Book of Abstracts

NeXT-Chem

INNOVATIVE CROSS-SECTORAL TECHNOLOGIES

Exploratory Workshops Series

Vth EDITION, 22-23 MAY, 2023

Bucharest, ROMANIA

Coordinators of the edition:
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FOREWORD

Welcome to the latest edition of the Exploratory Workshop "INNOVATIVE CROSS-SECTORAL TECHNOLOGIES - NeXT-Chem", a forum that has established itself as a beacon for young scientists to showcase their groundbreaking achievements in inter- and trans-disciplinary research. With each passing year, this workshop continues to foster collaboration, inspire new ideas, and shape the future of scientific exploration.

In its fifth edition, the NeXT-Chem workshop remains dedicated to providing a platform for young researchers, MSc and PhD students, to present their latest discoveries and gain invaluable insights through invited lectures. As usual, participation in this enriching experience is completely free, ensuring equal access for all passionate minds.

This year, the NeXT-Chem workshop has gained support from two institutional projects undertaken by our esteemed institute. The first project, "Supporting the competitiveness and excellence of INCDCP-ICECHIM research and innovation in the area of bioeconomy and related fields" (NeXT-BExcel 15PFE/2021) is financed through the National Plan for Research, Development and Innovation PNCDI III), aims to enhance the performance of INCDCP-ICECHIM in the field of bioeconomy, foster research skills development, and promote human capital advancement. To learn more about the NeXT-BExcel project, please visit our website by clicking here.

Secondly, 2023 marks the beginning of the INCDCP-ICECHIM Core Program for ChemNewDeal 2023-2026. This comprehensive program aligns with institutional strategies and plans, focusing on excellence, increasing the institutional capacity, and cultivating expertise in areas of smart specialization. By synergistically contributing to other programs and projects, ChemNewDeal strives to achieve ambitious goals, meet the demands of the economic environment and society, and make significant progress towards the Sustainable Development Goals (SDGs) and the National Strategy for the Circular Economy. To explore the objectives and ongoing projects funded by the ChemNewDeal program, please visit our dedicated webpage by clicking here.

Under the ChemNewDeal Program, two major research projects are currently receiving financial support. "AQUAMAT: Development of new materials for the integrated approach to the protection of water resources: from detection to depollution" aims to develop an innovative approach to water resource protection through the creation of advanced materials and innovative detection methods. The second project, "InteGral: Interconnectable modular technological platforms for an optimized conversion into bioproducts required by the market of side flows specific to the Romanian bioeconomy," focuses on developing interconnected modular platforms to efficiently convert bioresources into valuable bioproducts. These projects exemplify our commitment to addressing pressing environmental challenges while fostering economic growth and sustainable development.

The coordinators of this edition extend their gratitude to all the participants, speakers, and contributors who have made this workshop possible. May this edition of NeXT-Chem be a catalyst for transformative breakthroughs and an inspiration for future generations of scientists.

INVITED LECTURES

Monday, May 22nd, 2023

1. **Liviu POPA-SIMIL,** LAVM LLC.

   "Effectiveness of engineered methods of protection against aerosolized bio or actinide nano-bodies compared with vaccines and medical procedures in pandemic suppression"

2. **Paul VASOS,** ELI-NP, Institutul de Fizică și Inginerie Nucleară Horia Hulubei, Școala Doctorală Interdisciplinară (ISDS), Universitatea din București.

   "Timescales of biomolecular transformations via magnetic resonance spectroscopy and timely diagnostic of FLASH radiation effects"

3. **Bogdan TRICĂ,** INCDCP - ICECHIM Bucharest

   "Journal of imaginative experiments: an exercise in imagination using real scientific methods"

4. **Andrei SÂRBU,** Romanian Chemical Society

   "EuChemS: Empowering excellence in the chemical sciences"

Tuesday, May 23rd, 2023

5. **Ecaterina ANDRONESCU,** POLITEHNICA University of Bucharest

   "Nanochemistry in medical applications"

6. **George TEODORESCU,** INCDCP - ICECHIM Bucharest

   "Glass fiber/ash reinforced polymer composites for lightweight automotive parts"

7. **Rareș VASILICĂ,** E-Nformation

   "Publishing Opportunities. How to increase your chances of publication?"

Session 1 - Multifunctional materials, nanocomposites, innovative technologies and cultural heritage preservation

DESIGN OF VERSATILE BICOMPONENT PLATFORM CO-LOADED WITH THERAPEUTIC AGENTS FOR WOUND DRESSING APPLICATIONS

Elena COJOCARU [1], Jana GHITMAN [1,2], Gratiela GRADISTEANU PIRCALABIORU [2,3,4], Anamaria ZAHARIA[5], Horia IOVU [1,2,4], Andrei S\RBU[5]

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Keywords: 3D-printing; electrospinning; bicomponent scaffold; wound dressing.

Introduction: The research study proposed an efficient solution for antimicrobial wound dressings by engineering drug and prodrug-co-loaded bicomponent platform by combining electrospinning and 3D-printing technologies [1][2][3]. The outer component was constituted by a chitosan (CS) electro spun membrane loaded with indomethacin-based prodrug (pIMC), which served as support for printing the inner component, a gelatin methacryloyl (GM)/ sodium alginate (SA) 3D hydrogel loaded with tetracycline hydrochloride (TCH) molecules.

Materials and methods: In order to obtain the bicomponent scaffold, firstly it was necessary the design of pIMC-containing CS nanofibrous membrane (F/pIMC) by electro spinning as outer component, and secondly, the design of TCH-loaded GM/SA hydrogel (H/TCH) by 3D-printing and its double crosslinking (GM photopolymerization and ionic crosslinking of SA), as inner component. The assembling of the two components was achieved by printing the hydrogel onto the surface of nanofibrous membrane.

Results: SEM micrographs underlined both the nanofibrous architecture of non-crosslinked and crosslinked electro spun membranes, and the porous microstructure of 3D-printed scaffolds, as well as the joining of the two components in the final bicomponent scaffold. Concerning the drugs release profiles, it was noted that both F/pIMC and H/TCH released the therapeutics in a controlled and high cumulative amount, when they were in the presence of enzymes. According to *in vitro* cytocompatibility evaluation (MTT assay), the HeLa cell culture exhibited a good viability in the presence of bicomponent scaffold, which also manifested a good antimicrobial activity against *E. coli* and *S. aureus* bacteria.

Conclusions: Electro spun and 3D-printed bicomponent scaffold with applications in wound dressings was constructed by electro spinning and 3D-printing technologies. The outer component consisted of prodrug-containing CS nanofibrous membrane, while the inner component was comprised of TCH-loaded GM/SA hydrogel. The results of in vitro cellular response evaluation indicated that the bicomponent scaffold could promote HeLa cells adhesion and proliferation.

***Acknowledgements**: The experimental part of this work was possible due to European Regional Development Fund through the Competitiveness Operational Program 2014–2020, Priority axis 1, Project No. P_36_611, MyS-MIS code 107066, Innovative Technologies for Materials Quality Assurance in Health, Energy and Environmental—Center for Innovative Manufacturing Solutions of Smart Biomaterials and Biomedical Surfaces—INOVABIOMED.The first author acknowledges the European Social Fund from the Sectoral Operational Programme Human Capital 2014-2020, through the Financial Agreement with the title "Training of PhD students and postdoctoral researchers in order to acquire applied research skills - SMART", Contract no. 13530/16.06.2022 - SMIS code: 153734.*

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SULFOBETAINE FUCTIONALIZED GELLAN GUM: SYNTHESIS, SOLUTION AND GEL PROPERTIES

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Keywords: sulfobetaine, polyzwitterion, gellan, grafted polymer

Introduction: Gellan gum (GLL) is an anionic polysaccharide obtained as a fermentation product by the aerobic Gram-negative Pseudomonas elodea. It has a tetra saccharide repeating unit consisting of one α-rhamnose, one β-glucuronic acid and two β-glucose residues.[1] Polybetaines are suitable for biomedical applications due to improved biocompatibility, antimicrobial activity and hydration properties.[2] Due to the presence of many hydroxyl groups which act as possible sites for grafting reaction,[3] GLL is considered a suitable candidate as macromolecular support for introduction of zwitterionic moieties.

Materials and methods: The sulfobetaine methacrylate monomer (SBMA) was grafted onto GLL by free radical polymerization, using ammonium persulfate as initiator along with N,N,N′,N′-tetramethylethylene diamine as catalyst, varying the amount of the zwitterionic monomer used, i.e., x = 2, 3 and 5 mmoles of sulfobetaine methacrylate per gram of gellan. FTIR and ^{1}H NMR spectroscopy were employed to structurally evaluate the newly obtained grafted polymer. Dynamic and Electrophoretic Light Scattering were utilized to examine the gellan and zwitterionic polymer aggregates and also the polymers behavior in the presence of NaCl [4]. Nile Red and pyrene were used as probes to determine samples polarity and hydrophilicity.

Results: Both spectroscopic methods confirm the structure of the resulting polymer (Figure 1), ^{1}H NMR spectroscopy technique enabling the determination of the ratio between the zwitterionic and GLL units.

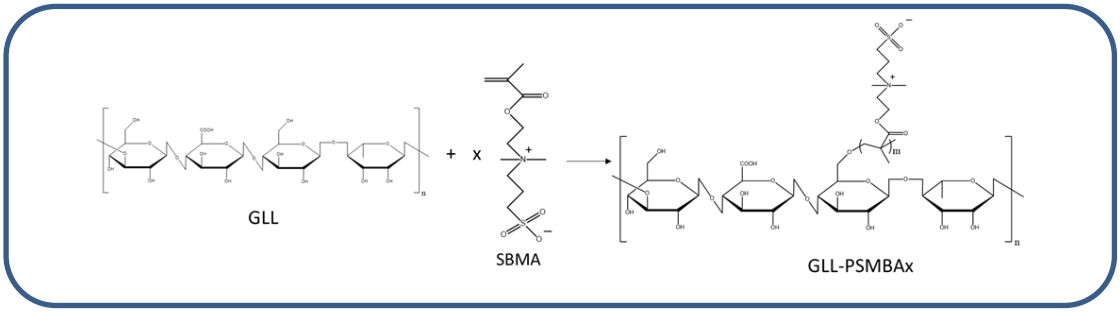

Figure 1. GLL-SBMAx synthesis reaction

The zwitterionic samples Zeta potential is around -25 mV, due to the presence of negative carboxyl group in their structure. Pyrene fluorescence analysis shows that the presence of betaine units increases the hydrophilicity as compared to the starting polymer. NaCl at concentration of at least 0.1M determines the gelation of GLL and GLL-PSBMAx 1mg/ml solutions.

Conclusions: SBMA was successfully grafted onto GLL, the presence of the zwitterionic units increasing the hydrophilicity of the polymer. Both polyelectrolyte (GLL) and anti-polyelectrolyte (betaine) behaviors were observed in the polymer-NaCl interaction.

***Acknowledgements**: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1541, within PNCDI III.*

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SILVER-COATED MAGNETITE MICROSPHERES FOR TARGETED ANTIMICROBIAL APPLICATIONS

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Keywords: magnetite microspheres, silver, nanoparticles, antimicrobial agents, antimicrobial therapy

Introduction: Magnetite has received increasing attention for medical applications due to its biocompatibility, low toxicity, and low cost. Additionally, owing to its unique magnetic properties, magnetite can be directed to the affected site using an external magnetic field. By functionalizing the surface of the particles and loading them with antibiotics, targeted drug-delivery systems can be created[1]. An example of commonly used particles are silver nanoparticles because of their biocompatibility and great antimicrobial properties[2]. This study focuses on the preparation of silver-coated magnetite microparticles that could be further used for targeted antimicrobial applications.

Materials and methods: Functionalized magnetite microspheres were obtained via a microwave-assisted solvothermal method using a single iron (III) source. The obtained microspheres were coated with silver nanoparticles in different molar ratios (1:0.25, 1:0.5 and 1:1) via a chemical reduction method.
The obtained particles were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and dynamic light scattering (DLS).

Results: XRD analysis confirmed the obtaining of single-phase magnetite after the solvothermal synthesis. FTIR spectra demonstrated the successful functionalization of the magnetite microspheres with polyethylene glycol (PEG) and the associated modifications of the spectra due to the presence of the silver. SEM analysis proved that the particles were spherical, with microscopic sizes, followed by morphological changes after the deposition of silver on the surface. EDX analysis allowed the assessment of the distribution of silver, which was present as a uniform coating onto the surface of magnetite, as well as agglomerates of silver nanoparticles at higher silver concentrations. DLS analysis allowed us to determine the Zetta potential and polydispersity index of the particles.

Conclusions: The preliminary results demonstrated the successful synthesis of magnetite microspheres through the microwave-assisted solvothermal method and the subsequent silver coating using the chemical reduction pathway. Future directions involve the evaluation of the biological properties of the obtained systems in terms of biocompatibility and antimicrobial activity.

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DESIGN OF LIQUID CRYSTALS BASED ON COPPER (I) COMPLEXES WITH BENZOYL THIOUREA

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Keywords: Copper; Metallomesogens; Benzoyl thiourea; Liquid crystal; complex.

Introduction: Liquid crystals are generally referred to as substances that integrates the structure andproperties of solid and liquid states. There are liquid crystalline materials based on copper(I) complexes prepared with various ligands[1].Although liquid crystalline property of fluorinated BTU ligands has also been studied previously[2],[3], in this report, we present a new BTU ligand and corresponding metallomesogens having just a single fluorine atom attached to a terminal part of the BTU and also present metallomesogens of ligands **L^1, L^2& L^3**(fig. **1**) whose properties have already been published[4].

Materials and methods: All the compounds reported in this work were prepared based on the reaction scheme provided in figure **1**. Each BTU ligand was reacted with $CuBr_2$, $CuCl_2$& CuI in a 2:1 proportion respectively in ethanol to afford the corresponding metallomesogens. The structure of the prepared compounds was confirmed by NMR and the liquid crystalline properties were investigated via a combination study of use of a polarizing optical microscope (POM), X-ray powder diffraction and Differential scanning calorimetry (DSC). The stability was studied via Thermogravimetry analysis (TGA).

Results: All the studied BTU ligands as well as the corresponding copper(I) complexes displayed liquid crystalline properties of the smectic phase type. Complexation of the mesogenic BTU with the metal results in a slight increase in stabilization of the liquid crystalline phase.

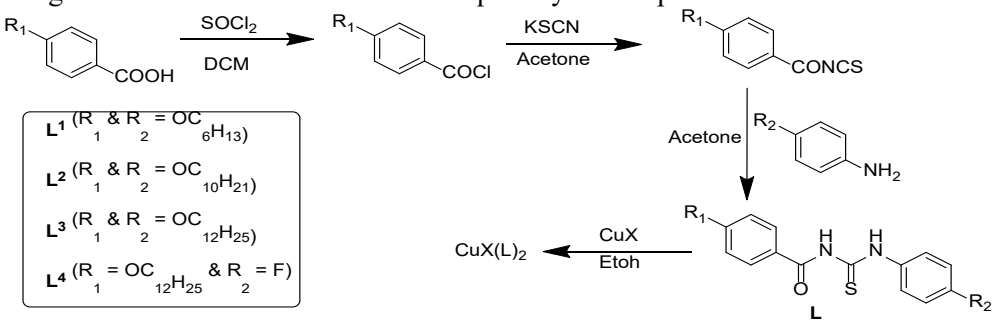

Figure 1: Reaction scheme for the prepared compounds.

Conclusions:Four mesogenic BTU ligands and twelve corresponding copper(I) halide metallomesogens have been prepared and investigated for their liquid crystalline properties. Overall studies indicate an appreciable stability of the LC phase of BTU with a single atom of fluorine on one end and an increase in stabilization of the LC phase of BTU upon complexation with a metal.

***Acknowledgements**: M.A. thanks the Romanian Ministry of Foreign Affairs and the University ofBucharest for funding and provision of other resources (project C1.2.PFE_CDI.2021-587/contractno.41PFE/30.12.2021).*

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INOVATIVE MATERIAL FOR THE CONSOLIDATION, CONSERVATION AND REINFORCEMENT OF UNDERWATER WOOD OF CULTURAL HERITAGE

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Keywords: cultural heritage, nanomaterials, apatitic materials, wood artefacts

Introduction: The concept of cultural heritage started as a simplistic one that was not given much attention, but in a very short time it ended up becoming a very complex one. Heritage objects have existed since the dawn of humanity, but they have always been seen as simple historical monuments and never grouped into such a complex concept as that of cultural heritage has become today. The increased attention given in the last decades to heritage objects is also largely due to their rapid and often irreversible degradation. The factors that lead to the deterioration of cultural heritage are multiple and often uncontrollable, divided into 2 major categories: natural factors and anthropogenic factors. Following the rapid development of environmental factors and population growth, the need for solutions to combat the degradation of cultural heritage has become a necessity, becoming a topical subject [1][2][3].

Materials and methods: The main objective of this study is the development of an innovative nanomaterial with a role in the preservation and consolidation of underwater wood of cultural heritage. The reinforcing material to be obtained consists of a polymeric part (natural or synthetic) to provide compatibility with the wood mass and an antimicrobial part (natural or synthetic phosphatic material) to provide protection against biodegradation. The challenge represented by this study consists in the use of the material, on objects made of wood and which were stored underwater. This presents a high degree of difficulty due to the physical, chemical and mechanical properties that differ from one wood mass to another, especially for heritage objects that have been in the aquatic environment for decades or hundreds of years [4].

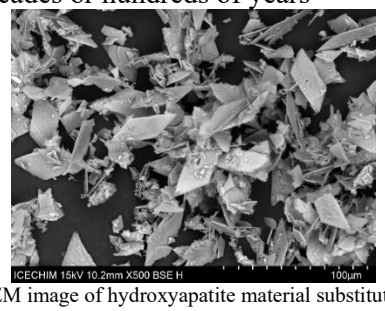

Figure 1. SEM image of hydroxyapatite material substituted with zinc

Results and Conclusions: In a first stage of the study we synthesized apatitic materials substituted with different metals in different molar ratios using the co-precipitation method. The compounds were analyzed by modern morpho-structural methods (XRD, XRF, FTIR, SEM) to confirm that the materials of interest were obtained.

Acknowledgements: *The authors gratefully acknowledge the support of the Ministry of Research, Innovation and Digitization through Program 1 - Development of the national research-development system, Subprogram 1.2-Institutional performance- Projects to finance excellence in RDI, Contract no. 15PFE/2021. The authors also gratefully acknowledge the financial support provided by a grant of the Ministry of Research, Innovation and Digitization, CCCDI—UEFISCDI, project number PN-III-P2-2.1-PED-2021-0627, within PNCDI III.*

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ADVANCED MATERIALS FOR THERMO RESPONSIVE SURFACES DESIGN

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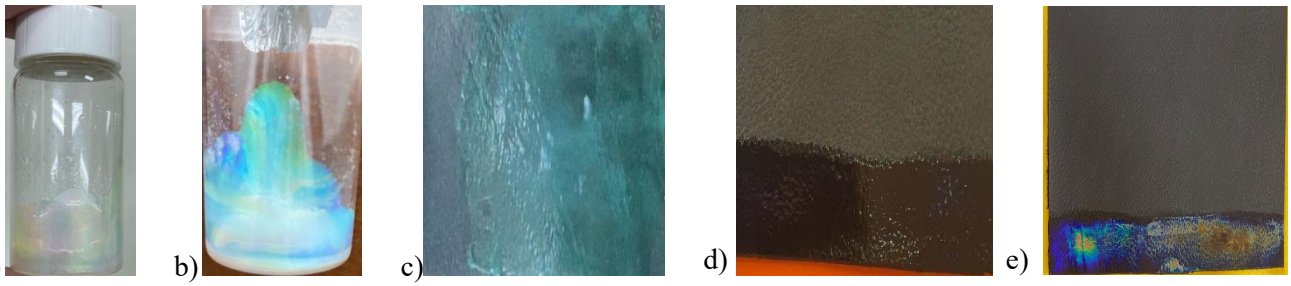
Keywords: liquid crystals; thermochromism effects; thermo responsive surfaces

Introduction: With special properties due to the supramolecular responsive structure, synthesis of liquid crystals found applications in versatile technologies, the most known being the flat panel electronic displays, optical imaging and recording, erasable optical disks, electronic slides, light modulators, lasers etc [1]. The phase transition of liquid crystals found also an interesting platform for developing sensors or thermo responsive surfaces. The synthesis and characterisation methods of liquid crystals are detailed described in literature [2], but almost no application can be found for leather surface finishing. The aim of the presentation is the development of leather surfaces with thermochromic response for versatile aestetic effects and for future aplications in flexible and wearable sensors.

Materials and methods: The cholesteric liquids were prepared by the mixing of cholesteril pelargonate with oleyl cholesterol carbonate which were incorporated into Norland Optical Adhesive 65 (NOA 65), and UV irradiated for polymerization in the presence of dichloromethane under slow stirring, in the dark. The polyvinyl alcohol was added and heated for solvent releasing, and then the photopolymerization under UV radiation at λ= 365 nm was used. Distilled and heated water was added to the obtained product. The new film forming polymer was dried and analyzed by ATR-FTIR when specific peaks of cholesteric liquid crystals were highlighted. The new mixture was used for leather and cardboards coating in view of thermochromism effects generation.

Results: The liquid crystals are shown in fig.1a) and the demonstration of their thermochromism at 38°C in fig. 1b and on two different surfaces, cardboard (fig. 1b) and leather (fig. 1c).



a) b) c) d) e)

Fig.1. Cholesteric mixture of liquid crystals at 35°C (a); at 38°C (b); deposited on cardboards (c); deposited on leather surface, before (black)(d) and after temperature exposure (e)

Conclusions: The preparation of thermochromic crystals embedded in film forming polymer showed the potential to elaborate new advanced surfaces with color thermal response, a first step for sensory applications.

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CONSIDERATIONS REGARDING ONE POT SYNTHESIS OF Ag/Ag2O@ZnAl-LDH COMPOSITES

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Keywords: LDH, cultural heritage

Introduction: Silver is a well-known antimicrobial agent extensively used in many applications such as biomedicine or conservation of cultural heritage elements prone to biodeterioration. In the recent years, a lot of interest has been placed on the silver (nano)particles incorporated or supported on 2D inorganic materials [1]. Among 2D compounds layered double hydroxides (LDHs) are interesting materials for developing 0D/2D nanostructured architecture. The use of LDH surface as a substrate or support for the antimicrobial component allow combination of the LDH biocompatibility and ion exchange properties with the bacteriostatic properties of silver [2]. Although literature covers the preparation of various Ag+/Ag@LDH composites for different applications, to our knowledge, facile one-step synthesis was not reported.

Materials and methods: The Ag-LDH composites were prepared by two different coprecipitation techniques, starting from the corresponding metallic nitrate salts and as coprecipitating agent, sodium hydroxide, respectively a mixture of sodium hydroxide and sodium carbonate (methods adapted from [3] and [4]), followed by the ageing and washing of the precipitate. The materials were characterized by powder X-ray diffraction (XRD), and X-ray fluorescence wavelength dispersed (WDXRF) in order to understand the phase, crystallinity and composition of the prepared materials.

Results: The X-ray diffractograms for both the synthesized materials present the diffraction lines at 2θ = 11.6°, 23.3°, 33.9°, 34.5°, 37.2°, 39.1°, 46.9°, 60.3° and 61.7°, assigned to the (003), (006), (101), (012), (104), (015), (018), (110) and (113) planes of typical crystalline structure of characteristic to ZnAl-LDH phase with nitrate as the compensating anion (JCPDS No.48-1022). However, the prepared composite in the presence of carbonate shows additional lines, characteristic to the same ZnAl-LDH phase but with carbonate as compensating anion, monoclinic m-phase Ag_2CO_3, metallic Ag and various other Zn containing phases. While the material prepared via coprecipitation at low suprasaturation and pH=10, presents the additional lines of Ag_2O. The elemental analysis shows that the molar amounts for each element are closed to the theoretical values.

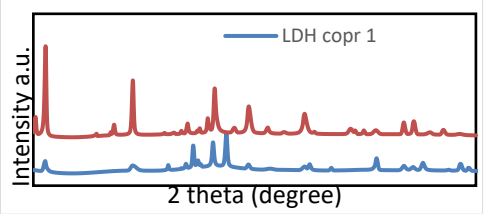

Fig 1. X-ray diffractogram of as-prepared materials

Conclusions: Ag+/Ag-LDH composites were prepared via two different methods, a fast coprecipitation in presence of carbonate anion and a coprecipitation at low supersaturation and constant pH, surprisingly, the addition of silver along the LDH precursors did not affect the formation of the LDH phase, however, the presence of the carbonate and subsequently the pH used during synthesis had impacted its crystallinity and the type of silver containing phases. The materials obtained will be further tested in various applications for our future tests in the conservation of cultural heritage.

***Acknowledgements**: Acknowledgements: This work was supported by a grant of the Romanian Ministery of Research and Innovation, PCCDI – UEFISCDI, contract no. 687PED/2022, Project PFE 15PFE/2021 - ID 583 and Nucleu project PN 23.06.02.01 – InteGral..*

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MOLECULARLY IMPRINTED NANOGELS FOR SPIKE S1 PROTEIN RECOGNITION

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Keywords: nanogels, molecularly imprinted polymers, inverse-mini emulsion polymerization

Introduction: The COVID-19 pandemic has highlighted the critical need for rapid and accurate detection of the SARS-CoV-2 virus. One approach to achieve this is through the development of synthetic antibodies that can selectively bind to the Spike S1 protein, a key component of the virus responsible for transmitting the viral entity into host cells [1]. Nanogels are described as particles that are composed of a 3D network of crosslinked polymer chains, typically with a size range between 10-200 nm. They can be designed to have a variety of properties, such as high-water content, biocompatibility, and stimuli-responsiveness. Nanogels have a wide range of potential applications in fields such as drug delivery, tissue engineering, and biosensing, due to their ability to encapsulate and release therapeutic agents in a controlled manner, as well as their ability to mimic natural biological structures [2]. Molecularly imprinted polymers (MIPs) are a promising class of synthetic materials that can be designed with high specificity and sensitivity towards their target molecule [3]. Therefore, the present study describes the synthesis of MIP nanogels (MIP-SNA) by an inverse mini-emulsion polymerization process which involves imprinting the template molecule into a hydrogel matrix. The resulting MIP-SNAs can be used as a sensitive and selective tool for the detection of the Spike S1 protein, offering potential advantages over traditional antibody-based assays.

Materials and methods: The molecularly imprinted synthetic nanogels (MIP-SNA) were obtained through polymerization in inverse mini-emulsion in presence of SARS-CoV-2 Spike S1 protein RBD (PSS1) as a template and using two polyethylene glycol diacrylate monomers.

Results: The physico-chemical characterization of PEGDA macromonomer, and MIP-SNA was carried out using different techniques such as FTIR, TGA/DTG, DLS, and SEM. The similarity between FTIR spectra of NIP-SNA and MIP-SNA confirmed that the chemical structure of MIP-SNA which is based on non-covalent bonds was not modified during the imprinting process. TGA/DTG analyses confirmed the presence of both macromonomer and protein/emulsifiers in the structure of MIP-SNA. Particle size was analyzed using DLS, and SEM images highlighted the individual spherical structures of the synthesized particles.

Conclusions: In this work, studies were conducted to obtain and characterize the physicochemical and morphological properties of MIP-SNAs based on polyethylene glycol diacrylate, in the presence of Spike S1 protein used as a template, through polymerization in inverse mini-emulsion. The characterization of the samples confirmed the presence of the compounds of interest and indicated the desired size for the potential application. The future is indeed promising and in the coming years there will be unprecedented progress in the control and manufacture of such systems and the translational application of these intelligent structures on a large scale in pharmacy, medicine, tissue engineering, sensors and diagnostics, micro and nano-diagnostics, and separation processes.

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LIPOPOLYSACCHARIDES DETECTION BY SPCE BASED ON INNOVATIVE CARBON PASTE FORMULATIONS WITH EMBEDDED MOLECULARLY IMPRINTED PARTICLES

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Keywords: molecularly imprinted particles, LPS detection, particle embedment, electroactive particles

Introduction: Drug resistance can be classified as the persistence and tolerance developed over time by microorganisms within the interaction with lethal doses of antibiotics [1]. The overuse and misuse of antibiotics without the prior recommendation of a doctor especially in the pandemic, is the main factor in the emergence of multi-resistant strains (superbug bacteria) and the causes of infections with bacilli such as the pyocyanin bacillus, both in hospital environments and community [2]. Therefore, accurate and cost-effective methods of bacterial detection are essential to prolong the lifespan of existing antibiotics in use and to help healthcare providers to prescribe antibiotics more judiciously.
Regarding these concerns, this work describes the obtaining and deposition of a carbon paste formulation based on embedment of molecularly imprinted particles (MIPs) designed as polymer shells that possess complementary shape, size, and chemical properties with the used target molecule [3]. In this study, based on the World Health Organization (WHO) priority pathogenic bacteria list [4], the chosen target molecule was represented by lipopolysaccharides from the second most concerned superbug bacteria namely *Pseudomonas aeruginosa*.
Materials and methods: To obtain the carbon paste formulation, the obtained MIPs particles previously synthesized in laboratory through a sol-gel method, were embedded in a carbon mixture based on a commercial carbon paste, nano-ZnO electroactive particles, a polyether-based binder, and a compatible solvent. Further on, the obtained formulation was drop-casted on the working surface of ceramic screen-printed carbon electrodes and cured using thermal treatment.
Results: Modern techniques, including structural and morphological analyses, were employed to characterize the obtained modified screen-printed carbon electrodes which demonstrated the successful embedment of MIP particles into the drop casted carbon paste formulation. The obtained modified screen-printed carbon electrodes were also submitted to cyclic and differential pulse voltammetry analyses in order to determine the capacity of the resulting carbon paste formulation to efficiently recognize the target molecule.
Conclusions: Therefore, the obtained screen-printed carbon electrodes modified with carbon paste formulation can act as an efficient tool for LPS detection from *Pseudomonas aeruginosa* due to their practical size, the low-cost of manufacture and a significantly low quantity of the required carbon paste.

***Acknowledgements**: This work was supported by the Ministry of Research, Innovation and Digitization through Program 1 - Development of the national research and development system, Subprogram 1.2 -Institutional performance- Projects to finance excellence in RDI, Contract no. 15PFE / 2021.*

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SYNTHESIS AND CHARACTERIZATION OF METAL-OXIDE PHOTOCATALYSTS WITH HETEROJUNCTIONS FOR WASTEWATER TREATMENT

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Keywords: photocatalysis, heterojunctions, organic pollutants, antibiotics, depollution

Introduction: Among the conventional treatment methods, the photocatalytic methods use catalysts to decompose photochemically organic pollutants in water. An intermediate problem that needs to be solved is the recovery of these chemicals after treating contaminated waters [1]. Conventional treatment methods are reported to be ineffective because some contaminants found in wastewaters are resistant at some extent [2]. Our group developed photocatalysts with metal-oxide heterojunctions, on a doped hydroxyapatite support for application in depollution processes of waters contaminated with selected organic pollutants, in particular antibiotics, which are found in effluents generated by different industries.

Materials and methods: In this study, we synthesized five metal-oxide photocatalysts, using copper acetate, cobalt acetate, chromium acetate, nickel acetate and ferric chloride as metal-oxide precursors and hydroxyapatite as supporting material using a Discover 2.0 Microwave Flow Reactor, at the temperature of around 160◦C, 300 W power, for 10 min. In order to make sure that the photocatalysts have the desired properties, we characterized them through modern analytical methods. In addition, the photocatalytic properties of the synthesized materials were determined by mixing separately the metal-oxide photocatalysts with a styrene-acrylic film-forming material, prepared using a method developed by us, as previously described [3]. The resulted materials were deposited on glass plates and were immersed in a vessel containing water contaminated with ceftriaxone, an antibiotic used in the treatment of bacterial infections. The reaction vessel was illuminated using a Xenon arc lamp and the degradation of the pharmaceutic product was monitored by UV-Vis absorption spectroscopy.

Results: The obtained materials presented adequate properties and they showed good results regarding the photocatalytic activity.

Conclusions: Based on the results obtained using water samples contaminated with ceftriaxone, the synthesized nanomaterials possess adequate morphological and structural characteristics for their use in water depollution by photocatalytic methods.

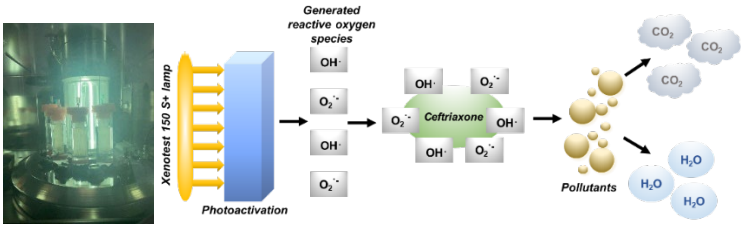

Figure 1. The mechanism of photocatalytic decomposition of ceftriaxone

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"GREENER" POLYURETHANE COMPOSITES WITH SPECIAL FEATURES

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Keywords: polyurethane; bio polyols; PET recycling; composites; vegetable oil

Introduction: Polyurethane (PUR) is one of the most used polymers in the world, owing to its good mechanical properties that can be tailored to suit different applications that require high tensile strength, wear and abrasion resistance or elasticity. By combining the aforementioned properties with its other advantages such as high chemical resistance to hydrolytic, enzymatic or photo-oxidative degradation or the degeneration produced by solvents or corrosive agents, polyurethane is a versatile polymer that finds uses in a variety of applications such as rigid and flexible foams, thermoplastics, fibers, biomedical devices, elastomers, sealants, adhesives and coatings [1].The process of obtaining polyurethane typically involves the polyaddition reaction of a polyol and a poly- or di- isocyanate. The vast majority of polyols and isocyanates used for the polyurethane production are petroleum derivates. Being a finite global resource, as more and more petroleum is extracted, the scarcity of petroleum will force the industries based on it to use renewable sources as alternatives or to chemically recycle the non-biodegradable plastics such as polyesters, polyurethanes, polyamides etc. The most studied feedstocks for the synthesis of polyols aimed at the production of polyurethanes are vegetable oils [2] because of the high crop yield associated with their manufacturing and also because of the simplicity of the chemical modifications required. Other biomaterials studied for this scope are wood derived lignocelluloses (from agro waste), starch, chitosan, microalgae etc. [3].

The chemical recycling of polyethylene terephthalate (PET) by glycolysis for polyol obtaining is an efficient way to reduce the need of petroleum for PUR production and to limit the disposal of PET waste in the environment, as PET is considered a non-biodegradable plastic [4].

Materials and methods: Polyols based on recycled PET have been synthesized using a two-step method: the glycolytic depolymerization of PET in presence of polyethylene glycol and esterification of the resulting oligomers with linear saturated dicarboxylic acids. The resulted polyols were reacted with an aromatic polyisocyanate based on methylene diphenyl diisocyanate (MDI) and glycerol. The resulted polyurethanes were characterized using FTIR, TGA, DSC and DMA.

Results: Previously obtained polyols based on recycled PET were reacted with isocyanates and a crosslinker. The polyurethane films thus obtained showed very good flexibility and good tensile strength. The FTIR spectra of the polyurethanes revealed the characteristic absorption bands for the urethane linkage. The glass transition temperature was determined using DSC and DMA. The loss and storage modulus were analyzed using DMA.

Conclusions: The synthesized polyurethanes samples showed promising mechanical properties and a good film-forming ability. They are to be reinforced with antibacterial inorganic fillers based on natural and synthetic phosphates and introduced in protective coating formulations to achieve conservation and restoration of wooden artifacts.

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RAPID AND SIMPLE DETERMINATION OF NITRITE IN SOIL BY USING PORTABLE AND MINIATURIZED ELECTROCHEMICAL TOOLS

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Keywords: nitrite; miniaturized sensors; soil; MWCNT-chitosan; lysimeter

Introduction: Nowadays, the rapid and easy determination of nitrite in environment and foods represent a necessity, since its chemical importance has been highlighted in many fields, especially in food and agriculture development. Nitrite is part of the nitrogen cycle and eutrophication, through its accumulation being able to lead to high toxic effects to plants and animals. Moreover, nitrites and nitrates are use as additives in food processing and as inhibitors for the microorganism growth, an overexpression of them in the body being able to affect the transport of oxygen in the blood and generating methemoglobinemia, known to cause death [1,2]. Thus, electrochemical sensors based on carbon nanomaterials and different matrices of dispersion were developed for sensitive and rapid determination of nitrite in soil samples extracted with low volume suction lysimeters.

Materials and methods: Commercial screen-printed carbon paste electrodes (SPEs) on PVC support were modified with nanocomposite material based on multiwalled carbon nanotubes (MWCNTs) and different matrices of dispersion (polymers, sol-gel, etc.). Electrochemical (cyclic voltammetry, electrochemical impedance spectroscopy and amperometry) and morpho-structural (SEM, FTIR) studies were performed in order to characterize and optimize the analytical parameters of the developed sensors. Determination of nitrite in real samples of soil solutions was carried out at room temperature, by using low volume suction lysimeters for root level soil monitoring.

Results: Electrocatalytic behavior of the modified sensors over the oxidation of nitrite was studied in acetate and respectively, phosphate buffer solutions of 0.1M, with pH ranging from 4 to 9. An enhanced electrochemical behavior and a decrease of the potential used for nitrite oxidation have been obtained by using chitosan (CS) as dispersion matrix for MWCNT. Completing the electrochemical studies with the morpho-structural analysis, it has been revealed a synergistic effect between MWCNT and chitosan. Optimization of the working potential, as well as of the buffer's pH were done in order to achieve a sensitive and selective determination of nitrite by using MWCNT-CS based sensors. Thus, sensitive and selective determination of nitrite was achieved in acetate buffer 0.1M, pH 5, at an applied potential below +0.6V vs Ag/AgCl. Detection of nitrite was performed with a specific sensitivity of 204.4 $mA \cdot M^{-1} \cdot cm^{-2}$ in a linear range up to 1.7 mM, in acetate buffer 0.1M, pH 5, at an applied potential of +0.58V vs Ag/AgCl. The limit of nitrite detection achieved by using MWCNT-CS based sensors was 2.3 µM (S/N=3), the sensors showing good stabilities and reproducibility. A miniaturized portable system using the developed MWCNT-CS based SPEs was dedicated for the detection of nitrite in soil solutions samples extracted by using suction lysimeters.

Conclusions: A simple and miniaturized electrochemical sensor based on MWCNT-CS nanomaterial was developed for sensitive, selective and rapid determination of nitrite in soil solutions. Detection of nitrite in real samples was performed by using portable electrochemical detector and the developed sensor inserted directly in the suction lysimeters.

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EFFICIENT COPPER REMOVAL FROM SIMULATED WASTEWATERS USING ALGINATE-BASED POLYMERIC BEADS

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Keywords: alginate beads, wastewaters, copper removal

Introduction: Copper is a common pollutant in water sources due to its extensive use in various industries. When copper enters water bodies, it can negatively impact aquatic life and human health. High concentrations of copper can damage gills, scales, and reproductive organs of fish, impairing their ability to survive and reproduce. Copper contamination in drinking water can cause health issues such as stomach cramps, nausea, and liver and kidney damage. Copper can also react with water to form compounds that alter the color, taste, and odor of water, making it aesthetically unappealing. Therefore, effective removal of copper from water sources is critical for the protection of both human health and the environment. Several methods are available for the removal of copper from water, including chemical precipitation, ion exchange, adsorption, and membrane filtration [1]. Among these methods, adsorption using polymer composite beads has gained significant attention due to its effectiveness, simplicity, and cost-efficiency. Alginate-based polymer composite beads have been developed as an effective method for copper removal from water sources. These beads consist of alginate, a biopolymer derived from seaweed, and other materials such as chitosan or activated carbon, composite inorganic-organic, which enhance their copper adsorption capabilities. The composite beads have a high surface area and can be easily regenerated for multiple cycles of use. The adsorption process is dependent on factors such as pH, temperature, and contact time, and can be optimized to achieve maximum copper removal efficiency. Overall, alginate-based polymer composite beads offer a promising solution for the efficient removal of copper from water, with potential applications in wastewater treatment and environmental remediation. The main purpose of the work is to develop and evaluate the efficacy of alginate-based polymer composite beads for the removal of copper from water sources.

Materials and methods: In this study alginate and inorganic-organic composite beads were synthesized by an efficient and innovative process.

Results: Physical were performed using X-Ray Diffraction (XRD). In addition, Fourier-Transform Infrared Spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA) were used to evaluate the chemical composition and thermal properties of the adsorbents. Determination of the adsorption capacity of composite polymeric beads was analyzed using Atomic Absorption Spectroscopy (AAS).

Conclusions: The new polymer biocomposite beads exhibited outstanding copper adsorption capabilities and can serve as promising materials for environmental remediation.

***Acknowledgements**: This work was supported by the Ministry of Research, Innovation and Digitization through Program 1 - Development of the national research and development system, Subprogram 1.2 - Institutional performance- Projects to finance excellence in RDI, Contract no. 15PFE / 2021. and PN-III-Human Resources Programme-YOUNG RESEARCH TEAMS-PN-III-P1-1.1-TE-2021-0915, grant no. 135/2022 - I-ON-MEM.*

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CRYOGELS BASED ON CHITOSAN FOR ANTIBIOTICS RETENTION

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Keywords: chitosan; cryogels; clay; antibiotics; water purification.

Introduction: In recent years, chitosan gained a lot of interest, especially when it comes to medical uses (wound healing, excipients for drug administration), due to its great biocompatibility and low toxicity [1]. However, low mechanical properties of this polymer limit to some extent its use. For this reason, in this study, chitosan was used in mixture with a natural clay, i.e., kaolin. The clay (Kaolin) was chosen due to its low toxicity and the occurrence of hydroxyl groups, which is suitable for preparing cryogels with adsorption properties [2][3]. Carbamazepine (CBZ) and Ciprofloxacin (CIP) are two types of antibiotics which are widely used in treatment of upper infection, epileptic diseases and many others [4]. As a consequence, a significant part of these antibiotics ends up in wastewaters. In order to retain all the traces of the antibiotics, new materials based on chitosan and clay have been studied.

Materials and methods: To develop new cryogels with adsorption capacity towards antibiotics, commercial chitosan (CC) and an organophilized clay (K-MAPTES) were required. The other reagents used: acetic acid, was used in mixture with water, for chitosan dissolution; methacryloxypropyltrimethoxysilane (MAPTES, Sigma Aldrich), the organophilization agent for Kaolin modification; crosslinking agent and two antibiotics (CBZ and CIP). The organophilization stage was needed because kaolin is an inorganic compound and, in order for it to be incorporated into the chitosan matrix it needs some organic moieties on its surface. The cryogels obtained were lyophilized and tested for antibiotic retention.

Results: Several characterization techniques (FTIR, SD, UV-Vis) were required to demonstrate the preparation of the developed materials. The FTIR spectra confirmed the incorporation of the inorganic component into the polymer matrix, by the appearance of the characteristic bands for the silylation agent- MAPTES and for the involved materials. The Swelling Degrees were used to determine the swelling capacity of the samples and also to establish how much time they were able to keep their integrity in water. The UV-Vis results indicate great adsorption capacity of cryogels for both antibiotics (CIP and CBZ).

Conclusions: In conclusion, following the results obtained, new cryogels based on chitosan and clay were obtained. These materials show great adsorption capacity for antibiotics and present potential for future use in wastewater treatment.

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BIOACTIVE GLASS PARTICLES FOR BONE TISSUE ENGINEERING

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Keywords: bioactive glass; sol-gel; biomaterials; tissue engineering

Introduction: Biomaterials play an essential role in today's world, facilitating the healing of injured tissues and restoring vital functions. Metals, ceramics, plastics, glass or even living cells and tissues can be used to create a biomaterial to support, enhance or replace damaged tissue. For a material to be considered a usable biomaterial for clinical applications, it must possess properties such as availability, low cost, no toxicity, inert to prevent body reactions or infections when implanted, easy to shape and not requiring additional surgical time [1]. Bioactive glass (BG) fulfills these conditions and is being considered for bone tissue engineering applications based on their ability to bind strongly to bone, which is mediated by the formation of a carbonated hydroxyapatite surface layer [2]. Bioactive glass, regardless of its composition, can be produced by two processing methods: the traditional melt-heat method at high temperatures and the sol-gel method, in which the precursors react at room temperature to form a gel [3].

Materials and methods: The method used in this work is sol-gel, resulting in more reactive materials and various textural properties. Following this idea, we present here the production of bioactive glass by the sol-gel method, with different textural characteristics. The syntheses were carried out in an acid medium using the same precursors and different procedures.

Results: In this study we synthesized bioactive glass particles by sol-gel method. The modification of the procedure results in materials with different textural characteristics. As water and alcohol evaporate, a rigid gel begins to form, with a network of interconnected pores. The processing of gelled sol has allowed several morphologies to be achieved by changing processing parameters such as gelling time or initial precursors.

Conclusions: According to the experimental results, we concluded that reaction conditions play an important role in particle size and morphology.

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MARBLES VS GRANITE. WEATHERING IN DIFFERENT CLIMATIC ENVIRONMENT

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Keywords: marble; granite; surface damage; cultural heritage

Introduction: The majority of exterior stone structures and decorations are subjected to temperature variations, both day-night cycles temperatures change as the sun heats the exposed surfaces and long variations as the air temperature changes through the seasons. Alterations such as granular disintegration, contour scaling and alveolus formations, can be observed either at the base of blocks and columns, or at the median-high zones of monuments [1]. In general, materials expand as they are heated but by differing amounts, depending on the material coefficient of expansion and its colour [2]. The aim of this paper is to study the changes in the aesthetic parameters of three types of marble (Ruschita marble, Albesti marble and Carrara marble) and three types of granite that come from Italy (Rosa Aswan (RA), Gray Granite (GT) and Beige Granite (BG)). The aim of this paper is to study the weathering mechanism of marbles and granite exposed to weathering in a climatic chamber.

Materials and methods: The samples were obtained by cutting pieces of marble with a diamond blade. The natural day, night weathering was simulated using a climatic chamber with controlled humidity, temperature and light, the sample were exposed to 20 cycles (each cycle consisted in 6h of exposure to 45 °C and 60% humidity after which the samples were exposed to room temperature and cool down). The final samples were analyzed by visual and stereoscopic analysis with (Euromex Binocular Stereomicroscope), by chromatic analysis (with a Konica Minolta CR-410 Chromometer) and by Glossometry (with Glossmetr HG268).

Results: By analyzing through visual and stereo microscopy, only small changes in the surface appearance can be observed for all the samples. The chromatic parameters also vary little after the exposure to artificial weathering, the DE parameter is less than 5 in the case of marbles and less than 2 in case of granit. A higher change in gloss has also been observed for marble.

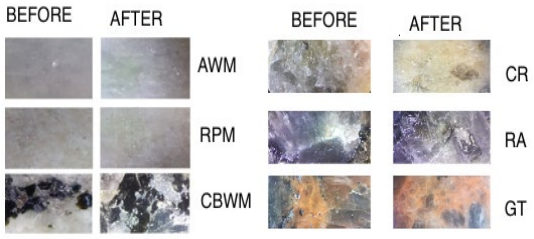

Figure 1. Stereomicroscopy marble and granite,(before and after the climatic chamber).

Conclusions: Based on the results of this study, it could be concluded that the artificial weathering cycles, will lead to the growth of superficial cracks at the specimens surface, and slight changes in the aesthetic parameters. The granite samples surface shows much less change in esthetics than the marble specimens, but nonetheless, the changes are not visible to the naked eye.

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DISCRETE AND EXTENDED STRUCTURES BASED ON COBALT AND HEXAFLUOROACETYLACETONE

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Keywords: metal clusters, coordination polymers, carboxylate ligands

Introduction: Coordination compounds of cobalt have attracted a focus of research due to their fascinating structures and potential applications in catalysis, electricity and magnetism [1][2]. With multiple possible oxidation states, the Co ion can display a positive magnetic spin, which can contribute to applications in molecular magnetism. The hexafluoroacetylacetone ligand, with its high fluorine density has been shown to enhance molecular magnetism properties through intermolecular fluorine-fluorine interactions, and it can easily coordinate to metal ions due to the favorable bidentate carboxylate structure.

Materials and methods: Our study therefore was focused on the synthesis and characterization of novel compounds of cobalt with the hexafluoroacetylacetone ligand. The complexes were synthesized using cobalt hexafluoroacetylacetonate ($Co(hfac)_2(H_2O)_2$), diethanolamine (H_2dea), acetic acid (HAc), triethylamine (NEt_3) for deprotonation, and various solvents.

Results: By optimizing the reaction conditions and the ratio between reagents, seven new complexes were obtained, containing cobalt ions and the hexafluoroacetylacetone ligand, one of which is also a 1D coordination polymer.

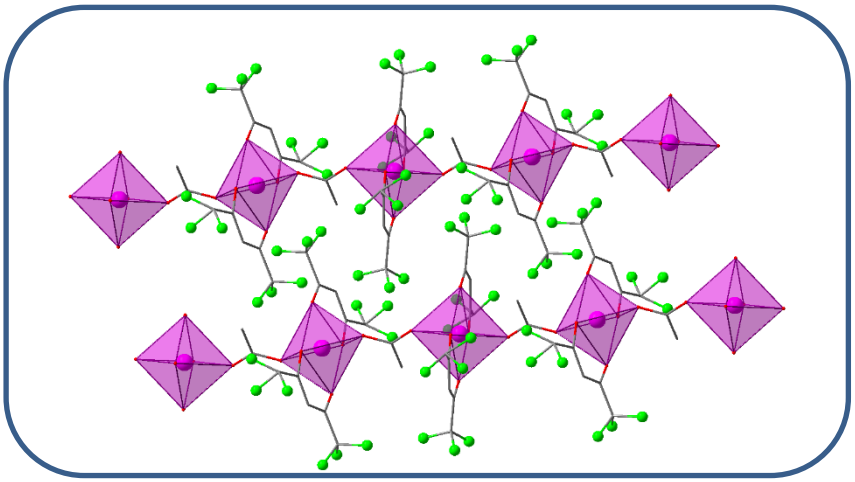

Figure 1. $Co(hfac)_2$ units of the 1D coordination polymer

Conclusions: The complexes and their structures were characterized and confirmed through SC-XRD, FT-IR and UV-VIS spectroscopy. More studies will be performed on these novel compounds to establish possible applications in magnetism or catalysis.

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OXIDOVANADIUM COMPLEXES WITH POTENTIAL INSULINOMIMETIC ACTIVITY

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Keywords: oxidovanadium coordination compounds; Schiff base ligands; crystal structure; biological activity

Introduction: Biological activity of oxidovanadium complexes has been intensively studied in recent years, revealing the fact that they show antimicrobial, antidiabetic, antitumor, and antiparasitic activity [1]. At the moment, there is no drug that can stop the progression of type 2 diabetes [2]; there are only a few that can slow it down, so coordination compounds of oxidovanadium may be suitable candidates for the treatment of diabetes.

Materials and methods: Oxidovanadium complexes with Schiff base ligands obtained from *o*-vanillin and essential amino acids, such as L/D/DL-leucine and L/D/DL-isoleucine, were synthesized. The compounds were characterized spectrally and structurally in solid state. Elemental analysis was carried out on a EuroEA Elemental Analyser (soft Callidus™) system. Molecular structures were determined by single-crystal X-ray diffraction with a Rigaku XtaLAB Synergy S diffractometer using SHELT-2018 and Diamond 3.2 software for graphical representations and the IR spectra were obtained in the range of 4000-400 cm^{-1} on a Bruker Fourier Transformance Tensor V-37 spectrophotometer, using OPUS software and KBr as reference. The circular dichroism (CD) spectra of vanadium complexes were measured on a Jasco J-1500 spectrophotometer.

Results: Several oxidovanadium complexes were obtained in the reaction between $VOSO_4 \cdot 3H_2O$ and the ONO donor Schiff base H_2L obtained by condensation of *o*-vanillin with L/D/DL-leucine or L/D/DL-isoleucine, resulted in the formation of a family of coordination compounds with the general molecular formula ([(VO)L(CH_3O)(CH_3OH)]. All compounds are characterized in the solid state and in solution, by elemental analyses, spectroscopic techniques (IR, UV-Vis, circular dichroism), as well as single crystal X-ray diffraction analysis. It was observed that structural differences occur when the amino acid used to obtain the Schiff base has different configurations. Thus, the compound that has an amino acid with L configuration in the composition of the Schiff base is dinuclear, while the one in which the amino acid has both D and L configuration is mononuclear. The structure of the mononuclear compound can be seen in figure 1.

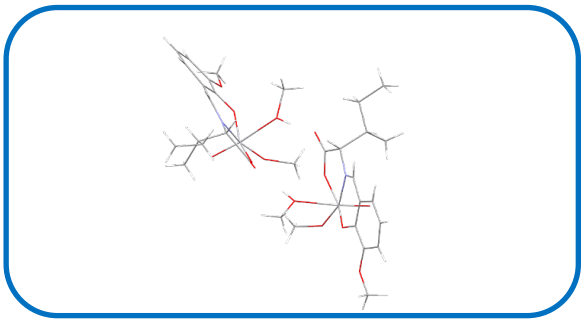

Figure 1. Crystal-structure of [(VO)L(CH_3O)]·CH_3OH

Conclusions: We have synthesized and characterized a new family of oxidovanadium coordination compounds with Schiff base ligands derived from leucine and isoleucine. We hope this work would provide new insight for potential applications of vanadium complexes as insulin-mimetic compounds.

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SYNTHESIS AND EVALUATION OF NOVEL CHITOSAN-BASED MATERIALS FOR EFFICIENT REMOVAL OF HEAVY METAL IONS FROM WASTEWATERS

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Keywords: chitosan synthesis, chitosan-based materials, wastewaters, heavy metals removal

Introduction: Heavy metals are considered toxic pollutants as they are not biodegradable and tend to accumulate in living organisms, causing various adverse effects such as cancer, neurological disorders, and damage to the kidneys, liver, and other organs. Additionally, heavy metals can also alter the physical and chemical properties of water, making it unsuitable for consumption or agricultural use. The negative impact of heavy metals on water has led to the development of various technologies for their removal and remediation from contaminated water sources[1][2].Chitin, a naturally occurring polymer found in the shells of crustaceans like shrimp and crabs, is the source of the biopolymer chitosan. Due to its ability to adsorb heavy metals, dyes, and organic molecules from contaminated water, it has generated interest in wastewater treatment. Various wastewater treatment processes, including coagulation-flocculation, membrane filtration, and adsorption, can use chitosan-based materials as adsorbents, flocculants, and membranes. Chitosan is an opportunity material for efficient and long-lasting wastewater treatment because of its characteristics, including its high cationic charge density and biodegradability [3][4].The mainobjective of the present research is to develop novel polymeric materials utilizing chitosan as a base for the purpose of adsorbing heavy metals from wastewaters.

Materials and methods: Chitosan was synthesized through the chemical deacetylation of chitin, which is a cost-effective process that does not involve the extensive use of reagents.

Results: Novel chitosan-based adsorbentswere obtained, and innovative methods were used to evaluate the adsorption capacities of thematerials. Using X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) analysis, and Scanning Electron Microscopy (SEM), the physical, morphological, and textural characteristics were determined. Adsorption capacity over time was observed using Atomic Absorption Spectroscopy (AAS). For insight into how synthesis parameters affected the final material properties, Thermal Gravimetric Analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR) were used.

Conclusions: The obtained innovative materials possess exceptional adsorption performance.

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COMPOSITE MATERIALS BASED ON CHITOSAN FOR SLOW RELEASE OF NPK FERTILIZERS IN AGRICULTURE

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Keywords: chitosan, cryogels, organic waste, liquid digestate, fertilizers

Introduction: The global food systems is under increasing pressure and, therefore, the agriculture sector will be challenged to provide food security for a growing world population without harming the environment. Modern technology will also be required in agro-ecosystems to assure enough food production and to reduce the harmful environmental effects brought on by the use of chemical fertilizers and incorrect disposal or recycling of agricultural waste [1][2]. Numerous studies in the literature have focused on the development of controlled-release biofertilizers and the use of crop residues as cover and carrier. Nitrogen (N), phosphorus (P) and potassium (K) are essential nutrients for plant growth. However, the application of these nutrients in the form of chemical fertilizers affects crops and soil [3][4]. Which is why, controlled release of nutrients is need. As result to this societal and environmental necessity, new composite materials with high nutrient content were developed in this study.

Materials and methods: For the preparation of innovative composite materials (cryogels) with nutrient content, commercial chitosan (CC) and liquid digestate (obtain from anaerobic digestion of organic waste) were used. Other reagents: acetic acid, was used in mixture with water, for chitosan dissolution; crosslinking agent. Two series of samples were prepared, some based on chitosan being considered as reference samples and in the case of the second series there were also nutrient-containing cryogels.

Results: In order to highlight the preparation of the aimed materials, several characterization techniques were needed (FTIR, SD, SEM). The FTIR spectra confirmed the incorporation of the liquid digestate into the polymer matrix, by the appearance of the characteristic bands for the materials. The Swelling Degrees were able to determine the ideal time for the samples (with and without liquid digestate) for resisting in water. Following this study, the cryogels will be further tested on UV-Vis for the controlled release of fertilizers.

Conclusions: In conclusion, new composite materials based on chitosan and liquid digestate were developed. These materials show great properties in terms of their structure, morphology and swelling capacity, making them potential candidates for future agricultural applications, as controlled release systems for NPK.

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GLASS FIBER/ASH REINFORCED POLYMER COMPOSITES FOR LIGHTWEIGHT AUTOMOTIVE PARTS

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Keywords: polypropylene; polyamide; glass fiber; ash; fiber reinforcement

Introduction: To address critical issues affecting both consumers and climate, the automotive industry is undergoing a major transformation regarding minimizing energy consumption of cars. One way to achieve this goal is to reduce the weight of vehicles by utilizing composite materials that have good strength to weight ratio for the manufacturing of lightweight components, that would decrease fuel consumption and harmful emissions [1]. An example of such composites are fiber reinforced polymers, particularly those based on glass fiber, which are regularly used in the automotive sector, due to their high-performance mechanical properties and lesser weight as against metallic car components [2]. To further reduce the weight of car components and to facilitate a simpler recycling process, a reduction in the amount of glass fiber within the composites should be achieved without jeopardizing the general properties required for these materials. The introduction of ash as a reinforcing agent in glass fiber reinforced composites not only helps reduce the glass fiber quantity but also provides usefulness and purpose to a waste material that would otherwise be discarded and would contribute to pollution of the environment [3]. This study reviews recent applications of various types of glass reinforced composite materials in automobiles as well as presents preliminary work involving the reduction of glass fiber in polymer composites via the introduction of ash waste as a substitute.

Materials and methods: For the preliminary tests, commercial polypropylene (PP) and polyamide 6 (PA6), glass fiber (F) and ash waste (C) were used. Samples, with 15-30% glass fiber and 15-25% ash were prepared in dynamic conditions through extrusion and injection molding for physico-mechanical (Impact testing, DMA), morphological (SEM), thermal (TGA, DSC) and tribological characterization (Nanoindentation and nanoscratching).

Results: Many advancements, including those provided in recent studies, were made possible by the disclosure of several production processes, including resin transfer, injection and compression molding. Each technology has advantages and disadvantages, and it is appropriate for a specific kind of material, set of performance requirements, and set of structural configurations. For the preliminary tests, the gradual introduction of ash leads to similar thermal stability of the composites. Scanning electron microscopy showed that the glass fiber in all composites is well embedded and evenly spread across the polymer matrix for both polypropylene and polyamide 6 while ash can be found in under the form of small agglomerates or as cubic structures. The storage modulus and stiffness of the composites gradually decreases (up to 27%) when lowering the glass fiber concentration, while nanoindentation tests seem to point that both hardness and reduced modulus values increase with the introduction of ash waste when compared to the 30% glass fiber polypropylene and polyamide 6 sample composite.

Conclusions: Discovering cost-effective, lightweight materials and more environmentally friendly manufacturing techniques are key aspects in the competition to create cars of the future. Fiber reinforced polymers are considered suitable substitutes for heavy metal car materials and ideal for the construction of superior, energy-efficient automobiles. Regarding the preliminary tests, we inquire that further investigations are needed to see the effect of the usage of compatibility agent and lubricant in the composites, that should lead to improving the composites homogeneity, and further improve their general physico-mechanical properties.

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Session 2 - Bioresources, biotechnologies and biorefinery

COMPOSITE NANOPARTICLES BASED ON ZEIN AND POLYSACCHARIDES

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Keywords: Polysaccharides; Zein; Nanoparticles; Alginate; Chondroitin sulfate

Introduction: Zein is a hydrophobic plant protein that has the ability to self-assemble into micro-/nanoparticles[1],[2]. However, because of its aggregation tendency and insolubility in water, it is difficult to be employed as a sole material[3]. In order to improve the stability, polysaccharides can be incorporated into the zein particles[1]. The present work focuses on optimizing composite protein/polysaccharide nanoparticles synthesis by varying different parameters: polysaccharide functional groups, alcohol/water ratio and polysaccharide/zein ratio.

Materials and methods: Zein and two polyanions, sodium alginate (Alg) and chondroitin sulfate A (CSA), were used to prepare interpolymeric complexes by titration of the polysaccharide solutions with different volumes of zein solution (60 or 70% ethanol, denoted as Z60 or Z70). The particle size, polydispersity index and zeta potential for the obtained particles were assesed by dynamic light scattering. Morphological characteristics of the particles were observed by scanning electron microscopy.

Results: Depending on the ratio between polymers and the ethanol content in zein solutions, particles of different sizes were obtained, as shown in Figure 1.It can be observed that the excess of polyanion led to the formation of particles with sizes between 60 and 150 nm (Figure 1a). Also, the polydispersity index of these composites is <0.4 and the zeta potential between -5 and -25 mV. SEM images revealed that the particles have a spherical shape (Figure 1b) and confirmed the information collected with Zetasizer.

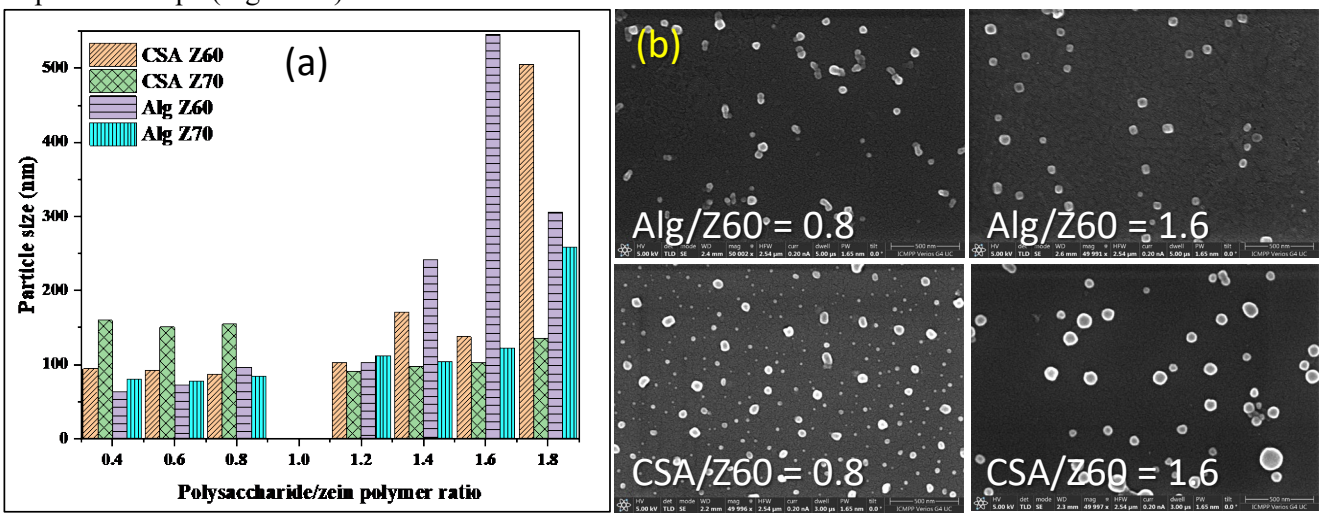

Figure 1. (a)Particle size and (b) shape of polysaccharide/zein interpolymeric complexes

Conclusions: Based on the obtained results we can conclude that the composite particles characteristics can be tuned by the synthesis conditions: polysaccharide functional groups, alcohol/water ratio, polysaccharide/zein ratio.

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XANTHAN AND LIGNIN ESTERS – BASED MATERIALS FOR DEGRADED ARGAN OIL SORPTION

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Keywords: lignin esters, xanthan, adsorbents, altered argan oil adsorption

Introduction: Argan oil is widely used in cosmetic or pharmacological industries [1]. A great number of chemical reactions (oxidation, hydrolysis, and a breakdown of fatty acids) occur in the oil at high temperature, exposure to air, light or moisture. Degraded oils become toxic due to the formation of harmful compounds such as peroxides, aldehydes or ketones. This is why researchers have been seeking to design suitable and inexpensive materials/methods to retain the degraded oils from wastewaters [2,3]. The present study is focused on the preparation of new adsorptive materials based on xanthan and lignin esters. Their mechanical and morphological properties were evaluated. The adsorption of altered argan oil and sunflower oil onto the obtained materials was also investigated.

Materials and methods: Ligno Boost (LB) lignin was esterified with oleic or stearic acid through an enzymatic reaction. Further, LB and its esters (LBOL or LBST) were embedded into xanthan (XG) matrix under magnetic stirring. The adsorptive materials (XG/LB, XG/LBOL and XG/LBST respectively) were obtained by freeze-thawing cycles, followed by lyophilization.

Structural differences between LB and its ester were investigated by FTIR and ^{13}C NMR techniques. Mechanical properties of materials were assessed using a Shimadzu Testing Equipment (EZ-LX/EZ-SX Series, Kyoto, Japan). SEM images (×500) were collected using a VEGA TESCAN microscope with a low-vacuum secondary electron detector at an acceleration voltage of 20 kV, at room temperature.

Results: FTIR and ^{13}C NMR spectra confirmed the chemical modification of LB by the presence of characteristic peaks assigned to aliphatic carbon atoms. According to SEM images, all the obtained materials presented interconnected pores. Uniaxial compressive analyses revealed that obtained materials presented remarkable toughness and elasticity due to the addition of LBST into the XG matrix.

After the oil sorption experiments it was revealed that over 60% of the total oil quantity was retained. XG, XG/LB and XG/LBST materials retained the highest amount of degraded argan oil (61.19, 55.15 and 53.02 g/g). The adsorption kinetics was performed to investigate the oil adsorption mechanism. Our data evidenced that pseudo-second order (PSO) kinetic model has a better correlation than the PFO (pseudo-first order) kinetic model, demonstrating the chemical nature of the adsorption process. The adsorption equilibrium of altered argan oil onto XG, XG/LB and XG/LBOL materials was best expressed by the Langmuir model (R^2 presented values between 0.9894 and 1.0000), while the adsorption equilibrium of argan oil onto XG/LBST was described by the Henry isotherm model (R^2 value of 0.9997).

Conclusions: In this study, LB was esterified with oleic and stearic acid through an enzymatically catalyzed reaction. Further, materials based on XG and LB esters were obtained and their adsorptive properties were studied. It was found that all the adsorbents retained over 50 g/g of altered argan oil. Kinetic studies reveled that experimental data were well correlated with PSO model, while equilibrium data were well fitted to Henry and Langmuir isotherm models. This study opens new insights concerning the use of lignin and its derivatives for application in wastewaters treatment.

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MODIFICATION OF NANOCELLULOSE'S SURFACE BY OXIDATION AND SILYLATION

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Keywords: nanocellulose; chemical modification; oxidation; silylation

Introduction: In light of humanity's transition towards a sustainable chemistry that aims, among others, at exploiting renewable feedstock for the obtaining of chemical products that, ideally, can suffer biodegradation at the end of their life cycle, cellulose emerges as a very interesting material.Cellulose may be isolated from a multitude of renewable resources (wood, cotton, hemp, jute, biomass residues etc.), and distinguishes itself by its biodegradability, biocompatibility, and the multitude of hydroxy (-OH) groups on its surface which open large possibilities for chemical modification and the generation of new functionalities. Nanocellulose is the generic name given to cellulose having at least one size in the nano range (< 100 nm) and can be either isolated from cellulose by chemical/enzymatic treatment and/or mechanical defibrillation, or produced by several bacteria through the fermentation of various sources of sugar. Unlike cellulose, nanocellulose (NC) possesses the advantages of an increased surface area and superior chemical reactivity due to the greater number of -OH groups located on its surface (relative to its weight) available for chemical modification reactions, which have propelled its exploitation as a key material in biomedicine, water purification, electronics, food industry, and as a reinforcing agent for polymer nanocomposites [1]. Despite its many advantages, important shortcomings of NC such as its high hydrophilicity, its tendency to self-associate via hydrogen bonding interactions and agglomerate in most organic solvents and hydrophobic polymer matrices, and its propensity to absorb moisture severely limit the use of NC in a wider variety of applications. A method to overcome these disadvantages and meet the requirements for different applications is the chemical modification of NC via oxidation, esterification, silylation, etherification, carbamylation or polymer grafting reactions at the -OH groups from its surface[2]. In this work, cellulose nanofibers (CNFs) obtained from microcrystalline cellulose (MCC) by mechanical defibrillation were chemically modified by (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)-mediated oxidation and silylation and the changes in the NC's surface properties following the two surface modification reactions were thoroughly evaluated.

Materials and methods: CNFs were obtained from MCC by microfluidization and chemically modified either by TEMPO-mediated oxidation or by silylation with a trialkoxysilane possessing a long-hydrophobic alkyl chain.The changes in the surface chemistry and thermal stability of CNFs post-functionalization were evaluated by Fourier Transform Spectroscopy (FTIR) and Thermogravimetric Analysis, while the dimensions and the surface morphology of the (un)modified CNFs were assessed by Scanning Electron Microscopy (SEM).

Results: FTIR spectroscopy confirmed the successful modification of the CNFs surface by TEMPO oxidation and, respectively, silylation, while the SEM images revealed that the CNFs maintained their nano dimensions post-functionalization.

Conclusions: TEMPO oxidation and silylation appear as two simple and effective routes for modifying the surface properties of CNFs without altering their nano dimensions. Chemically modified CNFs can be used as reinforcing agents for various polymer matrices.

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INFLUENCE OF PLANT EXTRACT ON THE PROPERTIES OF NANOCELLULOSE

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Keywords: nanocellulose, plant extract, thermal analysis

Introduction: The synthesis of all – green systems for medical application is an important and constant concern in the research field. Biocompatibility, biodegradability and low-toxicity are the most sought after characteristics in the "green" chemistry. Cellulose, a polysaccharide, can be obtained from a multitude of natural resources such as plants, wood waste, agricultural and food industry by-products. Given its properties, it can be paired with various other natural compounds and find uses in the food and medical fields, among others.
Cellulose has been used for the obtaining of nanocellulose, a central interest in various applications in the last years [1].Nanocellulose has some useful and interesting properties that can be employed in the medical field e.g.,moisture control of a wounded area, absorption of the fluids present in an infected tissue, capacity to entrap and release active compounds and as scaffolds in tissue engineering[2]. For its use in biomedical applications for wounds healing, cellulose needs to be paired with an agent that shows antibacterial activity and does not disturb its valuable properties [3]. Many plant extracts have antibacterial activity, and the natural resource background to be considered for green approaches. Thus, cellulose nanocrystal films loaded with curcumin had an inhibitory effect over *Streptococcus sp.,* MRSA, *P. mirabilis, E. coli,* and *C. Albicans*[3]. Basil extract, available over the counter in drugstores, is rich in polyphenolic acids and flavonoids that make it useful for biomedical applications[4].
Materials and methods: Foam-type structures were prepared by adding different concentrations of basil extract (BE) to a nanocellulose (NC) 1.5 wt % suspension in water for obtaining different NC/BE ratios (4/2, 4/3, 4/4). The NC/BE foams were obtained by freeze drying and further characterized by means of thermal, mechanical and morpho-structural analyses.

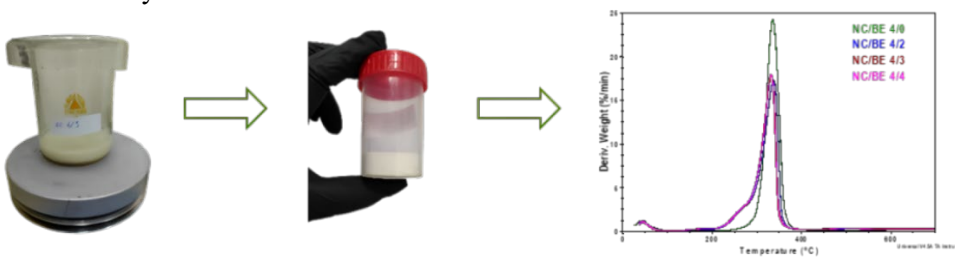

Figure 1. The combination of nanocellulose and basil extract; DTG diagram of NC/BE systems

Results:FT-IR investigation pointed out the appearance of new absorption bands characteristic of BE in the prepared NC/BE foams. The thermal stability of the NC/BE foams was slightly lower as compared to that of neat NC due to the phenolic compounds of BE which decompose at lower temperatures. Moreover, the morphological analysis showed that the BE "filled" the NC foams pores leading to a denser structure.
Conclusions: A facile and environmentally friendly method was successfully applied for the development of NC/BE foams intended for biomedical applications. From the overall results it can be concluded that the optimum NC/BE ratio was 4/2.

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MULTI-BIOTIC PRODUCT ENRICHED WITH SELENIUM NANOPARTICLES FORMED BY KOMBUCHA FERMENTATION WITH POLLEN

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Keywords: multi-biotic; Kombucha fermentation; selenium nanoparticles; biocompatibility; antioxidant activity

Introduction: A multi-biotic is a product that contains living microorganisms (probiotics), prebiotics which are components of food that act as a growth substrate for the living microorganisms, and postbiotics which are by-products released by probiotics, components that act in a synergic way to produce beneficial effects on the host's health [1]. Selenium nanoparticles (SeNPs), especially the biogenic ones, have been shown to be active against dysbiotic biofilm and decrease inflammation, mainly due to their antioxidant activity [2,3]. Fermentation of pollen by a symbiotic culture of bacteria and yeasts (SCOBY/Kombucha) leads to the release of pollen content including biosilica, increases the polyphenol content and enhances the prebiotic and probiotic effects of Kombucha [4]. The aim of this study was to obtain a multi-biotic product enriched with selenium nanoparticles formed by Kombucha fermentation with pollen in order to support the homeostatic microbiome and tissue regeneration.

Materials and methods: Response Surface Methodology (RSM) was used to optimize the production of bioactive compounds from pollen fermented with a Kombucha consortium. SeNPs were characterized by TEM-EDX, FTIR, DLS, and the nanoparticle bio-corona by FTIR and Zeta potential. The multi-biotic product was characterized by measuring the total content of polyphenols (TPC), flavonoids (TFC), hydroxycinnamic acids (HAT), soluble silicon, D-glucose/D-fructose, D-/L-lactic acid, Se^0. Bacterial (nano)cellulose was characterized by FTIR and XRD. Biocompatibility assays were performed on gingival fibroblasts (HGF-1, ATCC CRL-2014). Cell viability and proliferation were assessed after 24 h by CCK-8 and LIVE/DEAD assays. The cell morphology was evidenced by staining actin filaments with Alexa Fluor 488-conjugated phalloidin, while the nuclei were stained with DAPI. Antioxidant activity of the multi-biotic product as well as SeNPs was determined both by biochemical methods (DPPH, FRAP, CUPRAC) and *in vitro* by labeling reactive oxygen species with 2',7'-dichloro-dihydro-fluorescein diacetate (DCFH-DA) after induction of oxidative stress with H_2O_2.

Results: ANOVA analysis provided relevant data about the influence of variables on the production of bioactive compounds by Kombucha fermentation with pollen, as well as on maximizing the production of biogenic SeNPs. TEM-EDX analysis revealed quasi-spherical SeNPs of about 100 nm. FTIR analysis of SeNPs evidenced the amide bands, suggesting a proteic bio-corona around SeNPs. Polydisperse SeNPs with high stability were observed by DLS and Zeta potential analysis. There was an increase in the number of metabolically active cells treated with different concentrations of the optimal composition generated by the experimental design. A strong antioxidant activity was also noticed with an 80-90% reduction of reactive oxygen species (ROS).

Conclusions: The increased biological activity of the multi-biotic product from Kombucha fermentation with pollen enriched with SeNPs shows its potential for rebalancing the microbiota, offering Se supplementation, as well as supporting tissue regeneration which makes it a suitable candidate for several biomedical applications.

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BREWER'S YEAST – BIOACTIVE TREASURE YET TO BE SPENT

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Keywords: spent yeast cells; yeast cell walls; yeast extract; prebiotic activity; antioxidant activity

Introduction: In an over-consumption era, by all means, sustainability becomes the global motto of the future. Under such circumstances, by-products from the food and beverage industries turn into low-cost, sustainable, and easily accessible sources of bioactive compounds used as staples in various value-added products such as nutraceutical supplements for humans and domestic animals, in agriculture or food industry. Spent brewer's yeast (SBY) is one of the main by-products of the brewing industry and a rich source of macronutrients and micronutrients [1]. Hundreds of thousands of tonnes of this valuable by-product are produced world-wide every year [2]. The main aim of this work was to obtain and characterize the antioxidant and prebiotic activity of the extracts and yeast cell walls (YCW) from spent brewer's yeast subjected to an optimized lysis. Nutrients that have antioxidant properties are crucial for homeostasis, given their ability to combat and even prevent the oxidative stress that might imbalance the biological systems [3]. Probiotics have beneficial effects on both human and animal health, such as preserving intestinal microbiota and boosting the immune system [4].

Materials and methods: A combination of ultrasound, enzymatic and microfluidisation treatment was performed to disrupt SBY cells. The protein content of the spent brewer's yeast extract (SBYE) was assessed by Biuret and Bradford methods, in comparison with commercial yeast extracts (CYE). The antioxidant activity (AOA) of the samples (SBYE and YCW) was evaluated by several methods: radical scavenging activity – DPPH and ABTS, reducing antioxidant power – FRAP, PFRAP. The prebiotic activity was performed on the strain *Lactobacillus plantarum* DSM 1055.

Results: SBYE had higher protein content than CYE. The AOA of SBYE was superior in comparison with CYE. The YCW from the optimized lysis procedure had higher AOA than the YCW obtained by simple lysis methods. The growth of *L. plantarum* increased with the YCW concentration, being 40% higher compared to control at the maximum YCW concentration of 2 mg/mL.

Conclusions: Our preliminary results show that the bioactive properties of products derived from SBY, i.e., SBYE and YCW, are significant. SBYE proved to be a better source of nutrients than CYE, in terms of protein content and AOA. The optimized cascade lysis developed in this study enhanced the AOA of YCW solutions, which also have significant prebiotic activities.

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ISOLATION OF NANOCELLULOSE FROM KOMBUCHA BEVERAGE BY-PRODUCT

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Keywords: nanocellulose; Kombucha; purification; bleaching agent; weak acid

Introduction: In the last three decades, nanocellulose (NC) has been a focal point for many researchers due to its unmatched features. From the 90s, when the immense potential of NC as a reinforcing agent for polymer matrices was demonstrated for the first time, NC has quickly found its way in applications such as biomedicine, food industry, electronics, energy storage, water purification, etc. Hence the race of the scientific world in finding and developing new sources and methods for the isolation of pure NC with a higher yield and lower impact on the environment. Currently, most NC is obtained from plants either by chemical/enzymatic treatments or/and by mechanical disintegration, but these approaches are preceded by intense treatments with strong alkali and acids, bleaching agents or solvents intended to remove lignin, hemicellulose, pectin and impurities from cellulose. Another method to obtain NC is through the microbial fermentation of different carbon sources. Known as bacterial cellulose (BC), this NC is characterized by a higher purity as compared to plant cellulose, being more appealing for biomedical applications. An attractive BC source might be the Kombucha pellicles, a by-product of the fermented kombucha tea and others refreshment drinks [1]. These pellicles are obtained as a biofilm during the fermentation of black or green tea and a sugar source, using SCOBY a symbiotic consortium of bacteria and yeast [1][2]. This microbial biofilm consists of a multi-stratified matrix of entangled cellulose fibrils with a diameter between 20 and 100 nm [1][2]. The purification of these cellulosic pellicles containing different products such as bacteria, yeast cells, proteins, and polyphenols is however a challenging task [1][2][3]. Our group has shown that washing this by-product with NaOH solutions of different molarity led to a purer cellulose with higher crystallinity [1]. In addition, purification of cellulose with a 1.0 M NaOH solution at 23 and 90 °C followed by bleaching using NaClO or H_2O_2 led to a purer cellulose showing increased whiteness [3]. However, to the best of our knowledge, no method of obtaining pure NC from the Kombucha beverage by-product has been reported until now. Therefore, in this work, the influence of different treatments with oxidizing agents and strong and weak acids on the structure, morphology, and thermal properties of the Kombucha pellicles was thoroughly studied and discussed.

Materials and methods: The purification of the Kombucha membranes was conducted by treating the pellicles with an oxidizing agent i.e., sodium chlorite ($NaClO_2$), a strong acid i.e., sulfuric acid (H_2SO_4), or a weak carboxylic acid. The effects of these purifying treatments on the chemical structure and thermal stability of the Kombucha membranes were studied by Fourier transform spectroscopy (FT-IR) and thermogravimetric analysis (TGA), while the size and aspect of the cellulose fibirls from the Kombucha membranes before and after purification were assessed by scanning electron microscopy (SEM).

Results: The FTIR and TGA analyses showed the ability of the bleaching agent and acids to remove the fermentation residues from the Kombucha membranes. The SEM images revealed the changes in the size and appearance of the cellulose fibrils from the Kombucha pellicles after purification.

Conclusions: Kombucha membranes proved to be an attractive, low-cost source for the isolation of BC, while the purification of these membranes with a bleaching agent, strong or weak acid appeared to be effective in obtaining BC with a higher degree of purity.

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PHYSICAL PROPERTIES OF MECHANICALLY PRESSED GANODERMA FRUITING BODIES REINFORCED BY ELECTROSPUN BIOPOLYMERIC MATERIALS

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Keywords: fungal-based materials; nanofibers; electrospinning

Introduction: The potential of fungal-based materials as possible leather replacing materials has been the focus of many research groups in recent years and some companies have been managed to produce leather replacing materials starting from grown mycelia of various Basidiomycota and others [1]. However, most fungal-based materials produced by traditional methods exploit the natural structure of the fruiting bodies and not necessarily the mycelium which consumes the substrate. This is the case because the mycelium/depleted substrate mixture retains the long range network of hyphae and allows the use of scaffolds which produces materials with custom dimensions which is in many cases easier to process. This study focuses on developing a composite material made from the fruiting bodies of *Ganoderma spp.* which has been reinforced fungal chitosan extracted from the mycelium/substrate. The results presented are the first step in reaching this goal.

Materials and methods: *Ganoderma spp.* was obtained from a commercial source as a dried slices cut from *Ganoderma spp*. fruiting bodies. The fungal biomass was soaked in distilled water and cut in smaller pieces. The partially dried pieces were then milled in liquid nitrogen to a fine powder which was subsequently dried at 40 °C in a ventilated oven. The dried powder was then mechanically pressed under different conditions. The weight, height, axial compression Young modulus and loss and storage moduli evaluated by oscillometric rheology were evaluated. The electrospinning process was developed in parallel by trying different parameters such as voltage, distance, flow rate and sodium chloride on a 900 kDa polyethylene oxide purchased from Sigma which a water-soluble synthetic polymer which can be easily electrospun. This approach ensured that the practical interval of each of these conditions were met such as to facilitate nanofibers obtained from fungal chitosan. The morphology of the fibers were investigated by SEM.

Results: The mechanically pressed *Ganoderma spp.* material was evaluated in terms of apparent density and mechanical properties. The results showed that under the relatively high pressures of the mechanical press, the material changed very little which is favorable in terms of process reproducibility but shows that the practical interval of both time of applied pressure and value of applied pressure can be less intensive. In parallel, PEO was evaluated by flow rheology at different concentrations. By comparing with literature, the entanglement concentration and also the specific viscosity of PEO are very favorable for electrospinning. This shows the conditions which fungal chitosan will have attain to become more easily electrospinable, especially in terms of deacetylation degree.

Conclusions: Dried *Ganoderma spp.* fruiting bodies was shown to have the potential to be the base of composite materials. However, better properties are needed which could be obtained by blending this material with fungal chitosan nanofibers and other ingredients which would facilitate a kind of felting process.

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ANALYSIS OF THE ANTIOXIDANT ACTIVITY AND POLYSACCHARIDES CONTENT OF WATER KEFIR

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Keywords: antioxidant activity; polyphenols; polysaccharides; water kefir; SCOBY

Introduction: The constantly growing demand for biotech products in the modern world has led the processing industries to develop new products based on starter cultures of consumer-safe microorganisms. Research in this area is currently focusing on fermented products, including water kefir, which remains relatively under-researched [1]. This fermented product is distinguished by its frothy and slightly acidic character, which comes from the fermentation of the water kefir grains, sugar and dried fruits that are used to flavour the drink [2]. The kefir grains are white, translucent, of various sizes, made up of stable cultures of microorganisms such as lactic acid bacteria (LAB), acetic acid bacteria and yeasts, which constitute the SCOBY consortia (Symbiotic Colony of Bacteria and Yeast). The microbial consortia from grains lead to the formation of bacterial polysaccharides (i.e. dextran and levan) [3].

Materials and methods: The water kefir granules (Primal Life UG. Germany) were inoculated in a solution of 5% (w/v) sugar, 1 liter of sterilized water and 50 grams of lemon (2 slices). The vessel was covered with a sterile gauze and left to ferment for 3-4 days at 21°C being stirred several times. After completion of the fermentation process the grains were separated and re-inoculated for a new fermentation process. The beverage was kept at 4°C and used for further analysis. The antioxidant activity of the samples at 3 and 4 days of incubation was determined by the DPPH method for radical scavenging activity, and by FRAP and CUPRAC for the reducing antioxidant power. Folin-Ciocalteu reagent was used for the determination of the total polyphenolic content and the aluminium chloride colorimetric method for the determination of the total flavonoid content. The total hydroxycinnamic acids (HAT) was determined by colorimetric method using NaOH. Dextran was extracted from the water kefir granules and freeze-dryed, its purity was assessed by the phenol-sulfuric acid assay and the structural features were characterized by FTIR in the ATR mode.

Results: After fermenting water kefir for 4 days, the resulting beverage demonstrated a remarkable 3-fold increase in the antioxidant activity and a 2-fold increase in TPC, flavonoids and HAT content compared to the beverage fermented for 3 days, the recommended period. The phenol-sulfuric acid method indicated highly pure dextran extracted from the granules. The FTIR spectrum of the extracted dextran showed modification of the α-1-6 glycosidic structure when compared to the water kefir granules from which it was extracted and characteristic for dextran obtained from other biological sources [4] .

Conclusions: The results obtained so far demonstrate that water kefir, an under-researched fermented beverage, is an important source of bioactive compounds with high antioxidant activity, which can be optimized by the fermentation period.

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BIOREMEDIATION STRATEGY FOR CHROMIUM CONTAMINATED SOILS

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Keywords: bioremediation, soil, tannery industry, chromium, filamentous fungi

Introduction: The tannery industry releases important amounts of chromium into the environment, its hexavalent form being highly toxic to all forms of life. The soil microbiota is an important component of terrestrial ecosystems because it influences the services and overall functioning of the soil [1]. Numerous fungal genera are able to survive in heavy metal contaminated environments, and even to reduce their concentration or to metabolize them to less toxic forms, through to various resistance mechanisms [2]. For this reason, biological soil remediation methods are taken into consideration for their low costs, low negative impact on the environment as well as their role in ecological restoration [3]. The aim of the present study was to isolate heavy metal resistant filamentous fungi from chromium contaminated soil to be applied in bioremediation.

Materials and methods: Soil samples were collected from the surface layer in February 2023, from the proximity of a leather processing unit located in Bucharest. As physicochemical characterization, moisture and organic matter were determined by loss on ignition method, and pH was analyzed using a glass electrode of hydrogen. Total chromium content was determined by ICP-MS. Several filamentous fungi were isolated on agar media supplemented with chloramphenicol and $K_2Cr_2O_7$. The tolerance index was assayed on agar media containing concentrations of chromium in a range of 50 to 1000 mg L^{-1}. Growth diameters were measured daily for 7 days and the ratio between sample and control was compared. Values of the tolerance index between 0.80-0.99 indicated a high tolerance and values equal or above to 1 indicated a very high tolerance [4]. Micro- and macroscopical observations were performed to identify any morphological modifications determined by interactions between the fungal strains and chromium.

Results: Following physicochemical characterization, the soil proved to be low in moisture and organic matter, with a slightly alkaline pH. A number of 20 fungal strains were isolated, displaying various levels of tolerance to the concentrations of chromium tested. Most of the resistant strains were determined to belong to the *Trichoderma* sp. genera. Low concentrations of chromium proved to stimulate growth in a small number of strains, whereas in others it produced macroscopic and microscopic changes represented by increased production of pigment and delayed sporulation.

Conclusions: Through our study, we have successfully isolated filamentous fungi that displayed various degrees of resistance to chromium. Further studies will be focused on analyzing the ability of the highly tolerant fungal strains to reduce the concentration of chromium in soil solution.

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BIODIESEL PRODUCTION FROM WASTE COOKING OIL USING ALUMINIUM PILLARED CLAY AS A CATALYST

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Keywords: biodiesel, aluminum pillared clay, WCO

Introduction: The depletion of petroleum reserves and the rise in oil prices are two issues associated with fossil energy. Biodiesel, an alternative energy source with the potential to be developed, returns approximately 90% more energy than the energy used to produce it [1]. The major constraint limiting large-scale application is the high costs involved. For this process, various types of solid acid/base catalysts, non-edible, and waste cooking oil (WCO) have been used, which has its drawbacks [2]. Clay is an ideal green catalytic material because it is abundant, nonhazardous, yields a maximum desired product with minimal waste, is easily separated, and has excellent reusability. Montmorillonite, the main constituent of bentonites, is found to be the most useful of the clays as a catalyst [3]. The catalytic activity of bentonites can be increased by a process called pillaring. In this process, robust oxide particles are formed between the clay layers, acting as pillars and preventing the expanded layers from collapsing [4]. Clay pillaring is accomplished through the on exchange of interlayer ions without disturbing the layer structure, and this process increases surface area, pore size and pore volume. Therefore, this research is designed to produce biodiesel from WCO using pillared aluminum clay as a catalyst.

Materials and methods: The Aluminum pillared clay was prepared according to the procedure reported by Katdare *et al.* (2000) [4]. The product obtained was characterized using X-ray fluorescence spectroscopy (XRF), Brunauer-Emmett-Teller (BET) and Fourier transform infrared spectroscopy (FTIR). The WCO was pre-treated and the free fatty acid was reduced. Exactly 50 g of WCO was placed in a three - neck round-bottom flask along with the 0.5 wt% aluminum pillared clay catalyst dissolved in a 9:1 methanol to oil molar ratio. The flask was heated at 65 ^{o}C for 2 hrs. The product obtained was characterized using FTIR.

Results: The XRF analysis of the catalyst revealed that there is an increase in the amount of Al_2O_3 and a decrease in other oxides in pillared bentonite compared to raw bentonite. The pillaring process has caused an increase in surface area (336.4 m^2/g) and pore volume (0.189 cc/g) in the pillared clay but there is a slight decrease in pore size (2.128 nm). FTIR revealed peaks in both the raw bentonite and pillared clay around 793 cm^{-1}, 907 cm^{-1}, 984 cm^{-1}, 1627 cm^{-1}, 3440 cm^{-1} and 3688 cm^{-1} corresponding to deformation of Al-Mg-OH, deformation of Al-OH, stretching of Si-O, deformation of OH of water, stretching of OH of water, and stretching of Al-OH respectively. The above results confirm the successful preparation of the pillared clay. The spectrum region (fingerprint) between 1500 and 900 cm^{-1} elaborates on the (transesterification) chemical distinctions between biodiesel and vegetable oil. The presence of C=O stretching vibrations of carbonyl groups in esters causes the appearance of a strong peak at 1742 cm^{1} at the functional group region.

Conclusions: Aluminum pillared clay was successfully prepared and characterized. This study which is part of ongoing research confirms the effective use of aluminum pillared clay as a catalyst for converting WCO to biodiesel. The catalyst gave a biodiesel yield of 71%. Although the process requires further optimization, this can kick start a cost-effective biodiesel production process.

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EXPLORING THE POSSIBILITIES OF OBTAINING NATURAL EXTRACTS ABUNDANT IN PHYTOCONSTITUENTS FROM GRAPEVINE WASTE

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Keywords: grapevine waste; natural extracts; phytochemicals;

Introduction: Vine cultivation, along with the process of wine production, are two traditional practices that have a beneficial effect on the socioeconomic sector in various regions around the world. Thus, by expanding and developing these two areas, residues and secondary products rich in nutrients are obtained in a short time [1]. Considering the global area under grape cultivation, the estimated total volume of viticultural waste (buds, stems, shoots or grape leaves) varies between 6.9-13.8 million tons. On the other hand, winery waste such as pomace, seeds, grape stems, wine yeast, represents about 30% of the initial weight of grapes, of which 20-25% comes from pomace [2]. Instead, significant amounts of phytochemical compounds are present in these residues that could be used in other fields such as cosmetics, medicine and even food. The aim of the current study is to obtain different extracts from grape waste (pomace and shoots), using classical (oven extraction) and modern extraction methods (microwave-assisted extraction and ultrasound-assisted extraction) with increased yields of phenolic compounds from grape waste.

Materials and methods: To determine the most efficient method of extracting bioactive compounds from pomace and vine shoots, three methods of solid-liquid extraction were applied, a classical one, at high temperature, and two modern extraction methods, one with microwave digestion system (MILESTONE ETHOS EASY) and another with ultrasound assisted extraction (Ultrasonic bath - BANDELIN DIGIPLUS DL255H). In order to obtain an increased total phenolic content, two solid/liquid ratios were studied, 1:10 (w/v) and 2:10 (w/v) and different operational parameters were used. Furthermore, to determine the total content of phenolic compounds from extracts, the Folin-Ciocâlteu spectrophotometric method was chosen.

Results and conclusions: Extracts of pomace and shoots from autochthonous grapevines were obtained by three different extraction methods, the phytochemical content varying depending on the vegetal material subjected to extraction and the extraction method used.

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BLUE-LIGHT LASER EFFECTS ON *TRICHODERMA* AND ON ITS PLANT BIOSTIMULANT FORMULATIONS

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Keywords: blue-light; enzymatic-cocktail; Trichoderma; microalgae hydrolysis; plant biostimulant formulation

Introduction: The environmental conditions, e.g., the level of oxygen, temperature, humidity, UV radiation and the concentration of reactive oxygen species (ROS) differ in soil and on the crust surface. These properties can also change during day and night [1]. Fungi developed the ability to adapt to the ever-changing environment in order to survive. One important factor is light, which can regulate morphological and physiological processes of fungi [2], and expression of some enzymes, like the lignocellulolytic ones [3, 4]. Light, especially in the blue regime, influences signaling pathways, affecting the metabolism, stress response and development of fungi [5]. This study presents the influence of blue-light laser radiation, a less used form of ilumination, on the development and enzyme production by *Trichoderma*. It also investigates possible aplications of microalgae and microalgae-*Trichoderma* formulations as plant biostimulants. A cocktail from *Trichoderma* enzymes, combined with enzymes extracted from algae was tested on *Arabidopsis thailana* seeds to observe the phenotypic morphology.

Materials and methods: Fresh mature spores of *Trichoderma* strains were inoculated in ISM or PDB medium. The developed mycelium from ISM was inoculated in water with rice husk and the mycelium from PDB in minimal medium (MM) with 7% whey (dry mass) and 1% yeast extract for 14 days at 28°C. Samples were exposed to blue-light laser for 60 seconds after 6 days of incubation. The cellulase, α-amylase, protease activities, lipid peroxidation and sporulation of *Trichoderma* were analysed. The degradation of RH was visualized by SEM-EDX. The supernatant was used to lyse microalgae cultures, which were tested as non-lysed or lysed formulations on the development and salt tolerance of *A. thailana*.

Results: The irradiation influenced the enzymatic activities, either increasing or decreasing them, depending on the sampling time, substrate and *Trichoderma* strain. The lipid peroxidation of *Trichoderma* upon irradiation was not significantly different than the control, but the sporulation was higher. The rice husk was degraded by *Trichoderma*, as visualized by SEM-EDX, with no apparent significant differences between irradiated and non-irradiated *Trichoderma* cultures. There was no effect of the formulations on *A. thaliana* in the absence of salt. All formulations partially alleviated 50 mM NaCl stress, but at 100 mM NaCl positive effects were obtained only for non-lysed microalgae and microalgae lysed with enzymatic-cocktail from non-irradiated *Trichoderm*a. The lysis by *Trichoderma* does not change significantly the effects on *A. thaliana*.

Conclusions: Blue-light laser modulates the enzymatic activities of *Trichoderma* in a complex, apparently hormetic manner. The irradiation does not induce significant lipid peroxidation and intensifies sporulation of *Trichoderma*. Microalgae and microalgae – *Trichoderma* formulations act as plant biostimulant on *A. thaliana* under salt stress, but more in-depth studies are needed to maximize the potential of *Trichoderma* cultures.

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PRELIMINARY STUDIES ON MICROALGAE GROWTH ENHANCEMENT BY MIMETIC STRIGOLACTONES

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Keywords: microalgae biostimulant; Chlorella sorokiniana; Desmodesmus communis; mimetic strigolactone

Introduction: Nowadays microalgae are the first thing one can think about when dealing with biofuel, biogas [1], solving water pollution [2], enhancing crop quality [3] or developing pharmaceutical supplements [4]. Because they are so broadly used, the biomass and metabolite production of microalgae is necessary to be enhanced. Our main interest in this study was to determine whether mimetic strigolactones (SLs) can stimulate microalgae growth rate in the same manner as the phytohormones applied to microalgae are known to regulate their metabolite synthesis and enhance cell growth at the same time [5].

Materials and methods: Axenic cultures of two species of microalgae (*Chlorella sorokiniana* NIVA-CHL 176 and *Desmodesmus communis* NIVA-CHL 7) were tested with four mimetic strigolactones (SL-F1, SL-F2, SL-F3, SL-F4) at 10^{-7} M SL concentration. The microalgae were cultured in BG-11 medium, under controlled conditions of light 130 µmol/m2·s, temperature of 25 °C and 150 rpm orbital agitation (Heidolph Unimax 1010 Orbit) in a growth chamber (Algaetron AG230). To determine the microalgae growth, we measured four parameters such as optical density, biomass production, chlorophyll fluorescence and pigment concentration. The effects of mimetic SLs on both *Ch. Sorokiniana* and *D. communis* were monitored for 14 days.

Results: Significant increase in cell growth was recorded for *Ch sorokiniana* starting from the 5[th] day of culturing with SL-F3($V3^{-7}$) compared with the control and the *D. communis* growth was enhanced by SL-F1 and SL-F4 by 20% and 23%, respectively, compared to the control. The total chlorophyll content was increased in *Chlorella* supplemented with SL-F3 by 66% compared to untreated cultures.

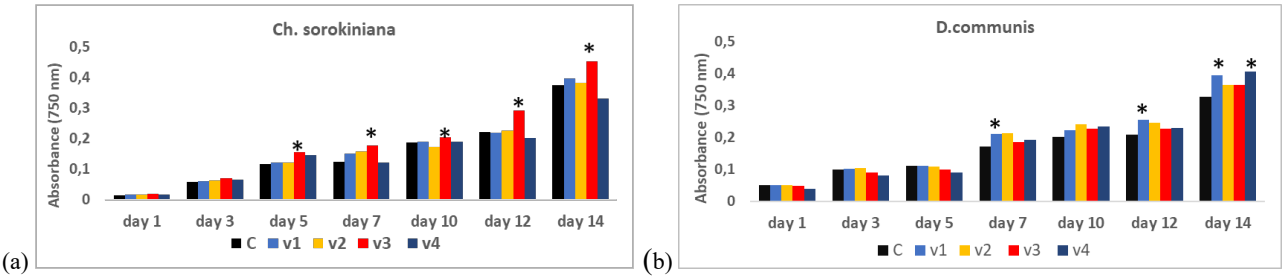

Figure 1. Optical densities of the microalgae cultures: (a) *Ch. Sorokiniana;* (b) *D.communis*

Conclusions: Preliminary studies showed that the microalgae growth can be enhanced by at least 20% compared with control, by supplementing the culture media with certain mimetic SLs at a 10^{-7} molar concentration, depending on the microalgae species. Further studies with different concentrations are ongoing.

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CATALYTIC PYROLYSIS OF WASTE BIOMASS

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Keywords: pyrolysis; biomass; catalyst; bio-oil; lignocellulosic

Introduction: This study investigates the impact of dolomite and zeolite on the pyrolysis process of lignocellulosic biomass. The addition of these catalysts to the biomass was found to enhance the yield and quality of the bio-oil produced [1]. The dolomite was investigated to promote the thermal decomposition of the biomass and increase the bio-oil yield, while the zeolite was found to catalyze the cracking and upgrading of the bio-oil. These findings suggest that the use of dolomite and zeolite in the pyrolysis process can significantly improve the efficiency and sustainability of biomass conversion to biofuels [2]. Furthermore, the study investigated the effects of different concentrations of dolomite and zeolite on the pyrolysis process.

Materials and methods: The oak sawdust in combination with dolomite $CaMg(CO_3)_2$ and/or zeolite was fed into the reactor and then the reactor was assembled. Before starting pyrolysis, the plant was purged with nitrogen from the cylinder at a flow rate of 5L/h for 7 minutes to remove oxygen from the plant. Heating was set to 450 °C. Temperature parameters were monitored in relation to time.

Results: The optimal concentration of dolomite was 5% while the optimal concentration of zeolite was 2%. Higher concentrations of these catalysts proved to have diminishing returns on the yield and quality of the bio-oil produced. The results showed that the bio-oil produced with the addition of these minerals had a higher heating value, lower acidity, and lower water content, indicating a higher quality fuel product.

Conclusions: The results of this study demonstrate the potential benefits of using dolomite and zeolite synergy effect in the pyrolysis process of lignocellulosic biomass. These minerals can increase the yield and quality of bio-oil produced, as well as improve the overall efficiency and sustainability of biomass conversion to biofuels.

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THE GENOTOXICITY ASSAY AS A SCREENING TOOL OF PLANT BIOSTIMULANTS – THE CASE OF FERMENTED HORSETAIL

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Keywords: genotoxicity assay; fermented horsetail; plant biostimulant; cytotoxicity; vicia faba

Introduction: The ongoing development of plant biostimulants requires not only tests of their stimulatory potential but also tests to prove their safety on plants, as the line between the biostimulant effect and the toxic effect needs to be known. When we talk about safety in terms of genotoxicity we mean lack of chromosomal aberrations, mutations, nucleus alterations, in a word: genetic damage. Any deviation from the classical cell cycle, mitosis and cytokinesis is cytotoxic and genotoxic. Moreover, the biostimulant effect is manifested and assessed in the presence of abiotic or biotic stress, including genotoxic elements. The potential toxic or biostimulant response of a biostimulant product can be determined using the genotoxicity assay performed on *Vicia faba* root meristems, a fast, convenient, and reliable *in vivo* test organism [1]. This technique comes with many advantages for industrialists as it would hold arguments of safety of the delivered plant product [2]. The aim of this study was to investigate the fermented horsetail (*Equisetum arvense*) as a possible plant biostimulant by determining the seed germination rate, root elongation inhibition, micronucleus frequency (MN) and mitotic index (MI), essential parameters of the assay.

Materials and methods: Horsetail ferment collected at different periods, one, two and three weeks, were used for the experiment. First, *Vicia faba* seeds were subjected to surface aseptization. For the germination process, a genotoxic product, lead nitrate ($Pb(NO_3)_2$) was used. Germination took place in a climatic chamber (Algaetron AG230) under temperature-controlled conditions. After 5-6 days of germination, 1-2 cm of the root tops were collected and fixed in ethanol:acetic acid. The staining with Schiff's reagent was carried out after preliminary hydrolysis of root tops in 1N HCl. The mitotic index results from the percentage of dividing cells of the total number of cells and the micronuclei frequencies from the percentage of micronuclei count of the total number of cells. Root elongation inhibition is determined by the difference between root length in the control sample and the root length in the treated sample, divided to control (REI = (C - T) / C) [1].

Results: The determinations regarding the geno- and cytotoxic effect validate the fact that the positive control containing $Pb(NO_3)_2$ gives a confirmed genotoxic action. After 5 days of germination, the one-week maceration sample induced better rate of seeds germination (93%) compared to the control containing sterile dH_2O. The same sample gave the best results following the REI index, the roots showing slower elongation in the sample with the 2 and 3-week maceration. The one-week horsetail maceration shows initially a similar effect as $Pb(NO3)_2$, but after 2-3 weeks of fermentation, this effect seems to disappear and the extract becomes slightly biostimulant. In the presence of stress (positive genotoxic control), the macerate shows protective action at the cellular level against the genotoxic substance, as the MN and MI results show.

Conclusions: *Equisetum arvense* maceration successfully responded to the genotoxicity assay on *Vicia faba*, an approach that can provide good tools in identifying possible genotoxic effects on plants and an excellent screening of chemicals, products and plant biostimulants. Considering the lack of chromosomal aberrations in the process of cell division and the lack of cytotoxicity according to mitotic index and the frequency of micronuclei results, in combination with the protection against genotoxic abiotic stress, the horsetail maceration proves to be a promising product.

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THE ENHANCEMENT OF THE BIOLOGICAL ACTIVITY OF HONEY AND ITS BIOMIMETIC DES WITH POLYPHENOLS FROM HONEYSUCKLE (*Lonicera Caprifolium*) FLOWERS

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Keywords: antioxidant; antibacterial; prebiotic, honey; natural deep eutectic solvent

Introduction: Honey is a natural product that has the characteristics of a deep eutectic solvent (DES) due to its physicochemical and structural properties[1, 2]. Polyphenols are compounds found in plant walls with various biological activities[3]. To enhance the biological activities of honey by increasing the antioxidant, antibacterial and prebiotic activity we mixed honey with a polyphenol extract from honeysuckle (*Lonicera caprifolium*) flowers. A biomimetic DES of honey was investigated as well, in order to demonstrate the similar behavior between honey and DES.

Materials and methods: The polyphenols were extracted from honeysuckle according to [4] and after solvent evaporation they were mixed with honey and DES in an ultrasonic bath and left to diffuse overnight. The phenolic acids and flavonoids were analysed by HPLC. The AOA was performed by spectrophotometric methods: FRAP, DPPH, CUPRAC, and ABTS. The interaction between the polyphenols from the honeysuckle extract and honey/ DES was analysed by determination of combination index, isobolograms and Webb analysis. The antimicrobial activity of the samples was performed by the agar disk-diffusion method and by determining the minimum inhibitory concentration (MIC) of the growth on Gram-positive strains: *Bacillus cereus* NCTC 10320, *Rhodococcus equi* ATCC 6939, *Enterococcus faecalis* ATCC 29212, *Staphylococcus aureus* ATCC 25923, and Gram-negative strains : *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* ATCC 27853, *Enterobacter aerogenes* ATCC 13048, *Salmonella enterica* NCTC 7400 and *Candida albicans* ATCC 10231. The prebiotic activity of the honey/DES - extract mixture was evaluated on strains *Lactobacillus reuteri* DSM 20016 and *Lactobacillus plantarum* DSM 1055 and compared to simple honey/DES, at product concentrations between 1 - 45 mg /mL.

Results: The interaction between honey/DES and polyphenols from honeysuckle extract in terms of antioxidant AOA range from synergism to antagonism, depending on the method of measuring AOA. The mixtures showed enhanced antimicrobial activity compared with honey/DES without extract for the bacteria strains : *B. cereus, R. equi, S. enterica, E. faecalis*, *E. coli, E. aerogenes* based on the agar disk-diffusion method. The MIC values of the mixtures were obtained for *E. coli* (25 mg/mL), *B. cereus* and *R. equi* (200 mg/mL). All concentrations of the honey/DES-extract mixtures exerted higher growth-promoting effects on *L. reuteri* strain than simple honey/DES. The highest prebiotic activity was observed at 25 mg/ml of honey/DES-extract mixture. In the case of *L. plantarum* growth, there were no significant differences between the mixtures and the simple honey/DES.

Conclusions: Our results show that the polyphenols from honeysuckle remain active when mixed with honey and can enhance the biological activity of honey, in some cases with synergic behaviour.

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CO_2 CAPTURE USING EGGSHELLS AS ECOLOGICAL SORBENT FROM AGRICULTURAL WASTE

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Keywords: bioeconomy; eggshells; CO_2 capture; circular economy

Introduction: Eggshells are considered in the European Union a side stream and hazardous materials. They are constantly produced by the agricultural and food industry, reaching hundreds of thousands of tons annually. This waste can be processed to become a valuable raw material and subsequently used in various fields, such as feed or fertilizer production, catalysts [1], CO_2 capture [2], etc. Calcium oxide is used in the chemical looping process, a method that uses metal oxides to capture CO_2 from various industrial sources. For improving the CO_2 capture capacity, we treated the eggshell powders with magnesium oxide [2,3].

Materials and methods: Eggshells from hatched eggs were prepared as adsorbent materials for CO_2 capture. They were washed with water, mechanically separated from the inner membrane by crushing, air-dried, grinded using a centrifugal mill (Retsch PM100) and calcinated at 850°C, 2h. Thus, CaO for chemical looping was obtained. The following step was the transformation of anhydrous $MgCl_2$ into (nano)MgO using distilled water and staged calcination, releasing the HCl from the system [2]. The two powders (CaO and MgO) were mixed together at 85% and 15%, respectively, dissolved in water for best mixing, re-calcinated at 600ºC and milled to 75-425 µm size particle. The capacity to capture CO_2 was determined using SDT Q600 (TA Instruments) with two purging gases (CO_2 / N_2 99.999% = 14% / 86%), 0.1 liters/min.

Results: FT-IR analysis (Shimadzu IRTracer-100) revealed the high reactivity and hygroscopicity of CaO, through the traces of CO_2 and water adsorbed [4]. XRD (SmartLab Rigaku) confirms the 15% (nano)MgO content and the presence of CaO, MgO, $CaCO_3$, and $Ca(OH)_2$. The MgO nanoparticles had a particle size of 15.2 nm in diameter. The CaO and MgO mixture, showed more than 3 times higher reactivity towards CO_2 than the CaO granules, after calcination in air (Figure 1).

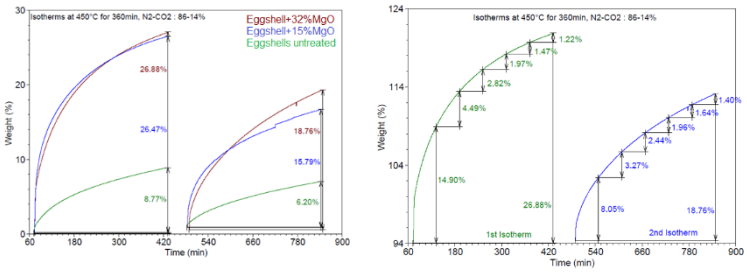

Figure 1. Carbonatation reactions in isothermal regime in CO_2/N_2 atmosphere:14%/86%

Conclusions: Nano-magnesium increases the CO_2 capture capacity of eggshells. Together with calcined eggshells (CaO), Mg in the form of nano-MgO helps to avoid the formation of preferential gas flow paths through the sorbent mass.

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