 2,3 enzyme showed the highest activity at 30°C in optimal pH conditions. The identified strain may have an important application in the bioremediation of polluted environments, and since environmental factors are very variable, it is advisable to determine the optimal degradation parameters in order to enhance the remediation processes.

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# Chitosan-based cryogels for heavy metals removal from wastewater

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The toxic heavy metals ions (HMIs) are the main pollutants in environment especially in soil and water which is producing detrimental effects, impairing the environmental welfare, reducing the quality of life and growing threat to humanity that may eventually cause death too. There are hundreds of sources of heavy metal pollution, including the coal, natural gas, paper, chlor-alkali industries and the untreated effluents from many industrial facilities that leads to severe water and soil pollution. Several methods have been extensively implemented to remove HMIs, e.g. chemical precipitation, flotation, ion exchange, membrane filtration, photocatalytic degradation, reverse osmosis or adsorption. Among these, adsorption using adequate sorbents is considered a simple and efficient technique to remove HMIs from wastewaters (Humelnicu et al, 2020; Sáez et al, 2020). In recent years, biopolymers have been considered the most promising raw materials for HMIs removal, as they exist abundantly and may form a cost-effective end product. Natural polymers, especially polysaccharides that are readily available, inexpensive and biodegradable, possess numerous reactive groups able to participate in metal ion adsorption. Chitosan (CS) based composites are being widely studied for water treatment and purification processes (Lazar et al, 2021).

In this regard, here we used composite sponges comprised of a natural zeolite (Z) and ethylenediaminetetraacetic acid (EDTA)-or diethylenetriaminepentaacetic acid (DTPA)-functionalized CS, as beads, for removal of Cu(II), Co(II) and Fe(III) ions from binary and ternary aqueous mixtures (Dinu et al, 2021). The HMI sorption capacities of CSZ-EDTA and CSZ-DTPA composite sponges were compared to those of unmodified sorbents. The influence of the initial HMI concentration and pH on the sorption performance of CSZ-based sorbents was evaluated. The Fe(III) ions were selectively retained when they were in two-component mixtures with Co(II) ions at pH 4, whereas Cu(II) ions were preferred when they were in two-component mixtures with Co(II) ions at pH 6. A high regeneration capacity was observed for all CS-based composite sorbents even after the fifth cycle of sorption/desorption, which clearly indicates their remarkable chemical stability and potential application in wastewater treatment.

## Acknowledgments

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# Assessment of porosity developed during microwave heating of biomass to obtain sorbent-type carbon materials

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The processing of materials in the microwave field is one of the technologies developed as sustainable and characterized by lower energy consumption [1]. Heat transfer in materials takes place from inside to outside, different to the conventional way of transferring heat from outside to inside by convection or conduction [2]. The unique characteristics of microwave processing recommend their use as a valuable energy solution for thermal processes of different materials [3], including for making sorbent-type carbon materials [4, 5]. This work describes the microwave pyrolysis at high temperature using a 1.1 kW laboratory equipment of walnut shells having an ash content 0.71%. The parameters used and the characteristics of the obtained sorbent-type carbon materials (CM) are shown in Table 1.

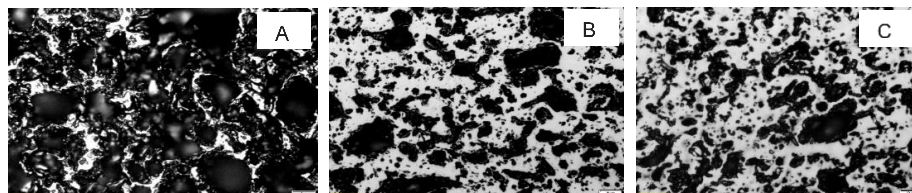
**Table 1.** Microwave field processing parameters and products characteristics

Sample ID	Processing parameters			Proximate analysis, %			Iodine index <sup>2)</sup> , mg/g
	Temp., °C	Heating time, min	Soaking time, min	Ash, (db)	Volatile, (db)	Fixed carbon, (db)	
CM 1	900	60	60	4.05	3.07	92.88	119.22
CM 2 <sup>1)</sup>	1000	60	45	5.19	3.14	91.67	352.50
CM 3 <sup>1)</sup>	1000	15	20	3.52	3.24	93.24	808.36

<sup>1)</sup> Starting material is biochar obtained at 600 °C in the microwave field and the gasification agent is CO<sub>2</sub> at 1 L/min.

<sup>2)</sup> After degassing at 100 °C for 1 h

The purity of biomass allows the development in CM of a pore network depending on degassing during heating. Their effect on the overall porosity development is evaluated by means of iodine index and optical structure and texture (Fig. 1). During heating of biochar at 900 °C an advanced degassing of material occurs generating large pores (Fig. 1, A) and low iodine adsorption capacity (119 mg/g). At 1000 °C the optical aspect determined by microscopical assessment of CA highlights that following the gasification reaction by CO<sub>2</sub>, preferably of the pore walls, a network of medium-sized pores is created (Fig. 1, B), which causes an increase of iodine index by 352 mg/g. By lowering heating and soaking time, was observed that CO<sub>2</sub> creates small micropores (< 5μm) in the thicker walls of the shell (Fig. 1, C) and increased iodine values of 808 mg/g.



**Fig. 1.** Textural and structural optical aspects of sorbent-type CM. Reflected light, immersion, 500X.

## Acknowledgments

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## Oxidation of metal sulfides in acidic environment

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Metal sulfides oxidation has a major environmental impact, causing acid mine drainage (AMD), the development of acid sulfate soils, and aquifer contamination. Metal sulfides oxidation is also important for the ores processing and for the metal recovery. During the chemical oxidation of the metal sulfides, various sulfur species, namely elemental sulfur, polysulfides, thiosulfate, polythionates, sulfite or sulfate, are generated.

The most abundant mineral sulfides in the earth's crust are pyrite ( $\text{FeS}_2$ ) and pyrrhotite ( $\text{FeS}$ ). It was observed that the oxidation of  $\text{FeS}_2$  and  $\text{FeS}$  depend on a number of parameters, such as: surface exposed to oxidant, oxidant concentration, temperature and pH [1,2].

This study presents a series of experimental results (Potentiodynamic Polarization, Electrochemical Impedance Spectroscopy and Cyclic Voltammetry) and quantum calculations which are used to analyze the mechanism of interaction of pyrite/pyrrhotite with the oxidizing solutions containing dissolved oxygen. It has been found that, there are clear differences in the electrochemical behavior of the two iron sulfides,  $\text{FeS}_2$  and  $\text{FeS}$ .

For example, in the presence of oxygen, at pH 2.5 and 25°C, the  $j_{\text{ox}}$  for the pyrite electrode is about 3 times higher than the  $j_{\text{ox}}$  for the pyrrhotite electrode. The observed differences indicate that the type of metal sulfide (iron sulfides,  $\text{PbS}$ ,  $\text{ZnS}$ , etc.) plays a very important role in environmental contamination.

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## The Ecological Footprint - a tool for the practical sustainability analysis

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The ecological footprint, a composite, objective and relevant indicator for the practical analysis of the sustainable development concept, has emerged as a working tool in the field of environmental management since the 1990s (William Rees). At present, it proves to be of maximum topicality and utility, as it allows - along with other indicators - the evaluation of the extent to which the objectives of sustainable development are achieved, but also the determination of the Happy Planet Index (HPI). Specifically, the ecological footprint indicates the area of land that the population needs in order to gain the resources necessary for development and the capacity to absorb waste, so it measures the pressure exerted by the population on the planet, through the consumption of resources, finished products and waste release. Determining the value of the ecological footprint involves relating the consumption of natural resources to the planet's ability to regenerate them and is expressed in global hectares. Given that the planet's surface is limited, it is natural to consider the way of land usage for all categories of use, along with the pace of population growth and elementary needs. Ecological footprint reports (WWF, 2020) show that the current area of land required to obtain the resources necessary to meet human needs is 60% higher than the planet's regenerative capacity.

The motivation for choosing this topic is given by the observation that, although globally the concept of sustainable development has been intensely debated for over 30 years, it has remained at a low level of practical validation, the most important reason being the ambiguity of measuring instruments. The ecological footprint, an indicator too little known and used in Romania for progress reports, allows the management analysis of the natural resources and also allows actions to be taken for their protection. The aim of the paper is to perform a analysis of the ecological footprint dynamics in Romania, for the period 2010-2020. The main objectives are: to correlate the results of the ecological footprint dynamics indicator with a set of significant indicators for measuring sustainable development objectives (total population, GDP / capita, unemployment rate, life expectancy at birth, energy consumption per capita, material consumption per capita, harvested wood mass, the surface of the artificial space) and highlighting the connection between the ecological footprint and the indicators of socio-economic progress. Methodologically, the paper is a non-experimental quantitative research, based on the dynamic analysis of a set of indicators and correlations. The data used are from official sources and reports and have been reorganized to achieve the proposed objectives. A dashboard simulator for calculating the ecological footprint was also used.

The results indicate that, despite the socio-economic progress in Romania, the management of natural resources is not sustainable, and the pressure on the environment is constantly increasing, an aspect correlated with GDP growth. For Romania, the EF value indicates a good situation, being 3.40 hag / pers. (2020). Romania is on the 95th place of the 188 countries for which EF is calculated. At European level, our country is advantageously positioned, the European average of EF value being 4.5 gha / pers. The global dispersion of the indicator indicates the extreme values: in Africa AE is 1.4 hag / pers., while in the USA it is 8.7 hag / pers. Annually, National Ecological Footprint values are calculated by Global Footprint Network for approximately 200 countries.

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<https://offset.climateneutralnow.org/footprintcalc>





# Equilibrium studies for the removal of Cd<sup>2+</sup> ions from wastewater using silica/polyelectrolyte multilayer core-shell composites

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Increasing water pollution with heavy metals resulted from the growth of industries and the use of fossil fuels is a worldwide concern. Among them, cadmium and other few metals are classified as priority pollutants due to their very low biodegradation, accumulation and toxic potential on human health and ecosystems. Cadmium causes extreme toxicity towards marine and fresh water organisms and has been linked with certain human cancers. To diminish this threat and to retain this micropollutant from wastewater, new innovative sorbents have been fabricated. This study reports the sorption of Cd<sup>2+</sup> ions from wastewater onto silica/polyelectrolyte multilayer composite microparticles at equilibrium. The sorbents were obtained by layer-by-layer (LbL) deposition of polyethylenimine (PEI) and polyacrylic acid (PAA) onto a Daisogel-type silica core, until 2.5 or 4.5 double polymer layers were deposited. The polycation layers in the composites were crosslinked by glutaraldehyde, at two different molar ratios  $r = [\text{CHO}]:[\text{NH}_2] = 0.1$  or  $1.0$ . In this manner, four composite sorbents were synthesized, i.e. IS/(PEI/PAA)<sub>2.5</sub> ( $r = 0.1$ ), IS/(PEI/PAA)<sub>2.5</sub> ( $r = 1$ ), IS/(PEI/PAA)<sub>4.5</sub> ( $r = 0.1$ ) and IS/(PEI/PAA)<sub>4.5</sub> ( $r = 1$ ). Adsorption of Cd<sup>2+</sup> ions onto silica/polyelectrolyte multilayer composite microparticles was performed by a batch procedure, considering a metal initial concentration in the range of 2 – 108 mg/L. The identification of equilibrium models is critical for the sorption process, especially for the interpretation of the underlying mechanism. In this study, the equilibrium data obtained from the influence of the initial concentration studies was used for modeling of several isotherms: Langmuir, Freundlich, Sips and Toth. The error was estimated using four functions: sum of the square error, Chi-square test, hybrid fractional error function and the average relative error. After non-linear regression optimization, the methodology of the sum of normalized errors was applied, which facilitated the selection of the optimum parameters set for each isotherm. Model adequacy was determined using two information criteria (IC): Hannan-Quinn and corrected Akaike. These criteria are based on maximum likelihood theory and reduce the overfitting caused by models with more parameters.

The equilibrium sorption capacities of the four composite sorbents are plotted in Fig. 1, indicating their dependence on the Cd<sup>2+</sup> ions initial concentration. At the same time, the sorption capacity increases with the number of polymer layers and the crosslinking degree. Therefore, the highest experimental sorption capacity was obtained when IS/(PEI/PAA)<sub>4.5</sub> ( $r = 1$ ) was used. The goodness-of-fit of the isotherm models suggested that the error functions presented a tendency to favor the models with three parameters. Among the error functions, Chi-square test provided the optimum isotherm parameters in most cases. The model selection was done considering the minimum values of the IC. According to the evaluation of the IC, Freundlich isotherm performed well in describing IS/(PEI/PAA)<sub>4.5</sub> ( $r = 0.1$ ) and IS/(PEI/PAA)<sub>2.5</sub> ( $r = 1$ ). It was found that Freundlich model was 36 times better than Langmuir model and 52 times better than Sips model. Toth isotherm model was favorable for the other two sorbents, predicting a maximum sorption capacity of 26.67 mg/g for IS/(PEI/PAA)<sub>4.5</sub> ( $r = 1$ ) and 3.87 mg/g for IS/(PEI/PAA)<sub>2.5</sub> ( $r = 0.1$ ). In summary, the LbL composite sorbents proved to be a promising solution for heavy metals, removal from wastewater, herein cadmium.

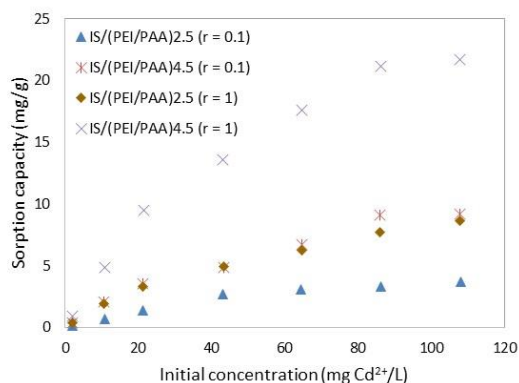


Fig. 1. Influence of the initial concentration on the removal of cadmium ions from aqueous solution

## Acknowledgment

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# Comparative study of Cu(II) removal from aqueous media using different biomasses as biosorbents

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The contamination of water sources with metal ions discharged from industrial activities is still one of the most important problems all over the world (Massoud et al., 2019). More and more cases of accidental pollution of inland or international waters, air or soil with substances or products containing heavy metals are frequently reported in the media and are also the subject of concern in the scientific world. To overcome this problem, different treatment methods of industrial effluents have been developed to eliminate such contaminants (Bogusz et al., 2015; Wael et al., 2016). Removal of metal ions using materials of biologic origin as biosorbents seems to be a viable alternative to this problem (Mudhoo et al., 2012; Gupta et al., 2015). In this study, different biomasses (such as: marine green algae biomass, yeast biomass and mustard biomass) were examined in the biosorption process of Cu(II) ions from aqueous media. The choice of this metal ion for the experimental studies was made taking into account the widespread uses in industrial activities and its economical importance. The effect of initial solution pH, biosorbent dosage and contact time were studied in batch system, at ambient temperature ( $22 \pm 1^\circ\text{C}$ ), to determined the optimum experimental conditions. A maximum removal efficiency of more than 90 % was obtained at initial solution pH of 5.0, 4.0 g/L biosorbent and at least 60 min of contact time (Fig. 1a). Under these conditions, the biosorption parameters ( $q$ , mg/g and  $R$  %) (Fig. 1b) increase with the increasing of Cu(II) ions concentration, and follow the order: mustard biomass > yeast biomass > algae biomass.

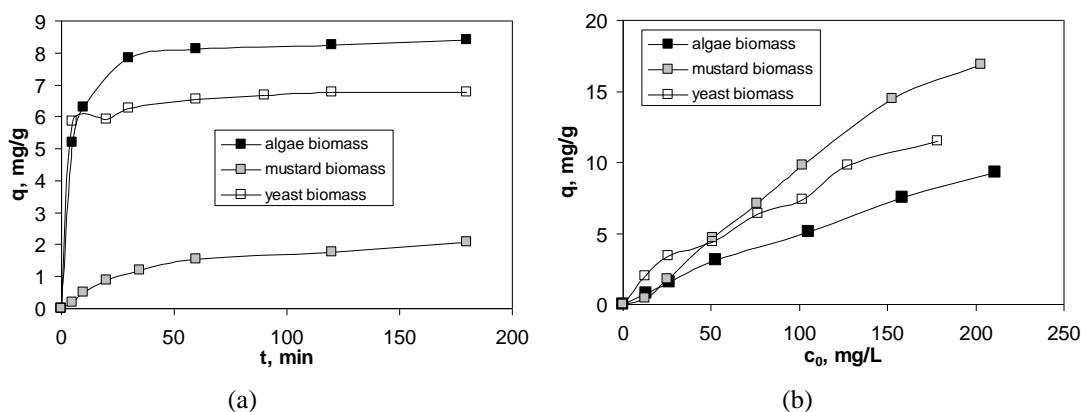


Fig. 1. Biosorptive performances of examined biomasses in the removal of Cu(II) ions from aqueous media.

To explain these differences, the elemental analysis of these three types of biomasses was performed, as well as their morphological characterization. The quantitative evaluation of the biosorptive performances of these three biosorbents in the Cu(II) ion removal processes was performed by isotherm and kinetic modelling. Langmuir and Freundlich isotherm models were used in the modelling of experimental isotherm, while pseudo-first order and pseudo-second order models were applied in the kinetics modelling of the biosorption processes. The obtained models parameters were analyzed in detail.

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# Scenario-based analysis of Iasi County car fleet evolution and environmental performance evaluation

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The recent and major changes of the European policy on transportation which calls for phasing out of the internal combustion-powered vehicles to reduce the greenhouse gases (GHG) emissions have led to a significant change in the consumers behavior in Western Europe through a raise in the new electric vehicles market uptake (from 3.5% to 11% in 2020). At the same time, most of the replaced vehicles have found their way as used passenger cars (or second-hand vehicles) in Eastern European countries, where they become most of the newly registered vehicles each year. For example, the national car fleet of Romania has increased by almost 9.5% in just one year (2017) to more than 7.6 million vehicles, of which approx. 6 million were passenger cars. According to official data from the National Registration Department, in 2020 approximately 1.76 million passenger cars (24%) were older than 20 years, 4.045 million units were 10 - 20 years old (56%), 1,184 million units were 3-10 years old (16%), and only 0.277 million (4%) were new cars.

The objective of this study is to perform an in-depth assessment of the environmental performance and evolution of the passenger car fleet in Iasi County (Romania). The analysis considers statistical data regarding the car fleet structure to model the current and future fleet dynamics. This fleet data, together with various circulation conditions are used as input data into the Copert 5.5 model which is used to estimate the specific use-phase emissions. Subsequently this updated emission data is used as input data into an LCA analysis. The study considers three scenarios regarding the fleet evolution and environmental performances: (1) no changes scenario in which used vehicles are imported at the current rates, (2) an import ban is imposed for older vehicles, and scenario (3) considers a fast increase of electric vehicles. The analysis focuses solely on the use phase of passenger cars, exhaust emissions being modeled in various driving situations (rural, urban, hot-cold operation and peak-off-peak traffic values) and by considering the actual environmental performance classes and age of vehicles in the fleet.

The results show that by considering these particular vehicle performance elements (pollution class and mileage damage due to age), impacts are better represented. Results presented in Fig. 1 clearly show that the evolution according to Scenario 1 represents the worst case with impacts up to 2.5 times higher in 2035 compared to 2020.

Limiting the imports of used cars and increasing the electric and hybrid vehicles share lead to a much softer impact increase or even a substantial decrease in some impact categories (e.g. tropospheric ozone generation).

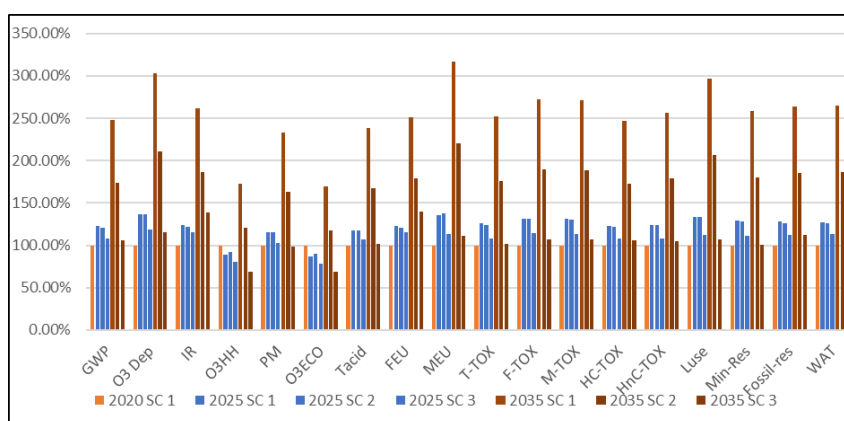


Fig. 1. 2020 – 2035 Iasi County Car fleet impacts evolution comparison

In conclusion, our analysis shows that the adoption of a series of car-fleet management and regulating instruments can help to mitigate and even reverse some of these impacts. Thus, the accelerated rate of hybrid and electric vehicles uptake represents the main driver for improving the overall environmental performance (especially in the air-related categories), while only increasing the share of newer ICEVs (and eliminating the old cars) is not sufficient to limit these growing impacts.

## Preliminary evaluation of the efficiency of a brewery wastewater treatment plant

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Evaluating the performance efficiency of the wastewater treatment plant (WWTP) is a challenging duty, mainly due to the uncontrolled fluctuations of its composition throughout the year.

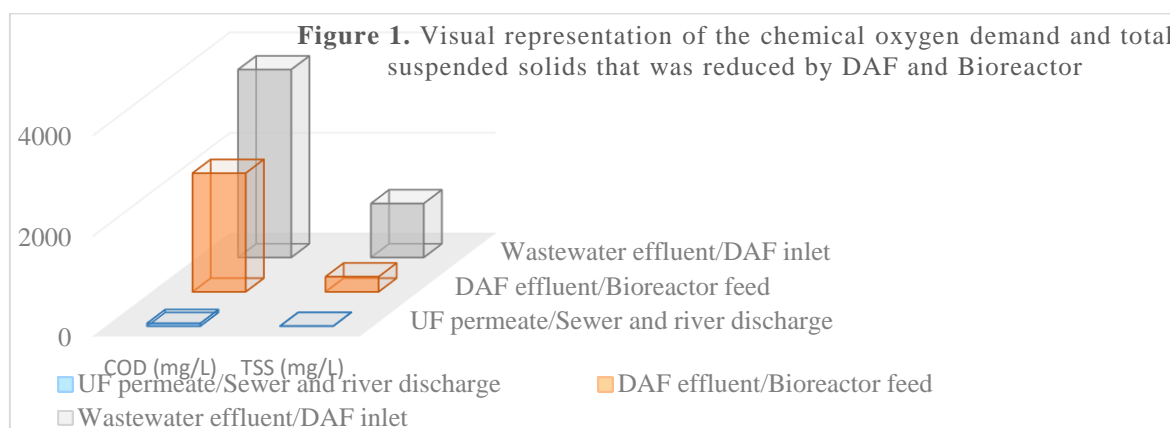
In this study, a brewery WWTP from South-East England was monitored over a period of one year. The brewery WWTP has the following flowsheet: **Mechanical treatment** (rotary screen) => **Equalisation tank** => **Chemical treatment & Dissolved air flotation (DAF)** => **Bioreactor feed tank** => **Biological treatment (AMBR™ Bioreactor Tank)** => **Membrane Separation System** (Biomass separation & Ultra Filtration (UF) => **Discharge** to the river/sewage or reuse inside the WWTP.

To assess the operational performance of the WWTP, the wastewater quality indicators including chemical oxygen demand (COD), total suspended solids (TSS), and pH, were examined. Ammonia, nitrate, and phosphate analysis were added during the chemical treatment step and on the Ultra Filtration Membrane Separation System step we added the turbidity and conductivity analysis, these indicators being used to monitor and sustain the microbial activity from the bioreactor.

COD, TSS, pH and ammonia were analyzed at the end of the process because they must meet certain discharge limits according to the standards to be released into the local river or sewer system. British Environmental agency which published the 'Wastewater treatment works: treatment monitoring and compliance limits' (2019) states that the compliance limit for COD is 125 mg/l, (Gov.uk, 2022), TSS has the limit at 100mg/l (Gov.uk, 2022), which makes the WWTP well under the limits.

	Wastewater effluent/ DAF inlet	DAF effluent/ Bioreactor feed	UF permeate/ Sewer and river discharge	Removal efficiency (%)
COD (mg/L)	3736.4	2,357.98	58.41	98.43
TSS (mg/L)	1072.9	301.46	4.56	99.56

**Table 1.** Chemical oxygen demand and total suspended solids that has being reduced by the DAF and the Bioreactor



For the WWTP the most important objective is to protect the environment by reducing as much as possible the pollutants from the wastewater. The conclusion of this study showed that this WWTP has a remarkable efficiency. The combination of DAF, bioreactor and UF reduces 98.43% of the COD and 99.56% of the TSS.

# Functionalization of PET waste and possible applications in the removal of Pb(II) ions from aqueous media

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Research on decontamination of water resources has led to an extraordinary boost in finding new and cheap materials that are able to remove pollutants (Cochrane et al., 2006). Pollution of water sources caused by heavy metal ions has raised global environmental problems around the world because they cannot be destroyed or degraded, have a tendency to accumulate in the environment and affect the quality of ecosystems. The main sources of water pollution with such toxic metal ions have emerged as a result of technological progress in the development of the industry, such as the chemical industry, the oil processing industry and the metallurgical industry (Volesky, 2001). Adsorption is considered a promising alternative for removing Pb(II) ions from aqueous media due to its efficiency, high selectivity, low cost, ease of operations. The main problem that ensures the fulfilment of these conditions is the choice of the adsorbent material. The extensively utilization of PET for package manufacturing has caused important environmental problems, due to huge quantity of PET packages which must be recycled (Shukla et al., 2008; Safruk et al., 2017). In order to find some practical applications in environmental remediation, in this study, PET waste was functionalized with organic dye (Orange G) and clay (Vlădiceni, Romania). Both functionalized materials have been tested as adsorbents for the removal of Pb(II) ions from aqueous media, in batch systems, compared with raw PET waste. The adsorption capacity ( $q$ , mg/g) of these adsorbents, calculated after 24 hours of contact time (Fig. 1a) increases with the increasing of initial Pb(II) ions concentration, and follow the order: PET functionalized with clay material > PET functionalized with Orange G > raw PET waste. The same variation is observed and in the case of the effect of contact time (Fig. 1b).

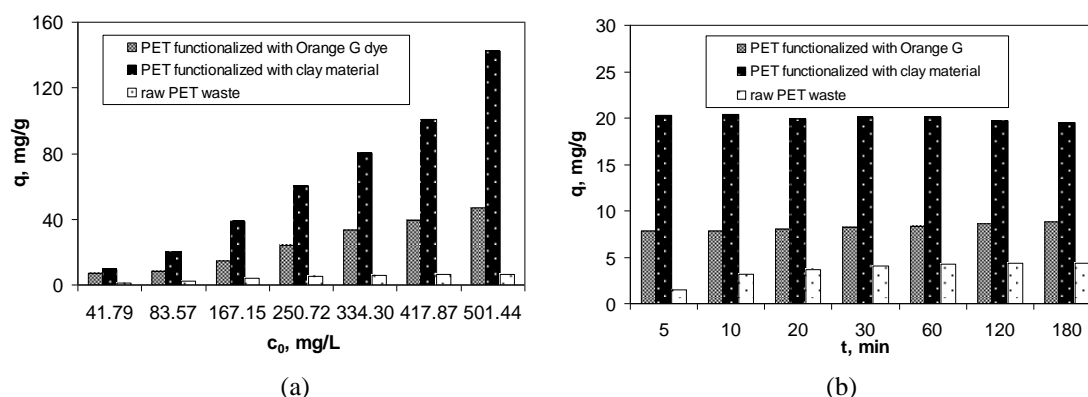


Fig. 1. Efficiency of Pb(II) ions removal on the three adsorbents

These differences can be explained considering the structural particularities of these adsorbents. The quantitative evaluation of the adsorptive performances of these three adsorbents in the Pb(II) ion removal was examined by isotherm (Langmuir and Freundlich isotherm models) and kinetic (pseudo-first order and pseudo-second order models) modelling. The modelling parameters will provide a clear image of the possibilities of functionalization of PET wastes, in order to obtain high-performance adsorbent materials

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## Coagulation-flocculation efficiency to remove manganese and natural organic matter for drinking water treatment

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Coagulation-flocculation processes play an essential role in drinking water sources treatment, creating a benefit through the efficient removal of inorganic and organic suspended colloids along with some of the dissolved substances. The efficiency of coagulation-flocculation processes to remove manganese, iron and natural organic matter (NOM) from raw water depends on: the pre-oxidation of raw water, the type and dosage of the selected coagulant and flocculant, pH, temperature, mixing conditions and pollutants properties. Manganese (Mn) and iron (Fe) are present in surface water from both natural sources, such as soil and rocks, and human activities. These trace metals are undesirable in drinking water due to aesthetic problems, corrosion of distribution networks and health issues. The adverse effects of manganese for human health depend on the concentration, the chemical species, the age and nutrition status of the exposed human being. Manganese exposure affects the nervous system functions and may even cause an irreversible Parkinson-like syndrome known as manganism. The presence of NOM in surface water contributes to the formation of disinfection by-products (DBPs), which leads to the potential presence of carcinogenic compounds in conventionally treated waters (involving chlorination as final stage of water treatment). This study presents a series of results obtained on a laboratory scale set-up for coagulation-flocculation of surface water from a river which is the drinking water source for a city in Central- East Romania. The objective of this study was to investigate the influence of operational parameters and water quality indicators on the process performances in terms of removal efficiencies and selection of optimum operating parameters for manganese, iron, and NOM removal. In order to assess the river raw water quality, the average annual values for quality parameters for the period 2020-2021 were analyzed. For this study, influent and effluent samples of the drinking water treatment plant (DWTP) were collected and characterized for the following indicators: pH, oxidability, turbidity, alkalinity, ammonia, nitrites, iron and manganese. These indicators were determined according to the current Standard Methods for water quality analysis. The coagulation-flocculation tests were performed at the natural pH of raw water. For the coagulation tests, an aluminum-based coagulant was used, because the iron concentration in the raw water exceeds the maximum admissible concentration stipulated in the Directive (EU) 2020/2184 and Law 458/2002 on drinking water quality. Polyhydroxy aluminum chloride (commercial name PAX XL 60) and polyacrylamide (commercial name AN910SEP) were used as coagulant and flocculant, respectively. Different parameters, such as coagulant dose (0.025 – 0.15 mL/L), river water temperature (4 and 20°C), rapid and slow mixing time and presence or absence of the flocculant were investigated. Multiple water quality indicators were determined, such as manganese, iron, turbidity, chemical oxygen demand (COD), dissolved organic carbon (DOC) and residual aluminium concentration. Some unconventional parameters relevant for NOM removal were also considered, like absorbance at 254 nm (A254), at 280 nm (A280) and at 365 nm (A365), as well as the ratios A254/DOC, A254/280 and A254/A365.

The results of this study show that, depending on coagulation-flocculation process parameters, in the presence of the flocculation reagent, it is possible to achieve manganese removal efficiencies up to 93.84% at low water temperature and up to 92.74% at high water temperature. Regarding the removal of iron concentration in the tests performed in the presence of the flocculation reagent with raw water at 4°C, the efficiency of the process varied between 40% and 99.04%. In the case of tests performed with raw water at 20°C, the efficiency of the process for removal iron varied between 35.38% and 98.99% in the presence of the flocculation reagent. The efficiency of the coagulation-flocculation process was determined considering the reduction of NOM determined as absorbance at 280 nm, which is related to the activated aromatic rings that influences the formation of trihalomethanes and haloacetic acids during water disinfection (involving chlorination as final stage of raw water treatment). Specifically, a coagulant dose of 0.10 mL/L, in presence of flocculant, at water temperature of 4°C, determined a decrease in NOM content (expressed as A280) of 81.52%. In the case of tests performed with raw water at 20°C, under the same operating conditions as the previous one, a decrease in NOM content (expressed as A280) of 63.21% was found. The residual aluminum concentration obtained after the coagulation-flocculation tests carried out in the presence of the flocculant at a raw water temperature of 4°C and 20°C is less than 50 µg/l in the case of the last three doses of coagulant used, which is lower than the Romanian legislative requirements, *i.e.* 200 µg/L.

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# Sustainability of packaging waste management in Romania: trends and impact

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Packaging waste (PW) has been an important topic in European Union for at least 30 years when the first Directive on packaging and packaging waste was issued, that included recommendations on design and waste management operations (Directive 94/62/EC). Since then, the Directive has been modified and completed in response to the societal challenges: increasing waste packaging quantities, limited recovery options for some of the current packaging materials (especially some plastic categories), materials ending up in landfills instead of being recirculated into the economy, etc. Among the significant amendments, establishing of more ambitious targets for all packaging and per material type (plastic, wood, ferrous metals, aluminum, glass, paper and cardboard), the mandatory setting up of Extended Producer Responsibility schemes in all members states, as part of the circular economy package together with the Plastic Strategy are expected to produce beneficial effects in terms of waste minimization and recovery.

However, the sustainability of these decisions should be quantified with suitable and measurable indicators, besides the regular material balance indicators measuring waste generation, collection, recovery (recycling and energy valorization) and final disposal. This study proposes a framework which starts from the material flows indicators and quantifies the environmental impact (in terms of greenhouse gas emissions and energy impact), the economic costs with wages and taxes related to the PW management operations and the social climate as labor hours put into the PW treatment operations (Fig. 1). The main objective is to evaluate the sustainability of a packing waste management system at national level. As case study the packaging waste management system in Romania was considered under an evaluation period of 10 years: 2010-2019.



**Fig. 1.** Packaging waste system and its environmental, social and economic impact

**Table 1.** Sustainability indicators calculated for the entire PW collected in 2015

Indicator	Value
Total GHG Emissions (t CO <sub>2</sub> e)	-2.46E+06*
Total Energy Impact (GJ)	-2.03E+07*
Labour (hours)	2.00E+07
Wages (Euro)	5.14E+08
Taxes (Euro)	9.33E+07

\*Negative values= environmental benefits  
Positive values=environmental impact

By using the Eurostat data base for the basic material flow indicators and the USEPA WARM software (vers. 15, 2020), sustainability indicators calculation could be performed per each PW category and treatment option. Overall results for a selected year (2015) from the investigated period are presented in Table 1.

To the best of our knowledge this is the first study that goes beyond the material balance of PW and gives an image on the evolution of the Romanian PW management system in terms of sustainability.



## Automating watershed delineation using ArcGIS Model Builder

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The watershed is the piece of land from which water captured from various forms is drained into the pour point. The choice of discharge point defines the boundaries of the basin, and the process of establishing a watershed's boundary is called watershed delineation. Depending on the needs of the user and the resources available, there are numerous way to delineate a watershed. Whilst the basin area can be easily designed and delineated using a paper map, GIS delineation is easier to replicate, takes less work and is less relying on subjective opinion.

There are numerous geospatial and hydrologic modeling tasks that can be carried out using Geographic Information System and Digital Elevation Model. Watersheds can be delineated by analysis performed on the topographic maps powered by digital elevation imaging plus the data that is already present in these pictures.

The use of GIS technology to develop and apply models for spatial natural challenges has increased significantly. These technologies support the organization and integration of spatial processes into larger systems that simulate the real words. The geoprocessing models support both the geographical analysis processes and the automated documentation of data management. Model Builder is very useful when creating, editing and managing geoprocessing models that conduce to automation. This is a geoprocessing tool process in the form of a chain that takes the output of one process and uses it as the input for another.

The purpose of this study was to develop a model for automatically delineate the catchment area from a Digital Elevation Model. This model facilitates input and output data management and allows for critical visual and spatial interpretations. The model created in this paper can be employed in all upcoming analyses of the same type.

## Evaluation of heat island effect through remote sensing methods

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Climate change is leading to more summer and tropical days across the globe. This has become abundantly clear in recent summers and, as a result, the heat island effects are becoming more intense and frequent. Urban heat island effect is one of the typical features of the urban climate and a phenomenon which lead to extreme weather and air pollution.

This directly threatens the health of humans and has a large number of consequences on living environment, including infrastructure, drinking water and surface water the quality.

Therefore, is necessary to identify the specific locations of urban heat islands. The purpose of this paper is to evaluate the heat island effect and to quantify the situation of the new development areas in Beilen, north-east of Midden-Drenthe.

Remote sensing and GIS methods were used for this analysis, together with a high resolution aerial image. GIS software was used for the study and to develop the heat islands map. Heat locations were satisfactorily determined by the model. Thus, understanding the studies on this subject will support decision makers and conservation planners manage effectively land and climate.

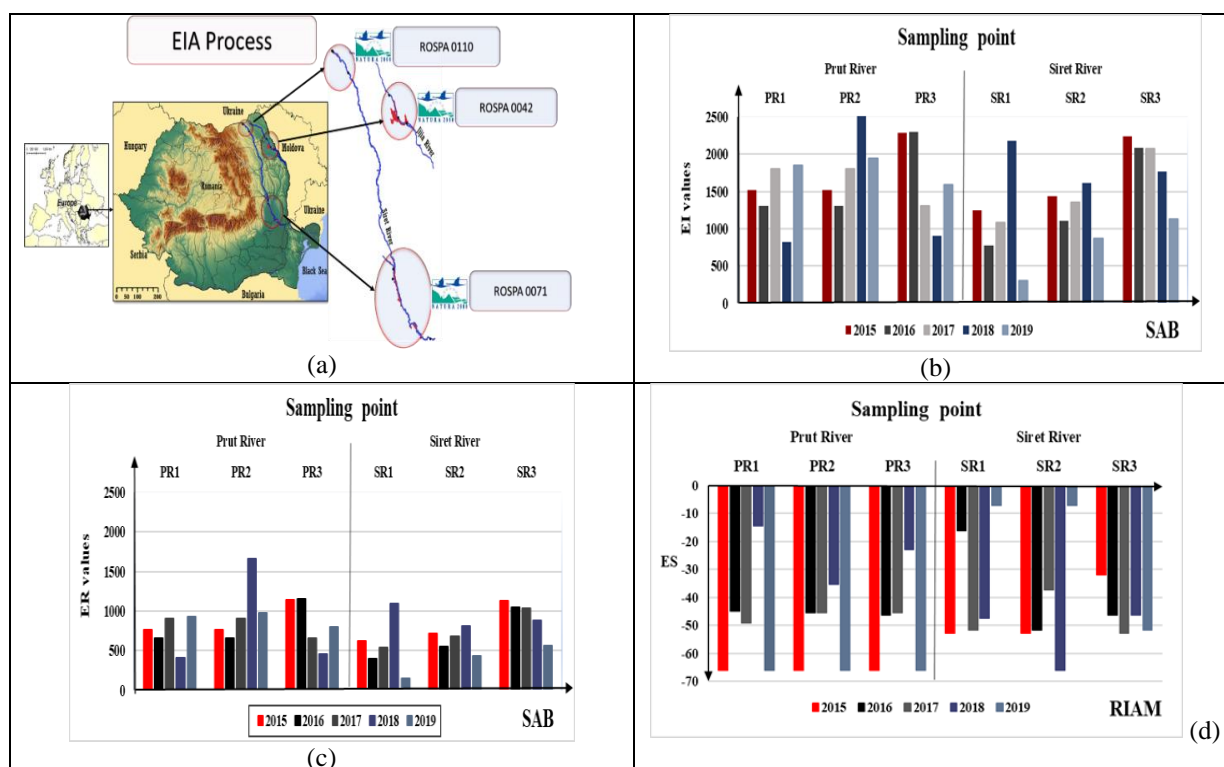
# Inorganic priority pollutants impact and risk assessment: comparative analysis of the Siret and Prut Rivers water quality

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Priority pollutants (i.e. heavy metals) can cause serious damages to the river water quality, even at very low concentrations (traces), considering their toxicity for the ecosystems. Apart from geological contributions, they can be dispersed in the environment through uncontrolled anthropogenic activities. Environmental impact and risk assessment is a tool often used for the evaluation and identification of harmful and negative effects on the environment. This study develops a comparative approach for assessing the impacts of heavy metals (As, Cd, Ni, Pb, Hg) on the water quality of the Siret and Prut rivers - the main rivers within the N-E region of Romania and tributaries of the Danube River. Also, the Prut River is the natural border with the Republic of Moldova. On the other hand, the evaluated sites cover protected areas, as Natura 2000 sites (SPA, SCI), as follows: ROSPA0042 (Jijia and Miletin Ponds), ROSPA0071 (Lower Siret Meadow) and ROSPA0110 (Rogojesti - Bucecea Accumulations) (Fig.1a). Three sampling sections were established for each river, and the environmental monitoring was conducted during 2015-2019. The impact assessment was run by using the Rapid Impact Assessment Matrix (RIAM) and Integrated method (SAB). The results showed that there were considerable differences obtained between the monitored years (Fig.1 b, c). It can be observed that for 2018, the environmental impact scores were higher in the three sections for both Siret and Prut rivers. The highest value for risk was recorded for the Prut River in 2018, in section 2 (Fig.1d), while in terms of impacts, the Siret River was the most affected in 2018, section 2. In comparison, the Prut River is more polluted than the Siret River, considering the same period and indicators, as reference.



**Fig. 1.** The results of environmental impact (EI) and risk (ER) for Siret and Prut River, from N-E Romania:

(a) protected areas from N-E Romania - study area, (b) comparison of the environmental impact values according to the SAB method; (c) comparison of the environmental risk values according to the SAB method; (d) comparison of the environmental impact values according to RIAM method