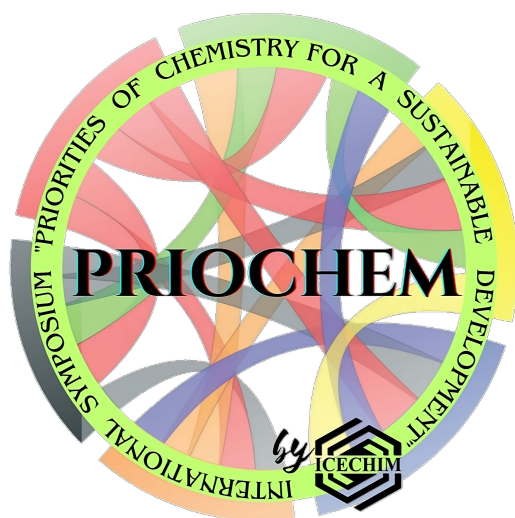




Book of Abstracts

No. 19/2023

The International Symposium PRIOrities of CHEMistry for a sustainable development



Organized by: INCDCP-ICECHIM Bucharest

Partners: Romanian Chemical Society

“C.D. Nenitescu” Foundation

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Volume of Summaries Technical Page

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Multifunctional materials, nanocomposites, innovative technologies and cultural heritage preservation

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Bioresources, biotechnologies and biorefining

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FOREWORD

The National Institute for Research and Development in Chemistry and Petrochemistry - ICECHIM Bucharest has a long history of organizing scientific meetings: from 1981 to 1994, the "ICECHIM Symposium" was held in the last week of January of each year. This tradition has been revived since 2005, with the 19th edition this year, and has grown in importance and prestige both nationally and internationally.

The 19th edition of the International Symposium PRIORITIES OF CHEMISTRY FOR SUSTAINABLE DEVELOPMENT - PRIOCHEM was held between October 11-13, 2023, in collaboration with the Romanian Chemistry Society and the "CD Nenitescu" Foundation.









Oral presentations (19), poster papers (65), plenary lectures (10), invited papers (4), and special presentations (4) were among the many academic and commercial presentations on the agenda. This diverse content encouraged the exchange of innovative ideas and the transfer of difficult knowledge, and it emphasized the importance of path innovation, which has significant competitive implications for accelerated development at the level of economic operators as well as socio-economic benefits for civil society. To promote collaboration, networking, and the exploration of new research directions, 13 satellite events were organized in addition to the main symposium.

We would like to express our heartfelt gratitude to the Romanian Ministry of Research, Innovation, and Digitalization for their invaluable financial assistance in organizing the international symposium PRIOCHEM 2023, which was made possible by financing contract no. 12M / 27.06.2023.








At the same time, we would like to thank our sponsors, S.C. NANOTEAM S.R.L. and VWR International (part of AVANTOR).

Your support was critical to the success of this event, and we are grateful for the opportunity to work with you to advance the field of chemistry for sustainable development!

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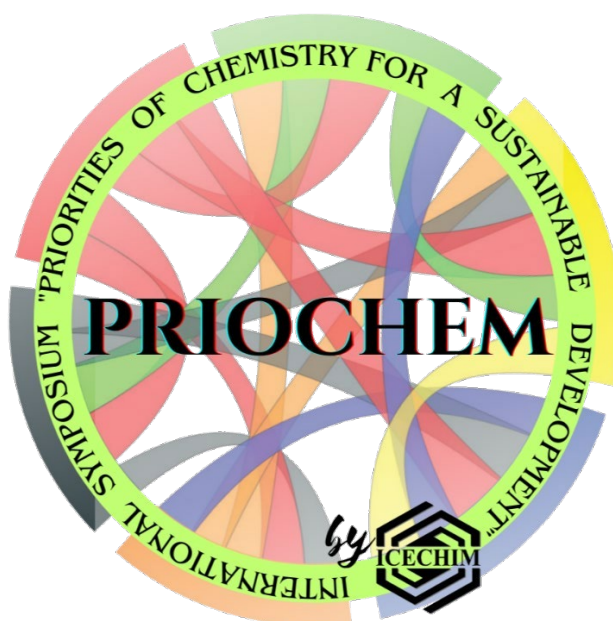
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NANOCARBON BASED THERMOSET COMPOSITES FOR PROTECTIVE APPLICATIONS

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Keywords: *graphene oxide, thermoset, corrosion protection, UV aging*

The non-regenerative and often leachable nature of the active ingredients used in conventional paint systems results in high levels of incorporated pigments. This poses technological, economic and environmental problems, particularly when the inhibitors released are toxic (such as Cr (VI) pigments). By increasing the exchange surface with the metal substrate, the use of nanostructured pigments can achieve inhibitory efficacy at low contents.

The development of stimuable pigments is another avenue that has been recently explored in our laboratory, as it should make it possible to limit releases into the environment and increase the inhibitor's protective efficiency. Functionalized or non-functionalized graphene oxide, GO, is an interesting platform, thanks to its 2D geometry and the reactivity of its sheet surface. We'll take a look at some examples to illustrate the compatibility problems that can arise between GO and thermoset polymerization systems.

Examples will also show the effectiveness of GO in protecting metals from corrosion, and we'll also discuss the effectiveness of GO in protecting polymer matrix from oxidative degradation.

POLYMER BASED GLASSY CARBONS – PREPARATION AND APPLICATION

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Keywords: *glassy carbon; XRD; Raman spectroscopy*

Introduction:

Glassy carbon is a black non-transparent material, which have found application as antireflective coatings. The carbonization of thermosetting resins (poly-aryl acetylene, furfuryl alcohol, phenolic resins) leads to formation of low-ordered, non-graphitizing carbon-based material, denoted 'glassy carbon'. Glassy carbon is a stiff, fragile material, and it exhibits a surface fracture, similar to that presented by the glass. Unlike graphite, glassy carbon is a hard and isotropic material. Besides, glassy carbon low impermeability towards molecules of gases and liquids, excellent chemical and thermal stability, very good thermal and electrical conductivity.

Glassy carbon is a carbon material characterized by high mechanical strength. In addition, it is chemically inert, especially in a reducing atmosphere. The glass-carbon is fragile, has an almost defect-free outer surface, which resembles an inorganic glass. Glassy carbon possesses high temperature resistance, hardness, low density, low electrical resistance, low friction, low thermal resistance, extreme resistance to chemical attack and permeability to gases and liquids. Glassy carbon is widely used as an electrode material in electrochemistry, as well as for high temperature crucibles and as a component of some prosthetic devices, and can be fabricated as different shapes, sizes and sections

Materials and methods:

Carbon composite is obtained using petroleum coke (filler) and coal tar-pitch (binder). The technology includes obtaining a suitable mixture of the binder and the filler, pressing at the softening temperature of the binder and heating the resulting material in a special temperature rise mode up to 1000 °C. The resulting material is covered with vitreous (glassy) carbon, through repeated contact with a toluene solution of the product, obtained as a result of thermal degradation of polyvinyl chloride and subsequent carbonization at 1000°C. The purpose of this treatment is formation of glassy carbon surface without pores.

Results:

Modern physico-chemical methods, like XRD and Raman spectroscopy, are used for characterization glassy carbon structures.

Conclusions:

Glassy carbon is applied in many fields – electrochemical devices and sensors, energy storage, wastewater decontamination, tools for precision molding, ablative shields. Due to its good biocompatibility, glassy carbon may be also used in medical applications - heart valves, implants, tissue regeneration.

Acknowledgements: *This work is financially supported by the Bulgarian National Science Fund under Project KP-06-H27/2, 08.12.2018 and also Romanian-Bulgarian Academy Joint Project INNOMAG (2022-2024).*

MOLECULARLY IMPRINTED POLYMERS: FROM DESIGN TO APPLICATIONS

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Keywords: *molecularly imprinted polymers; adsorption; quantification; organic contaminants*

Molecularly imprinted polymers (MIPs) are unique types of polymers designed with tailored sites that have the ability to selectively attach particular analytes. This selective quality is created during MIPs' synthesis. To obtain MIPs, a specific chemical components called functional monomers and cross-linkers are mixed with the target analyte, resulting in precise interactions between the polymer's side chains and the analyte molecules. The effectiveness of these interactions determines how well MIPs can ultimately recognize and bind to the desired analyte. Therefore, it is of utmost importance to ensure strong and dependable interactions within the structure of MIPs.

MIPs have garnered significant interest due to their outstanding stability in different chemical and physical environments, excellent selectivity, cost-effective production, and the ability to be reused multiple times. These appealing qualities have made MIPs highly sought after for applications requiring high selectivity of solid material. Thanks to their numerous features, MIPs find widespread use in various fields, including separation, purification, sensing, and catalysis processes.

Recently, we have developed a new analytical procedure involving application of MIPs as molecular scavengers for ambient mass spectrometry (ambient MS). Ambient MS encompasses various methods that allow the generation of ions under normal atmospheric pressure conditions. These techniques offer several significant advantages, including fast, real-time, direct, and high-throughput analyses, often requiring little to no prior sample preparation. Additionally, they permit the analysis of samples right from their surfaces or matrices. Among various techniques within the ambient MS category, the plasma-based methods stand out as unique. These techniques are grounded in the generation of a plasma species, achieved by applying electrical discharge between a pair of electrodes in contact with a flowing inert gas. As a result, a stream of ionized molecules, radicals, excited-state neutrals, and electrons is formed. Ultimately, this plasma species is directed towards the sample, leading to the desorption and ionization of the targeted analytes.

The presentation will focus on the synthesis, characteristics, and applications of MIPs, with particular emphasis on the advancements achieved by our research team. We have successfully integrated various adsorbents, notably MIPs, into ambient mass spectrometry, resulting in lowered detection limits for numerous organic analytes [1-3]. Furthermore, the exceptional properties of MIPs based on poly(2-oxazoline)s will be discussed, highlighting the progress we have made in this area [4, 5].

These poly(2-oxazoline)-based MIPs possess a remarkable capacity for binding, which is especially important when used in conjunction with ambient mass spectrometry. This combination allows us to detect hazardous contaminants in liquid environmental samples. We believe this analytical method can be further refined to quantify various organic pollutants in environmental samples and enhance our ability to detect them with greater sensitivity.

Acknowledgements: *This work was supported by the National Science Centre, Poland, under grant number 2020/37/B/ST5/01938.*

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POLYMERIC COMPOSITE MATERIALS FOR DEFENSE AND SECURITY APPLICATIONS

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Keywords: *energetic materials, materials for ballistic protection, materials for CBRN defense*

Introduction:

Defense and security systems are becoming more and more complex, and so are the materials used to build them. Advanced materials can significantly shape future operational effectiveness in military and security missions. On the other hand, dual-use products, services, and technologies can address the needs of both civilian and defense communities. In this context we take the opportunity to make an overview of the research activities accomplished in the Military Technical Academy regarding polymeric composites to be used in defense and security applications, during last years.

Materials and Methods:

Using smart polymeric binders, it allows the decrease of the risks for operators and environment while manufacturing or recycling this kind of composite materials. Regarding ballistic protection topic we discuss some achievements in polyurea based nanocomposite coatings to be used to improve the performance of metallic armours for military platforms. In CBRN defense, we present our contributions regarding polymeric strippable coatings to be used for CBRN decontamination of surfaces.

Results and Discussions:

Our focus was mainly directed on three categories of materials: energetic materials (i.e., explosives, propellants and pyrotechnics), materials for ballistic protection and materials for CBRN defense. In the area of energetic materials, we discuss the achievements regarding greener propellants for civil and military propulsion systems (rockets), and novel polymer bonded explosives (PBXs).

Conclusions:

Several types of energetic materials (i.e., explosives, propellants and pyrotechnics), materials for ballistic protection and materials for CBRN defense were designed and tested. The results pointed out that the materials may be further used to replace some of the conventional materials that are used in defense and security applications.

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CONCURRENT MEASUREMENTS OF NEUROMETABOLIC CHANGES AND LOCAL FIELD POTENTIALS DURING EPILEPTIC SEIZURES USING MICROELECTRODE ARRAYS

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Keywords: Lactate, Oxygen, Amperometry, Oxidase-bases microbiosensor, seizures

Introduction: Seizures are paroxysmal events in which increased neuronal activity is accompanied by an increase in localized energetic demand. The ability to simultaneously record electrical and chemical events using a single sensor poses a promising approach to identify seizure onset zones in the brain. Fast sampling amperometry allows concurrent measurement of rapid neurochemical and electrophysiological events using a single sensor and recording system. This is supported by the fact that the high-frequency component of an amperometric recording (>1 Hz) resembles the local field potential while the low frequency component (<1 Hz) reflects the electrochemical signal resulting from the oxidation or reduction of electroactive species present in the milieu [1]. The microfabrication of multi-site electrode arrays (MEA) platforms offers a high density of recording from restricted areas, the versatility of configuration designs that allow the E-chem/E-phys recordings *in vivo* with high spatiotemporal. Advantages of using implantable microelectrode biosensors include high sensitivity and selectivity, high spatial and temporal resolution, and minimal tissue disruption.

Materials and methods: In the present work, we used ceramic-based platinum microelectrode arrays (MEAs) to perform high-frequency amperometric recording of local pO_2 and local field potential (LFP)-related currents during seizures in the hippocampus of chronically implanted freely moving rats. We have also designed microelectrode biosensors using platinum-modified carbon fiber microelectrodes (Pt/CFM) and for *in vivo* detection and monitoring of neurometabolic markers such as lactate and glucose. We construct first-generation biosensors based on oxidase enzymes immobilized on the microelectrode surface using the cross-linking agent glutaraldehyde in the presence of BSA. In addition, biosensors are coated with a polyurethane (PU) layer to extend the liner range. Hydrogen peroxide is used as a reporter molecule, detected by amperometry at $+0.7$ vs. Ag/AgCl. Before insertion into the brain tissue, the selectivity of the biosensors against ascorbate is improved by electropolymerization of m-phenylenediamine (m-PD) [2,3].

Results: Using a non-enzyme-coated CFM null sensor or a sentinel site on the MEA allows for the estimation of basal extracellular levels of lactate and glucose in different brain regions. Moreover, real-time and simultaneous *in vivo* monitoring of neurometabolic markers such as lactate, glucose, and oxygen in anesthetized and awake rats in response to local depolarization with KCl or induction of seizure activity with 4-aminopyridine or pilocarpine will be presented.

Conclusions: We demonstrate that fast sampling amperometry coupled with microelectrode biosensors is an excellent tool for concurrent electrochemical recordings (E-Chem) with local field potential (LPF)-related currents (E-Phys) in a single sensor

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CYCLODEXTRIN-BASED NANOSPONGES AS EFFICIENT MATRICES FOR PESTICIDE REMOVAL

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Keywords: please provide up to five keywords separated by semicolon (max. 1 row)

Introduction: Persistent organic pesticides have long been responsible for controlling human disease vectors and significantly increased agricultural productivity. In recent years, however, the effects of pesticides on the environment, biodiversity, and human health became a major concern.

These chemicals include organochlorines, such as imidacloprid, a systemic chloronicotinyl insecticide that can persist in the environment for prolonged periods and is readily absorbed by living organisms. It acts by contact and ingestion as postsynaptic nicotinic acetylcholine receptors and blocks insect neurotransmission.

Sorption systems have integrated efficient technologies to prevent or eliminate pesticides from the environment, as they are based on low-cost materials such as clay minerals, zeolites, aluminum, and iron oxides or oxyhydroxides, and biomaterials.

NSs are defined as water insoluble, supramolecular, porous 3D polymeric materials with high thermal stability [1]. Among the various monomers suitable for their synthesis, cyclodextrins (CDs) are the most common, due to their amphiphilic properties and high ability to form host-guest complexes [2]. Moreover, CDs are characterized by a large number of hydroxyl groups, located at the rims of the truncated cone, which are susceptible to functionalization. Cyclodextrin-based nanosponges (CDNSs), nanoporous 3D-dimensional structures, with high degree of crosslinking and unique physicochemical properties, have recently been recognized as promising environmentally friendly sorbents for pesticides, taking advantage from the hydrophobic cavities of CDs and the hydrophilic network of the porous structure. That will allow the interaction with a large number of ions and molecules.

In this communication we report the synthesis and characterization of amine-based CDNSs with α - and β -CD, using hexane-1,6-diamine (HDA) and dodecane-1,12-diamine (DDA) as anchors (crosslinkers), and their performance in removing 2,4-D, imidacloprid and its commercial formulation: Confidor O-TEQ®.

Conclusions: The β CD₂-HDA NS shows a remarkable removal percentage of Confidor O-TEQ® from aqueous solution. However, the improvement in sorption efficiency for Confidor O-TEQ® compared to the results obtained for its active ingredient imidacloprid is also remarkable. Thus, the q_e value for sorbed Confidor O-TEQ® (288 mg/g) is about four times higher than the value obtained for pure imidacloprid (68 mg/g) per gram of sorbent. Thus, the sorption of imidacloprid by CD-NSs is significantly enhanced by the Confidor O-TEQ® formulation, i.e., the oil formulation of Confidor O-TEQ® improves the wettability of the sorbent by lowering the surface tension, which significantly increases the amount of imidacloprid sorbed by β CD₂-HAD NS. Furthermore, the maximum sorption for Confidor O-TEQ® in β CD₂-HDA is observed at a pH of 6.5 while for IMD it is at a pH of 3.5. The effect of anchor chain length was also evaluated by molecular dynamics simulations. It was found that the stability of the monomeric β CD-HDA:Imidacloprid complex is largely determined by N...O...H and C-H...O type interactions; on the other hand, no interactions between the CD cavity and imidacloprid were observed in the presence of β CD-DDA. On contrary to imidacloprid, the maximum removal efficiency for 2,4-D is found for the NS with the shorter anchor. These differences will be discussed with the help of molecular dynamics simulations.

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PROTEJAREA PRIN BREVETUL DE INVENȚIE A REZULTATELOR CERCETĂRII DIN DOMENIUL NENOMATERIALELOR POLIMERICE

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Nanomaterialele polimerice reprezintă - potrivit legislației naționale și europene privind brevetele de invenție - unul dintre obiectele care pot fi brevetate cu succes, fie că e vorba despre un produs/compoziție și/sau un procedeu special conceput pentru obținerea acestora și/sau o instalație în care se aplică procedeul. Brevetul de invenție conferă titularului un monopol de exploatare, acordat de stat, în schimbul dezvăluirii soluției tehnice.

“O dezvăluire suficientă a invenției” presupune ca persoana de specialitate din domeniu să poată realiza invenția în toate variantele acesteia, așa cum sunt revendicate. Invenția trebuie dezvăluită în egală măsură în descriere, în revendicări și desene.

„Dezvăluirea” rezultatelor cercetării în postere, expoziții, conferințe, simpozioane și reviste de specialitate cotate internațional trebuie să urmeze depunerii unei cereri de brevete de invenție la OSIM, altfel cererea respectivă este respinsă fiind lipsită de noutate.

Pe baza unei dezvăluiri clare și complete a invenției, se poate realiza un raport de documentare, în vederea stabilirii stadiului tehnicii, ca bază a procedurii de examinare de fond a cererii de brevet de invenție, în vederea analizării condițiilor de brevetabilitate, prevăzute de Legea nr. 64/1991, republicată în 2014. Întocmirea și publicarea raportului de documentare, în condițiile Legii, corespunde interesului transparenței procedurii de examinare și implicit, al furnizării de informații terților, susținând astfel cercetarea în domeniul respectiv.

PHYTOTHERAPY-A NATURAL THERAPEUTIC APPROACHES

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Keywords: phytotherapy, medicinal herbs, digestive, respiratory, locomotor, urogenital, cardiovascular

Introduction: The historical and ongoing importance of medicinal herbs is essential in healthcare. For centuries, plants have been used for their healing properties, and many modern pharmaceuticals are derived from plant substances. The points about the benefits of herbal remedies, including their cost-effectiveness, accessibility, and generally lower risk of side effects (when used properly), are also well taken.

It's essential to maintain a balanced view of the role of herbal remedies in healthcare. While they can offer significant benefits and can be effective in treating a range of conditions, they are not a panacea. It's critical to approach the use of herbal remedies with the same caution and scrutiny as pharmaceutical drugs and to determine exactly the active principles.

Materials and methods: The identification of the active principles of medicinal and aromatic plants involves the use of a wide range of techniques and procedures: paper chromatography (CPH) used for the separation and identification of organic compounds from plants, high performance liquid chromatography (HPLC) used for the separation, identification and quantification of the principles active ingredients from plant extracts as well as physico-chemical analyses, biological tests, microscopic analysis.

Results: The inventory of medicinal and aromatic plants studied includes species with a definite content in therapeutic chemical compounds. Among them, they are often used in the phytotherapy of some ailments as follows: in ailments of the digestive system (*Achillea millefolium*, *Althaea officinalis*, *Equisetum arvense*, *Matricaria recutita*, *Hypericum perforatum*, *Capsella bursa-pastoris*, *Populus nigra*, *Symphytum officinale*), in diseases of the respiratory system (*Achillea millefolium*, *Althaea officinalis*, *Hypericum perforatum*, *Matricaria chamomilla*, *Quercus robur*, *Rosa canina*, *Malva sylvestris*, *Tussilago farfara*, *Pinus sylvestris*), plants used in diseases of the locomotor system (*Betula pendula*, *Urtica dioica*, *Matricaria chamomilla*, *Populus nigra*, *Salix alba*), in diseases of the urogenital system (*Betula pendula*, *Equisetum arvense*, *Taraxacum officinale*, *Viola tricolor*, *Urtica dioica*), in phytotherapy of the cardiovascular system (*Convallaria majalis*, *Crataegus monogyna*, *Leonurus cardiaca*, *Valeriana officinalis*, *Vinca minor*, *Viscum album*).

Conclusions: Phytotherapy through the use of medicinal and aromatic plants is an important source for enriching the therapeutic arsenal that can be used by the medical world.

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FROM IDEAS TO IMPACT: UNDERSTANDING KNOWLEDGE VALORIZATION IN THE EUROPEAN RESEARCH AREA

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Keywords: *research management and administration, knowledge transfer, commercialization, change management*

The landscape of Research and Innovation (R&I) has undergone profound transformations since the release of the European Commission Recommendation on the management of intellectual property in knowledge transfer activities in 2008. In light of paradigm shifts, there is an urgent need for a comprehensive update, one that goes beyond the traditional concept of knowledge transfer and embraces the monetization of knowledge assets. These assets, whose origins are diverse, are now generated within a dynamic R&I ecosystem populated by a diverse set of change agents.

The overarching goal of this comprehensive update is to chart a unified path toward the formulation of unified measures and policy instruments that will improve knowledge sharing and valorization across Europe. In addition, the implementation of latest European Codes of Practice will provide invaluable guidance to R&I practitioners, assisting them in the effective implementation of critical aspects of knowledge valorization, inclusive of prudent intellectual property management and the implementation of standardization measures to facilitate knowledge acquisition.

This necessary update must deal with a slew of new challenges posed by the ever-changing R&I landscape. Among these challenges, the increasingly complex knowledge value chains, the emergence of novel market opportunities catalyzed by advancing technologies, the evolution of new paradigms in industry-academia collaborations, citizens' active participation in knowledge processes, and the imperative of fostering reciprocity in intellectual property management within the realm of international R&I cooperation have been recently addressed by the European Commission by means of a holistic approach that is seamlessly interwoven with research funding initiatives should be taken to strategically support and fund the valorization of knowledge. Consequently, adequate resources must be allocated in proportion to the magnitude of this undertaking, drawing inspiration from best practices relying on a diverse set of tools developed and refined across Europe's diverse landscapes.

The importance of technology transfer and efficient utilization of research outcomes cannot be overstated as the European Union navigates its path towards recovery from the COVID-19 pandemic and steers its course towards a green and digitally empowered economy. These prerequisites are critical to achieving the ambitious policy goals set forth by the 2030 Agenda. The insights gained from the rapid dissemination and commercialization of research discoveries during the pandemic necessitate their universal application across all spheres that may benefit from expedite problem-solving solutions within the domain of research management and administration.

This comprehensive update marks a watershed moment in the evolution of European R&I policy, with the potential to shape the trajectory of knowledge valorization across local sustainable development regions and underpin the achievement of lofty societal and economic goals.

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MULTIFUNCTIONAL SURFACES FOR SENSING APPLICATIONS

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Keywords: Biosensors, Point-of-Care Diagnostics, Surface Modifications, Functionalization

Introduction: In recent years, considerable research has been focused on the multifunctional properties that are improved and tailored by nanoengineering to be used as multifunctional surfaces in emerging sensing technologies. New advancements in material design and surface functionalizations have paved the way for public safety, simultaneous health monitoring, enabling efficient onsite detection and point-of-care testing. The selection of nanomaterials is an important factor for sensors coupled with bio-functionalities that demand high sensitivity, accuracy, reproducibility, mechanical flexibility, and low cost. Focusing on morphological and structural characteristics in order to tailor their properties, allows improved responses for detections of target biomolecules.

Materials and methods: 1-Pyrenebutyric acid (PBA), 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDC), N-hydroxysuccinimide (NHS), potassium chloride (KCl), bovine serum albumin (BSA, lyophilized powder, ≥96%), potassium ferrocyanide (K₄[Fe(CN)₆]) and ferricyanide (K₃[Fe(CN)₆]), phosphate-buffered saline (PBS) with pH 7.4, coc-mAb1, Benzoylcegonine- D8, amphetamine, benzodiazepine standard-3, and methamphetamine solutions. Laser patterning was performed by a CO₂ Universal Laser System on a commercial polyimide (PI) substrate. Electrochemical techniques, differential pulse voltammetry (DPV), and cyclic voltammetry (CV) were conducted by a PalmSens potentiostat instrument and a custom-made multiplex potentiostat, named KAUSTat. Elemental analysis and morphological characterizations were performed by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) instruments.

Results: Multifunctional surfaces for various sensor applications were successfully designed with high sensitivity and accuracy. A smart electrochemical sensor was designed for SARS-CoV-2 detection and the identification of SARS-CoV-2 variants with high sensitivity. For clinical validation, the detection system was successfully applied to 23 blood serum samples and 63 nasopharyngeal swabs from COVID-19 patients with alpha, beta, and delta variants. The sensor was coupled with a portable and wireless potentiostat to obtain a PoC diagnostic platform and ML-enabled diagnostic model designed for rapid and accurate detection of emerging variants. A smartphone-based multiplex LSG sensor for the simultaneous detection of AMP, COC, and BZD was developed for on-site illicit drugs. Real spiked saliva, healthy, and MET patient saliva samples were used for the clinical study. And simultaneous detection of cardiac biomarkers (troponin-I, troponin-T, and c-reactive proteins) was designed based on gold LSG electrodes for AMI diagnosis.

Conclusions: In our studies, we explored the design of multifunctional surfaces for development of nanoparticle-based biosensors. By harnessing the unique properties of diverse nanoparticles, such as magnetic, gold, silver, and polymeric structures loaded with specific dyes, we have achieved remarkable outcomes for detection of viral diseases as COVID-19, simultaneous health monitoring for heart diseases, on-site rapid drug detection for cocaine, amphetamine, methamphetamine etc. Furthermore, our studies contributed the smart sensing technologies by providing discreet and portable platforms for real-time monitoring and detection, these cutting-edge devices are an excellent example of the revolutionary potential of nanotechnology.

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SCIENTIFIC CONTRIBUTIONS

Section 1 – MTCH

Multifunctional materials,
nanocomposites, innovative
technologies and cultural
heritage preservation



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Keywords: natural dyes; ultrasound-assisted extraction; stabilisation; hybrid silica coatings

Introduction:

Natural dyes have fascinated mankind since early days. Our ancestors, in prehistoric times, used extracts of plant and/or animal origin for textile coloration [1]. From cave paintings to art and makeup, the evolution of humanity as we know it goes hand in hand with the development of dyes and pigments, either synthesized or natural. The latter, while widely available in nature, are known to be easily degradable at various factors, such as humidity, light, storage etc. [2,3]. To overcome these drawbacks, the aim of the study was to stabilize the extracted dyes by embedding them in hybrid silica coatings. Sol-gel applications are known to improve water, oil, soil repellency, flame retardancy, and provide UV and antibacterial protection [4]. In this way, textile coloring with an environmentally friendly dye with improved optical and tinctorial properties could be possible at large scale.

Materials and methods:

The natural dyes of plant origin were extracted using conventional and unconventional methods – ultrasound-assisted (UAE) and analyzed spectrophotometrically aided by the Jasco V-550 spectrophotometer. The employed hybrid silica coatings are based on tetraethyl orthosilicate (TEOS) and phenyl triethoxysilane (PTES). Together with tetrahydrofuran (THF), ethanol (EtOH), and citric acid, the prepared sol-gel was impregnated, using a fabric impregnation machine, on top of the textile material (cotton blend) already impregnated with the natural dye extract. After drying at 40 °C, the optical and tinctorial properties of the impregnated fabric strips, with and without sol-gel, were analyzed and compared.

Results:

The natural dyes extractions provided us with higher concentration when the unconventional method was employed. Utilizing UAE to the detriment of the common conventional ones, also lead to reduced extraction time and energy consumption. To overcome the sensitive nature of the dyes, sol-gel was involved as a stabilizing agent. Impregnating the fabric strips with sol-gel leads to improved optical and tinctorial properties for the natural dyes utilized in the current study.

Conclusions:

Dyes of natural origin have a probable future when discussing textile coloration at large scale, especially after sol-gel impregnation, as both the optical and tinctorial properties show improvement.

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SEPARATION AND IDENTIFICATION OF MOLECULAR SPECIES BY GC-MS FOR THE REACTION MIXTURE WITH METHYLTRIMETHOXYSIANE (MTMOS)

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Keywords: methyltrimethoxysilane (MTMOS), mass spectra, sol-gel process

Introduction:

The aim of this article is separation and identification of molecular species obtained in the sol-gel process by GC-MS for the reaction mixture with methyltrimethoxysilane (MTMOS). The HP 5890 gas chromatograph with a fused silica high-performance capillary column with 75,000 theoretical plates, and 70-SE VG Analytical double focusing mass spectrometer were used. In the presence of an unhydrolyzed methyl group, it is expected that for the molecular species starting with the cyclic trimers, a series of geometric isomers will be highlighted due to the position of the methyl groups in relation to the ring plane of each siloxane molecule; in addition, for the hydrolyzed products, isomers with different relative positions of the hydroxyl groups to the methyl and methoxy groups are possible. Subsequent stages of the hydrolysis-polycondensation process are essentially determined by the reactivity of the new molecular species formed.

The first purpose of the author's thesis [1] was the separation and identification of molecular species obtained in the sol-gel process by gas chromatography coupled with mass spectrometry (GC-MS).

The basic factors that influence the sol-gel process have been studied systematically by GC-MS: the type of precursor alkoxide (TEOS, MTEOS, VTEOS, MTMOS), other major influencing factors in the sol-gel process were also studied by GC-MS, such as the type of solvent (EtOH, MeOH, PrOH), the amount of water for hydrolysis (sub-stoichiometric or without water), the order of introducing the reactants and the type of catalyst (HCl, HF, CH₃COOH, NH₃). The results were published between 1994 and 2007 [2-8].

Materials and methods:

Working conditions for the HP 5890 gas chromatograph	
Injection port temperature	250 °C
GC-MS interface temperature	280 °C
Column and stationary phase	A fused silica high-performance capillary column Silicone oil OV-1
Temperature program	40 °C (3 min.), 15 °C/min, to 220 °C (5 min)
Carrier gas	Helium flow rate 1 ml/min.
Working conditions for 70-SE, VG Analytical double focusing mass spectrometer	
Acquisition mode	SCN
Ion source temperature	180 °C
Electron energy	70 eV
Electronic amplifier	250

Fig. 1. GC-MS method and optimization parameters

Results: Identification of molecular species by GC-MS for the reaction mixture with methyltrimethoxysilane (MTMOS)

The starting reaction mixture (1) had the composition:

MTMOS: H₂O: MeOH 1:1:1,75 (mol / mol) (HCl pH = 3.5)

(1)

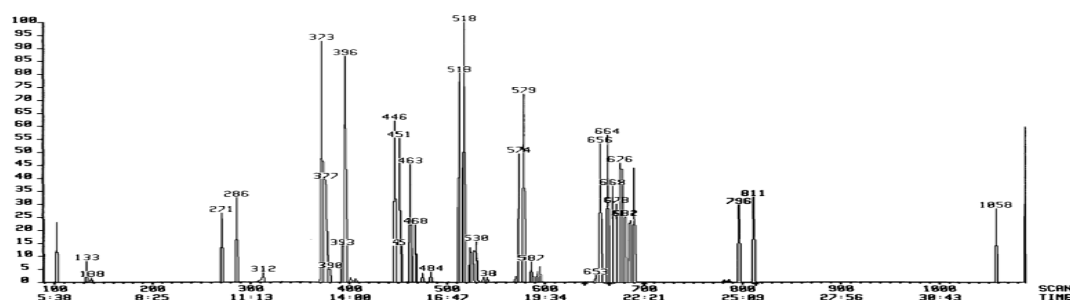
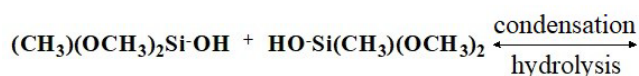
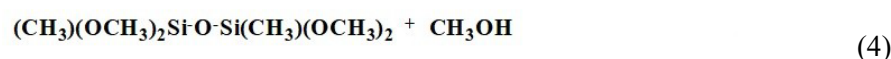
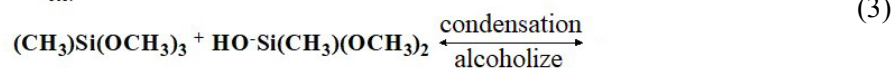
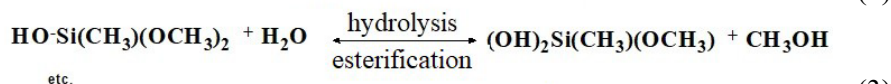
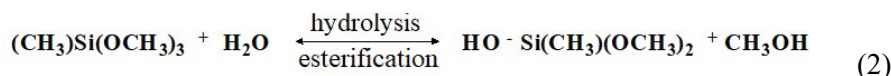


Fig. 2 Chromatogram of reaction mixture MTMOS: H₂O: MeOH 1:1:1,75 (mol / mol) (HCl pH = 3.5)

The reaction mixture (1) with MTMOS was used at 96 h after preparation to identify molecular species by GC-MS; under the working conditions specified in subheading 2, the chromatogram of the mixture was obtained (Fig. 2).

Equations (2)-(5) are materialized for the reaction mixture with MTMOS where $R = CH_3$ and $R' = CH_3$ as follows:



According to equations (2)-(5) it is possible to identify the hydrolysis and condensation products of MTMOS. At the same time, since the methyl group does not hydrolyze, it is expected that for the molecular species starting with the cyclic trimers, a series of geometric isomers will be highlighted due to the position of the methyl groups in relation to the ring plane of each siloxane molecule; in addition, for the hydrolyzed products, isomers with different relative positions of the hydroxyl groups to the methyl and methoxy groups are possible.

Conclusions:

1. Identification by GC-MS of 65 molecular species from 86 theoretical structures was performed for the reaction mixture with alkoxide precursor methyl-trimethoxysilane (MTMOS) in parental solvent (MeOH) and acid catalyze (HCl). The mass spectra of identified species from monomers to octamers are presented.

2. In the presence of an unhydrolyzed methyl group, the molecular species starting with the cyclic trimers, a series of 47 geometric isomers were identified due to the position of the methyl groups in relation to the ring plane of each siloxane molecule; in addition, for the hydrolyzed products, 4 isomers with different relative positions of the hydroxyl groups to the methyl and methoxy groups were identified.

3. The subsequent stages of the sol-gel process are essentially determined by the reactivity of the new molecular species formed in the sol stage for different alkoxides, including in the case of reactions with MTMOS.

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A COLD ACTIVE ALDEHYDE DEHYDROGENASE FROM FLAVOBACTERIUM PL002 AS A NEW ENZYMATIC LABEL FOR DNA APTAMERS: A PRELIMINARY STUDY

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Keywords: aptamer, biosensor, DNA, enzyme, UV spectrometry

Introduction: Aptamer-based biosensing mechanisms often involve DNA probes labelled with catalysts (enzymes, nanozymes, DNazymes) to obtain a high-output electrochemical or optical signal. Despite costs and stability limitations, natural enzymes remain the most powerful catalysts available [1]. In this context we report a preliminary study for obtaining an aptamer labeled with a cold active aldehyde dehydrogenase from the Antarctic *Flavobacterium* PL002 (F-ALDH), for the controlled labelling of a DNA aptamer for lysozyme [2]. The cold active recombinant enzyme functions in a wide temperature range and the recombinant enzyme has a histidine tag attached to the N-terminal which has an affinity for the complex nickel- nitrilotriacetic acid (Ni-NTA) [3].

The aim of this work is to investigate whether the labeling of a DNA aptamer with F-ALDH by this mechanism preserves indeed the enzyme activity and how it compares with the covalent attachment of the enzyme by amine coupling.

Materials and methods: The enzyme-tagged lysozyme aptamer was obtained by a 4-step procedure involving (i) the preparation of a conjugate between the thiol-ended aptamer and N_α,N_α -Bis(carboxymethyl)-L-lysine using maleimide; (ii) incubation with NiCl_2 to form the Ni-nitrilotriacetic acid chelate; (iii) attaching the enzyme to the aptamer via nickel-histidine affinity; (iv) purification of the reaction product, i.e., the labelled aptamer by centrifugation through a 30 kDa cut-off filter and by size exclusion chromatography (SEC).

Results: UV spectrometry was used to verify the attachment of F-ALDH to the aptamer, the changes observed at 260 nm and 280 nm being indicative of the success of the experimental protocol. However, the attempts to measure the mass of the conjugate and obtain direct proof by gel electrophoresis were unsuccessful. The binding to the aptamer resulted in a 23% reduction in the specific activity of F-ALDH compared to the free enzyme. In enzymatic activity measurements of lysozyme measuring the absorbance of *Micrococcus lysodeikticus* substrate at a plate reader, the labeled aptamer significantly inhibited the activity of lysozyme, indicating strong binding.

Conclusions: Experiments conducted under optimal conditions to visualize the enzyme or the DNA enabled the identification of the two components in the „labeled aptamer” solution, but there were no additional bands to prove that the aptamer was bound to the enzyme. More detailed investigations by LC/MS are needed to obtain such proof. Enzyme activity was largely preserved following the controlled attachment to the lysozyme aptamer. Further studies are required to evidence the effect of the labeling on the aptamer binding and to identify the optimal storage conditions for preserving the catalytic activity of the aptamer-bound F-ALDH.

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PRISTINE AND MODIFIED HOLLOW MESOPOROUS SILICA SPHERES AS CARRIERS FOR POLYPHENOLS

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Keywords: mesoporous silica; zinc oxide; polyphenolic extract; encapsulation; biocompatibility.

Introduction: Pristine and functionalized mesoporous silica has been widely studied as carrier for either active pharmaceutical ingredients or natural compounds with health benefits due to its large pore volume, high biocompatibility, and surface properties that can be tailored by linking organic groups or attaching inorganic nanoparticles [1,2]. Among natural compounds, polyphenols are valuable substances extracted from plants that have attracted attention due to their benefits on human health such as anti-inflammatory, antioxidant, antibacterial and antitumoral activities [3]. The objective of this work was to obtain pure and modified with ZnO hollow mesoporous silica spheres and then to use them as supports for a polyphenolic extract prepared from bilberry leaves, resulting composite materials for topical applications.

Materials and methods: Pristine mesoporous silica hollow spheres (HS) were obtained by sol-gel method assisted by solvothermal treatment using hexadecyltrimethylammonium bromide as template agent. Then, they were modified with ZnO by impregnation method (HS-Zn). HS and HS-Zn were used as carriers for a polyphenolic extract. The cytocompatibility of extract from bilberry leaves, carriers and extract-loaded supports was evaluated on NCTC L292 fibroblasts and HaCaT keratinocytes.

Results: HS and HS-Zn carriers with an average size of 400-500 nm and high porosity were obtained. In the case of HS-Zn, ZnO was evenly distributed inside the silica spheres. The polyphenolic extract with very good antioxidant activity was rich in chlorogenic acid and rutin hydrate, which are known compounds with antibacterial properties.

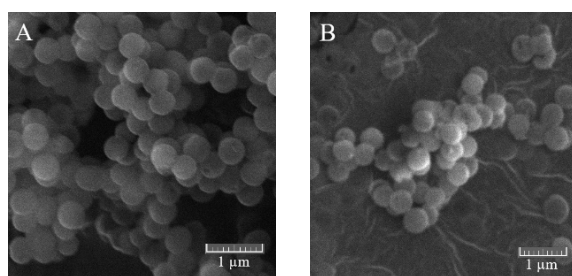


Figure 1. SEM images of pristine hollow mesoporous silica spheres (A) and ZnO modified mesoporous silica spheres (B).

Conclusions: Extract-loaded materials showed good cytocompatibility up to 50 μg/mL on both tested cell lines. A synergistic antimicrobial effect between ZnO and bilberry leaves extract was observed against standard *P. aeruginosa* strain. Therefore, extract-loaded materials could be used in biomedical applications.
Acknowledgements: The financial support from UEFISCDI (Romania) through project PCE no. 117/2022 is highly appreciated.

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NEW APATITE-BASED CONSOLIDANT FOR STONE PRESERVATION

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Keywords: triple substituted carbonated hydroxyapatite, stone consolidation and preservation, nanoemulsion method

Introduction: The performance of a consolidation treatment depends on several factors: product type, stone characteristics, the procedures used to apply the consolidants, the concentration of consolidants solutions, the condition of the stone and the ambient conditions before, during and after the application [1,2]. The apatite's efficiency as inorganic consolidates for carbonated stone was previously demonstrates [3], with strength and tensile improvement and reduced surface micro-cracks. This study aim was to synthesize triple substituted carbonated hydroxyapatite (triple-CHAp), via nanoemulsion method. Calcium substitution with three considered metallic ions was investigated in terms of structural, morphological and compositional properties. Then, the efficacy of triple-CHAp as inorganic consolidant for artificial stone samples was tested by specific methods.

Materials and methods: Triple-CHAp was synthesized by the nanoemulsion method, at room temperature, when carbonated hydroxyapatite is obtained, simultaneously with calcium substitution by the metallic ions provided by the nitrate form of the metals' precursors, chosen due to their high-water solubility of dopants. The final product was filtered, washed, dried and calcinated. Triple-CHAp water suspensions, of 3 concentrations, were prepared and applied on simulated stone samples to demonstrated their consolidation efficacy. Triple-CHAp was analyzed by FTIR, WDXRF, XRD, SEM. The chromatic changes, water repellency, consolidation properties, and durability of stone specimens before and after treatment were analyzed.

Results: The presence of the metallic ions into CHAp structure was confirmed by WDXRF and FTIR. Spherical nanometric particles, with high surface area and pores, and tendency to agglomerated, result (Fig. 1). When applied on stone, by brushing or spraying, triple-CHAp improves the physical and mechanical properties of the substrate, reduces the water absorption, and maintains the appearance and color of stone.

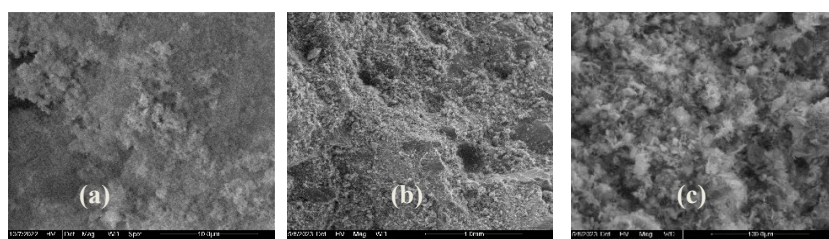


Figure 1 Morphology of triple-CHAp (a), control (b) and treated (c) stone specimens

Conclusions: The calcium ions from CHAp structure were partially substituted with three metallic ions and the compositional ratio, apatite structure changes and morphology of the new synthesized inorganic compound were demonstrated. Also, by treating stone specimens with triple-CHAp suspensions, the consolidation efficacy is proven. Thus, the consolidate can be further applied on real stone samples.

Acknowledgements: This work was carried out through the PN 23.06 Core Program - ChemNewDeal within the National Plan for Research, Development and Innovation 2022-2027, developed with the support of Ministry of Research, Innovation, and Digitization, project no. PN 23.06.02.01 (InteGral) and project number PN-III-P2-2.1-PED-2021-3885 (687PED/2022) from UEFISCDI-MCID, within PNCDI III.

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COMPOSITES – PRECURSORS FOR OBTAINING NEW SORBENTS AND CATALISTS

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Keywords: *composites; metal; carbon; active centres; isotherm; mesopores.*

Introduction:

Sorbents and catalysts are widely used in the chemical industry, in the processes of separation and purification of gaseous and liquid systems, in environmental protection. Obtaining new sorbents with selective sorption and catalytic properties is an important field of research. This report discusses the results of studies on obtaining new sorbent-catalysts for the removal of nitrite ions from water, but not only.

Materials and methods: A series of composites (7 pieces) was obtained by the hydrothermal method. The composites were obtained from walnut shells by impregnation with compounds of Mn, Co, Cu. Also, for comparison, samples of commercial catalysts containing Mn, Fe and other metals were investigated.

The composites were examined using SEM EDX, XRD, FT-IR spectroscopy and thermogravimetry methods.

The concentration of nitrite ions in the solution was determined spectrophotometrically [1].

Results: Four types of composites based on Mn compounds have been obtained. Three of them also contain impurities of Fe, C, K and others. The data in Figure 1 serve as an example. Also, 2 composites based on Co and Cu was obtained. All composites contain O and predominantly C.

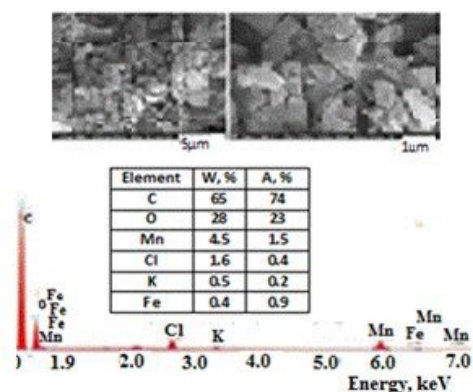


Fig.1. SEM EDX of Mn-containing composite.

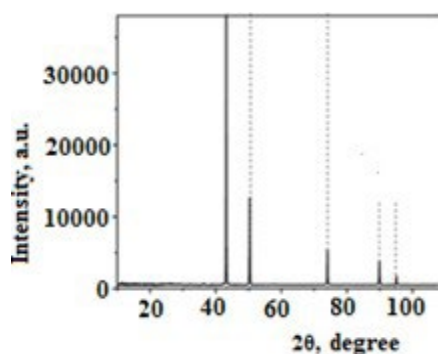


Fig.2. X-ray diffraction pattern of the Cu-containing composite.

Conclusions: The active centres have an irregular shape and are unevenly distributed in the volume of the composite particles. The EDX data allowed the calculation of the formal brut formulas of the active centres. Studies carried out using IR-Fourier spectroscopy show that, in addition to inorganic compounds, the composition of composites also includes organic compounds. Surprisingly, out of all the composites obtained, only one contains crystalline phases, namely metallic copper (Fig. 2). When heated in air at a temperature of 650 °C, crystalline phases appear in all composites. These phases are metal oxides. The composites are thermally stable up to 240 °C. Nitrogen adsorption and desorption isotherms were also obtained. Samples contain practically only mesopores, and the width of the pores is 3.8-5.6 nm. Tests have shown that the composites transform (remove) nitrite ions from the solution.

Acknowledgments: This research was carried out with the financial support of the National Agency for Research and Development, Chisinau, Moldova. (Grant number 20.80009.7007.21).

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DESIGN AND DEVELOPMENT OF MIP BASED ELECTROCHEMICAL SENSOR FOR CORTISOL DETECTION

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Keywords: cortisol; pencil graphite electrodes; SPEs MIP; sensor; polymers

Introduction:

Medical biochemistry represents a very important field because the connection between the various problems of medicine and the interdisciplinary field of science has led to the study and finding of new solutions for different dysfunctions and diseases that occur. Hormones represent one of the most important classes of chemical compounds existing in human body. Among these hormones that control key body functions, cortisol is an essential one for the body's survival as it represents a biomarker of stress. This compound can be determined in various samples, such as: blood, sweat, saliva and hair. Thus, electrochemical miniaturized sensors based on a polymer were developed for rapid and sensitive determination of cortisol.

Materials and methods:

Commercial pencil graphite electrodes (PGEs) and carbon paste screen-printed electrodes (SPEs) were used for development of cortisol-based sensors. Electrodeposition of the monomer proflavine was realized in the absence of cortisol to obtain Non-Imprinted Polymer (NIP) and respectively, in the presence of cortisol to obtain Molecularly Imprinted Polymer (MIP). In order to characterize and optimize the analytical parameters of the developed sensors, electrochemical (cyclic voltammetry, differential pulse voltammetry, electrochemical impedance spectroscopy) and morpho-structural (SEM, FTIR) studies were performed. A direct determination of cortisol was carried out using the developed sensors, but also an indirect determination was performed using potassium hexacyanoferrate at 37°C (human body's temperature).

Results:

Electrochemical behavior of the polymer-based sensors was studied in acetate and respectively, phosphate buffer solutions of 0.1M, with pH ranging from 3 to 7 in the presence of cortisol. Since the CV and DPV studies revealed that cortisol was electrochemically inactive, in the potential range used, at the surface of NIP and MIP based sensors, respectively, a direct determination of cortisol using the developed sensors is not possible to be achieved with a good sensitivity. Thus, an indirect determination of cortisol based on the decrease of the oxidation signal of the reversible redox couple $[\text{Fe}(\text{CN})_6]^{4-/3-}$ was performed in phosphate buffer 0.1M, pH 7, in the potential range from -0.1 to 0.5V vs Ag/AgCl. Considering that it was used a fairly high concentration of cortisol and the decrease of signal was quite small for the incubation times used, in order to obtain better results, the study was continued by modifying the electrodes surfaces with polymer films, obtained by electropolymerization's method, under potentiodynamic conditions, in the presence (MIP) and absence (NIP) of cortisol.

Conclusions: Electrochemical determination of cortisol was possible by using an indirect method consisting in the decrease of the oxidation signal registered for the reversible redox couple $[\text{Fe}(\text{CN})_6]^{4-/3-}$. The detection of cortisol by using MIP based sensors was achieved with a higher sensitivity than unmodified sensors (NIP). The electrochemical studies for this stress biomarker are very important as the increased interest in recent years for the development of faster and more sensitive detection methods has increased considerably.

Acknowledgements: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project M-ERANET-3-FULSENS-GEL within PNCDI III, Contract no. 318/2022 and within 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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INNOVATIVE ECO-FRIENDLY SYNTHESIS OF POLYOL/SILVER NANOPARTICLES FOR ANTIMICROBIAL POLYURETHANE SYSTEMS DEVELOPMENT

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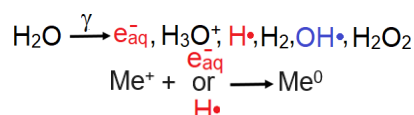
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Keywords: gamma rays, nanocomposites, polyurethane foam, antimicrobial

Introduction: In contemporary times, a steady influx of novel technologies centered around nanoparticles is persistently emerging and advancing across a wide spectrum of application domains, most notably within the rapidly evolving biomedical and pharmaceutical sectors. Polyurethanes (PU) are a category of polymer materials which are prepared by polyaddition reaction of a di-isocyanate and a polyol mixture with additives. In our current research, we have employed an innovative technique known as in-situ radiochemical synthesis to create dispersions of silver nanoparticles (AgNPs) within polyol solutions. These systems can subsequently be utilized in the fabrication of antimicrobial polyurethane foams (PuF). The radiochemical synthesis of metallic nanoparticles stands as an environmentally-friendly approach for generating nanoparticles distinguished by precise size management, consistent dispersion, complete reduction, and exceptional stability, all achieved under notably gentle operational parameters.

Materials and methods: AgNPs were synthesized via a single-step gamma irradiation method at doses up to 100 kGy in a solution consisting of polyol (Petol 56 – 3, Oltchim, Mw: 3000, f=3), silver nitrate (0-20 mM), and a small amount of water (1% by volume). The materials underwent characterization through a range of analytical techniques, including UV-Vis spectroscopy, laser diffraction, SEM analysis, and assessment of their antimicrobial properties.

Results: Radiochemical synthesis is a viable approach for producing diverse metal nanoparticles, including those composed of silver (Ag), gold (Au), platinum (Pt), copper (Cu), and more. The reduction of metal ions in this process is controlled by reducing agents generated through water radiolysis, i.e., hydrated electron (e^-), and hydrogen atoms (H^\bullet):



In the production of polyurethane foams, the quantity of water can influence the final properties of the foam, thus requiring strict control. Silver nanoparticles were obtained under conditions with a limited amount of water (1% v/v). Following irradiation of the polyol solutions, their color changed from transparent to brown, serving as an initial indication of AgNPs formation. UV-Vis spectroscopy revealed characteristic SPR absorption peaks of AgNPs (Figure 1). Particle size determination using laser diffraction analysis, indicated an average size of AgNPs at 4.1 nm.

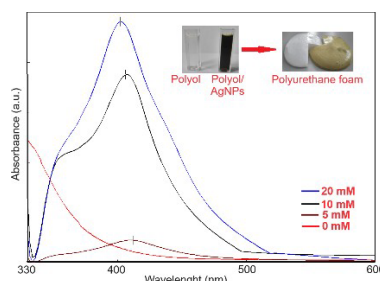


Figure 1. UV-Vis spectra of polyol/AgNPs systems

Conclusions:

Gamma irradiation can be used for the innovative synthesis of polyurethane foam nanocomposites with silver nanoparticles, starting from the direct synthesis of AgNPs in the polyol solution. Due to the intrinsic antimicrobial activity conferred by AgNPs, these materials have the potential for use in the biomedical field (e.g., antimicrobial mattresses, carpets, catheters).

Acknowledgements: The financial support was provided by MCID, through project PN-III-P2-2.1-PED-2021-0423 (612PED/2022)

THERMAL GRAVIMETRIC ANALYSIS OF GRAPHITE FILMS DEPOSITED ON METAL SURFACE BY ELECTRIC DISCHARGE IMPULSE IN THE UNDEREXCITATION REGIME USING PYROLYTHIC GRAPHITE CATHODE

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Keywords: *graphite film, thermal gravimetric analyses, electrical discharges*

Introduction: The formation of graphite films at micrometric and nanometric scale on the surfaces of alloys-made parts causes their diffusion in the surface layer accompanied by the formation of high hardness carbides, and, as a result, the wear resistance of this layer increases [1-5]. TGA tests on graphite films were conducted on a Du Pont Instruments 951 device. In order to avoid errors – due to the oxidative process that takes place at high temperature and results in a weight increase – TGA tests on graphite films were carried out in nitrogen atmosphere. The following parameters were set for the reference sample and for the graphite deposit material on the surface of the work piece: 20-800 °C temperature range; 10 °C/min heating rate; medium N₂ analysis at a working pressure of 760 mm Hg

Materials and methods: First of all, TGA tests were done on a pure graphite sample, which was thought to be the reference sample. The curve shape does not reveal any unusual thermal behaviour for graphite; within the temperature range of 100-280 °C a weight loss of 7.485% (0.4683 mg) occurs as a result of volatiles and water evaporation; between 280-600 °C no weight loss occurs which shows a high thermal stability of graphite; some non-significant decomposition (of about 18% of baseline) occurs within the temperature range of 650-800 °C, caused by decomposition of tars and heavy hydrocarbons that are found in most varieties of graphite and, finally, considerable amount of graphite is found in the residue – more than 75%, at the end of determination 800 °C. These aspects are characteristic for graphite behaviour. TGA curve of deposited graphite sample shows a completely different allure from that characteristic of pure graphite. The graph shows a number of very interesting aspects suggesting that the graphite film, deposited by electrical discharge in impulse, has a completely different structure from that of pure graphite or that, besides graphite, other chemical compounds of carbon are formed [6].

Conclusions: One may notice that within 200-300 °C temperature range (at 222.99 °C) a significant weight increase (of 1.999 %) occurs, showing that the graphite sample gains weight, instead of losing it due to decomposition or loss in volatiles – showing a material adsorption in graphite film structure (as the adsorbed material cannot be anything but nitrogen from the atmosphere in which the tests are run).

Acknowledgements: *This work was carried out through the PN 23.06 Core Program - ChemNewDeal within the National Plan for Research, Development and Innovation 2022-2027, developed with the support of Ministry of Research, Innovation, and Digitization, project no. PN 23.06.02.01 (InteGral).*

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AN ECOFRIENDLY APPROACH FOR THE ELECTROCHEMICAL DETERMINATION OF OLIVE OILS POLYPHENOLS USING DEEP EUTECTIC SOLVENTS

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Keywords: phenolic compounds, extra virgin olive oil, deep eutectic solvent, cyclic voltammetry

Introduction: Phenolic compounds are a diverse class of bioactive secondary metabolites and are of high and significant importance due to their biological and nutritional attributes [1]. Indeed, their antioxidant and anti-inflammatory activities have been associated with the preventive action on certain diseases, such as atherosclerosis and cancer [2]. Olive oil, the main source of dietary fat, is a complex mixture of natural substances having multiple beneficial effects on the body [3]. Most research has focused on the biologically active phenolic compounds naturally present in virgin olive oils to aid in explaining reduced mortality and morbidity experienced by people consuming a traditional Mediterranean diet [4]. The determination of phenolic compounds in extra virgin olive oils (EVOO) by means of rapid, low cost, environment-free methods would be a desirable achievement.

Materials and methods: A natural deep eutectic solvent (DES) based on glucose and lactic acid was considered as extraction solvent for phenolic compounds in EVOO. These phenolic compounds have been electrochemically determined using a screen-printed electrode (SPCE) modified with carbon nanotubes (CNTs), using cyclic voltammetry (CV) as a detection technique. Also, Folin-Ciocalteu method was used in order to spectrophotometrically detect the phenolic compounds in the ultraviolet range.

Results: The present work was aimed at setting up an easy and green method for the determination of p-coumaric acid, chlorogenic acid and gallic in EVOO by means of a liquid - liquid extraction with a natural DES and direct spectrophotometric analysis of the extracts. For the individual phenolic compounds excellent detection limits were obtained in the range from 1.63×10^{-8} M for gallic acid to 2.45×10^{-8} M for chlorogenic acid. Furthermore, based on the equation of the calibration curve, the total phenolic compound content (TPC) of the oil samples was determined by applying the Folin-Ciocalteu spectrophotometric method, expressed as mg gallic acid/kg oil, the values ranging from 105 mg gallic acid/kg oil to 280 mg gallic acid/kg oil.

Conclusions: The assessment of the content of phenolic compounds in olive oils is of main importance, due to their role in sensory properties, health effects and storage stability. We have demonstrated that the DES based on glucose and lactic acid could be used as an extraction medium for phenolic compounds of olive oils. Besides, the spectroscopic properties of the extracts were related with the total phenol content of the oils, as assessed by the common Folin-Ciocalteu assay carried out on the methanol-water extracts. The method proposed is fast and easy, requiring cheaper equipment in comparison with other methods.

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS—UEFISCDI, project number PN-III-P4-ID-PCE-2020-0923, within PNCDI III.

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DRUG-RELEASE SYSTEM BASED ON BIOCOMPATIBLE HYDROGEL CHARGED WITH LAYERED DOUBLE HYDROXIDE CONTAINING ENCAPSULATED *RHAMNUS FRANGULA* L. PHYTOEXTRACT

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Keywords: layered double hydroxide, poly (ethylene glycol) diacrylate; composite hydrogel; phytoextract

Introduction: Nowadays, classical drug-delivery systems can present an increased number of limitations such as the inability to provide a sustained drug effect over time. In order to overcome this kind of limitations and achieve a controlled drug release to a specific affected areas in the human body, various systems have been developed, such as inorganic nanoparticles [1], carbon nanostructures [2], polymeric nanoparticles [3] and so on. Layered double hydroxides (LDH) have been identified as particularly promising systems for this purpose, as they can include the necessary drug within their interlayer space, resulting in slowed diffusion [4]. A hydrogel (HG) can be described as a water-absorbent (retained) polymer network presenting a gel-like aspect which consists of a main polymer chain and a hydrophilic functional group [5]. Usually, LDH and hydrogel materials are commonly employed for encapsulating and achieving controlled release of synthetic drugs as ibuprofen, diclofenac, indomethacin, or cephalexin [6]. This type of materials combination offers a suitable environment for incorporating these drugs, releasing them gradually over time. This work focuses on the charging of LDHs previously encapsulated with *Rhamnus frangula* L. (RfL) phytoextract (chosen as the active substance) into biocompatible hydrogels (HG) for slow intestinal-transit treatment.

Materials and methods: In this respect, the composite hydrogels based on polyethylene glycol diacrylate (PEGDA) and three different types of LDHs or encapsulated RfL-LDHs, were synthesized by in situ radical polymerization, in aqueous media, together with ammonium persulfate (APS) used as initiator and tetramethyl ethylenediamine (TMEDA) used as catalyst [7].

Results: The obtained composite hydrogels were characterized from structural, morphological, and rheological point of view using modern techniques. Also, for the HG, the equilibrium Swelling Degree (ESD) was determined followed by the controlled-release experiments.

Conclusions: In conclusions, the obtained biocompatible hydrogels charged with layered double hydroxide containing encapsulated *Rhamnus frangula* L. phytoextract can lead to an efficient slow-release system, at the intestine pH, being a promising material alternative for slow intestinal-transit treatment.

Acknowledgements: This work was supported by the grants of the Ministry of Research, Innovation and Digitization, CCCDI-UEFISCDI, project number PN-III-P2-2.1-PED-2021-1870, within PNCDI III, grant number 646PED/2022—DUACTIVMER, and PN III-Human Resources Program—Young Research Teams—PN-III-P1-1.1-TE-2021-1239, grant number 144/2022—ANTISPIKE.

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CATALYTIC MICROPUMPS MADE OF UREASE FOR MIXING SOLUTIONS IN CONFINED SPACES

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Keywords: autonomous mixing; enzyme micropump; solutal buoyancy; osmotic flow

Introduction:

Mixing solutions in confined spaces (e.g., in microfluidic channels) is a challenge that is usually addressed with passive or active micromixers [1]. However, such micromixers are most often obtained by very complicated microfabrication methods and require external power sources. These features make “classic” micromixers costly to implement and difficult to use outside specialized laboratories. Motivated by these facts, we have investigated the use of catalytic micropumps made of urease for mixing solutions in confined spaces.

Materials and methods:

Urease micropumps were fabricated using a method we have previously used to build glucose oxidase micropumps [2]. The ability of the urease micropumps to produce both solutal buoyancy-driven (*i.e.*, bulk) flows and surface-driven (*i.e.*, osmotic) flows was thoroughly investigated by using particle trajectory analysis combined with two types of tracer particles.

Results:

The fabricated urease micropumps produced robust flows both in the bulk of the solution and at the solid / liquid interface carrying the micropump. Typical fluid velocities observed in our preliminary experiments are presented in Figure 1 (that also shows the schematic representation of an enzyme micropump). The fabricated urease micropumps outcompete the glucose oxidase micropumps previously fabricated by us [3] in terms of surface-driven flows, and are outcompeted by only one urease micropump previously reported in the literature [4] in terms of bulk flows.

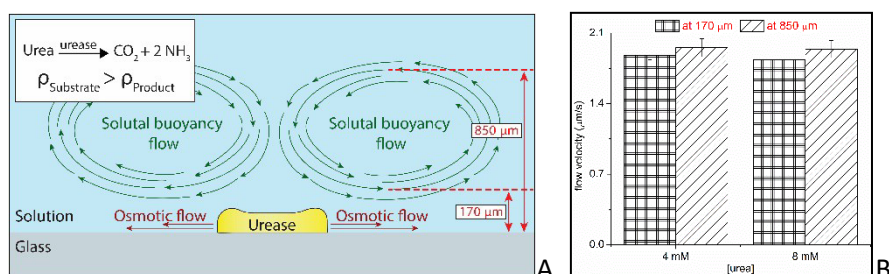


Figure 1. Schematic representation of an urease micropump, of its bulk flows, and of its surface-driven flows (A) and typical fluid velocities observed at two different heights from the interface carrying the urease micropump (B).

Conclusions:

The fabricated urease micropumps are promising for mixing solutions in confined spaces. An array of such micropumps could also be suitable for pumping solution through microfluidic channels.

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WASTEWATER DYES REMOVAL THROUGH HYBRID SYSTEMS OF HYDROGEL/Pt-Ni ALLOY NANOPARTICLES

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Keywords: wastewater, hydrogel nanocomposites, metal nanoparticles, dyes

Introduction:

Limited access to clean drinking water represents one of the most prevalent global issues, drawing the attention of researchers and government agencies to water purification. The utilization of a combination of absorption and nanotechnology presents promising prospects for wastewater treatment. Recently, a significant amount of research has been focused on the development of new materials based on polymer matrices to remove contaminants from wastewater. In the context of water treatment applications, hydrogels stand out as efficient materials for retaining a wide range of pollutants, including heavy metal ions, harmful dyes and pharmaceutical waste. This paper provides a succinct overview of the effective removal of methylene blue (MB) using hybrid systems consisting of polymeric hydrogels and Pt-Ni nanoparticles (Pt-Ni NPs). Additionally, the study introduces a synthesis method aimed at reducing reliance on scarce metals like Pt by alloying them with more readily available elements such as Ni.

Materials and methods:

Hybrid structures of Hydrogel/Pt-Ni NPs were generated through an irradiation process under standard temperature and pressure conditions. This involved subjecting aqueous solutions to irradiation, composed of acrylamide (20% w/v), 1-vinyl-2-pyrrolidone (20% v/v), and chitosan (2.5% w/v), in a volumetric ratio of 1:0.5:1, along with 2 mM of Pt and Ni salt precursors. The hydrogels were formed by exposing the reaction mixture to a radiation dose of 50 kGy. Ultrapure water served as the solvent. The catalytic efficiency (determined spectrophotometrically) of obtained nanocomposites was tested by introducing 100 mg of hydrogels material in 50 mL aqueous solution of MB (up to 100 ppm), in the presence of 2 mL of NaBH₄ (0.2 M).

Results:

Radiochemical synthesis represents a suitable method for simultaneously obtaining a cross-linked polymeric network (through a mechanism involving free radicals generated by ionizing radiation) and metallic nanoparticles (due to highly reducing species resulting from the radiolysis of water). Following exposure to radiation, the resulting material exhibited a hydrogel structure, assuming a black coloration as a consequence of the Pt-Ni nanoparticle formation, whereas the nanoparticle-free hydrogel remained transparent. The hydrogel structure containing Pt-Ni NPs displayed an impressive swelling capacity of over 900%, compared to only 420% for the nanoparticle-free material and, respectively, a gel content of 91% and 96%. The removal efficiency of MB from an aqueous solution is depicted in Figure 1, with the dye reduction rate being dependent on its initial concentration.

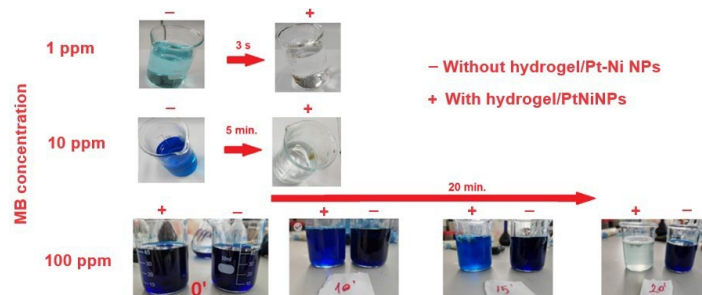


Figure 1. MB removal efficiency of hydrogel/Pt-Ni NPs structures

Conclusions: Gamma irradiation represents an eco-friendly technique that enables the simultaneous production of hybrid structures, involving polymeric hydrogels incorporating Pt-Ni nanoparticles. Due to their liquid-absorption capacity and catalytic activity in reducing organic compounds, these materials can be utilized in wastewater treatment applications, with the ability to reduce the content of dyes, pharmaceuticals, detergents and other organic contaminants in these solutions.

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CrSiCN COATINGS WITH ENHANCED MECHANICAL AND ANTICORROSIVE PERFORMANCE FOR WOODWORKING INDUSTRY

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Keywords: CrSiCN coatings, steel substrates, mechanical properties, corrosion resistance, woodworking applications

Introduction: Wood is a renewable resource with various applications in different industries. Wood machining involves complex processes influenced by factors like corrosion, wear, adhesion, and hardness. Coated surfaces must exhibit strong adhesion and high hardness across a wide temperature range to withstand the harsh conditions of wood cutting, especially with materials like oak. The cyclic temperature fluctuations during wood cutting pose challenges, and coatings must remain resistant to high temperatures, wear, and corrosion [1,2]. In this study, we investigate using nanocomposite coatings and advanced alloys as substrates for hard coatings that can enhance the mechanical and anticorrosive properties of the tools in real-life exploitation. The effect of different deposition parameters and coating compositions on the structure and behavior of the coatings was also investigated.

Materials and methods: The CrSiCN coatings were deposited by cathodic arc evaporation technique on three distinct steel substrates (C45, 16MnCr5, and X155CrVMo12) with varying carbon content. The reactive gas mixture of C₂H₂ and N₂ was used as a control parameter to obtain coatings with different C/N ratios. Morphological, microstructural, and mechanical analyses were conducted, including elemental composition, surface morphology, X-ray diffraction, and thickness measurements. Friction and wear tests under corrosive conditions were performed to assess the coatings' performance. Additionally, the corrosion resistance of the CrSiCN coatings was evaluated using potentiodynamic polarization in distilled water and sand.

Results: The CrSiCN coatings deposited on steel substrates showed improved corrosion resistance compared to uncoated steel. This finding suggests that these coatings could provide valuable protection against corrosion in real-world applications, potentially expanding their utility beyond wood machining. The results also showed that the C/N ratio influenced the formation of different phases and microstructures, affecting the coatings' hardness, adhesion, friction coefficient, and corrosion potential. CrSiCN C50N50 coatings exhibited superior morphology, hardness, corrosion resistance, and friction behavior compared to C70N30 or C30N70 coatings.

Conclusions: These results collectively point to the potential of CrSiCN coatings, particularly those with optimized C/N ratios like C50N50, to address challenges in industrial applications, enhance tool longevity, and improve performance under challenging conditions. Coated wood-cutting tools demonstrated significantly improved resistance and durability compared to uncoated tools.

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DEVELOPMENT OF COMPOSITE COATINGS WITH INCREASED DURABILITY AND SCRATCH PROTECTION OF METAL SURFACES

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Keywords: composite coatings; increased durability; anti-scratching properties

The main goal of the present work as the development of a composite coating material, which simultaneously presents high cohesion and a high degree of scratch resistance, dedicated to the steel-carbon type support materials, offering at the same time anti-corrosion protection [1].

The developed composite coating also presented increased durability on a metal surface, especially on a brake roller, by successively depositing of layers of liquid epoxy resin mixed with sand granules on a metal surface, supported and rotated by using some bearings assembled in a casing which in turn is mounted on a support plate [2].



Figure 1. Developed coatings



Figure 2. Application of the proposed coating

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NEW MULTIFUNCTIONAL CEMENTITIOUS COMPOSITES FOR PROTECTION AGAINST BIO-PATHOGENS AGENTS

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Keywords: oxide nano-particles, anti-bacteriological, anti-fungal, cementitious composites

Introduction:

The paper presents the results of a research regarding the method of synthesis and characterization of a new cementitious composite materials based on ZnO nanoparticles (ZNPs) from the antibacterial and antifungal properties point of view. The effect of the addition of ZNPs on the antibacterial, antifungal and physical-mechanical properties on to of the cementitious composites materials will be presented.

Materials and methods:

The experimental work has been carried out by the addition of ZnO in weight percentage of 0%, 3%, 5%, and 7% in the plaster mortar. The ZNPs with antibacterial and antifungal properties were synthesized by a modified sol-gel method in the presence of an anionic surfactant (sodium dioctyl sulfosuccinate) and at low temperature (40°C). Within this research the following materials have been used: Portland cement type CEM I 42.5R, and ZnO. The Portland cement was analyzed from chemical and physical-mechanical point of view according to SR EN 196-2, SR EN 196-1, 3 [1-3]. In the case of sand, investigations were done regarding particle size distribution. Plaster mortars based on cementitious anti-bacteriological and anti-fungal composites were analyzed from the anti-bacteriological point of view through a qualitative method, using an adapted version of the Kirby Bauer disk diffusion method, according to the CLSI standard (CLSI, 2020) by exposure to two strains, gram positive (*S. aureus*) and gram negative (*E. coli*), and from the anti-fungal point of view by employing two methods: a method adapted according to SR EN 60068-2-10/2006- Environmental tests. Part 2: Tests. Test J and guide: molds, and a method adapted from ASTM G21-09- American Society for Testing and Materials, Standard Practice for Determining the Resistance of Synthetic Polymeric Materials to Fungi, 2009, by exposure to a mixture of fungal spores (*Aspergillus brasiliensis*-ATCC 9642, *Penicillium funiculosum*- ATCC 11797, *Chaetomium globosum* – ATCC 6205, *Trichoderma virens* – ATCC 9645 and *Aureobasidium pullulans* ATCC15233). The physical-mechanical properties were tested according to the specific method standards.

Results:

Through the approached synthesis method, ZNPs with a hexagonal wurtzite structure was obtained, presenting a nanodot morphology and size below 40 nm. The physical-mechanical properties of mortars cement with ZNPs are influenced by the content of ZNPs. Regarding the initial and final setting time, the addition of ZNPs in mortars cement resulted an increase of it. The compressive strength of the mixtures was influenced by the quantity of ZNPs. After evaluating the samples by exposure to a mix of spores, it was observed that all the samples have a high antifungal effect. After 28 days, the surface remains 100% uncovered. The antibacterial effect of the tested samples is proven by the absence of bacteria development on the surface of the exposed samples, also showing an inhibition zone. The antibacterial effect is higher against the *E. coli* strain, and among the three samples, the 5% ZNPs content sample has the largest inhibition zone diameter of 1.5 ± 0.05 cm.

Conclusions:

The obtained results will allow the development of new alternatives for construction materials with special characteristics.

Acknowledgements: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CCCDI - UEFISCDI, project number PN-III-P2-2.1-PED-2021-0334, within PNCDI III.

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SUSTAINABLE SYNTHESIS OF POLYMERIC HYDROGEL/METAL NANOPARTICLE HYBRIDS

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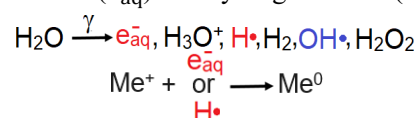
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Keywords: polymeric hydrogels, metal nanoparticles, nanocomposites, gamma rays

Introduction: Hybrid structures of polymeric hydrogel/metallic nanoparticles (MeNPs) (e.g., Ag, Cu, Au, Pd, Pt, Fe, Ni, Co, Ti, etc.) represent a category of intelligent materials that combine the properties of hydrogels with the optical, catalytic, photocatalytic, antimicrobial etc., properties of metallic nanoparticles. The synthesis of these materials involves a range of techniques such as block polymerization, chemical, physical, enzymatic, and radiochemical cross-linking. Among these, radiochemical cross-linking is an environmentally friendly and efficient technique for synthesizing 3D hydrogel structures concurrently with the synthesis of metallic nanoparticles [1]. This paper concisely presents the radiochemical synthesis method of polymeric hydrogels with silver and platinum nanoparticles. These systems hold the potential for various biomedical applications (such as antimicrobial dressings and implants) or wastewater treatment (reduction of organic dye-like compounds).

Materials and methods: Hydrogel/MeNPs hybrid structures were fabricated using an irradiation process within standard pressure and temperature conditions. This involved exposing aqueous solutions, containing specific components: water-soluble polymers, comprising 15% polyvinylpyrrolidone (PVP) and 1% chitosan (CTS), as well as 1 mM precursor salts (AgNO₃ or hexachloroplatinic acid 8%), to a radiation dose of 40 kGy. Ultrapure water served as the solvent.

Results: The energy from gamma radiation is sufficient to break chemical bonds and initiate the formation of free radicals. These free radicals, through recombination processes, lead to the creation of networks between polymer molecules, forming a 3D network. Also, the water radiolysis generates various species with high potential reduction such as hydrated electron (e_{aq}⁻) and hydrogen atoms (H[•]) [1]:



After irradiation, a solid-like hydrogel structure emerges with a noticeable alteration in color. The neat hydrogel becomes transparent, while the presence of Ag and Pt nanoparticles is indicated by a shift to yellow and black colors, respectively (Fig. 1). This change in color serves as an initial indication of the formation of metal nanoparticles within the gel matrix. In the case of AgNPs, the UV-vis spectrum exhibits a characteristic surface plasmon resonance (SPR) absorption band centered at 400 nm. The hybrid materials behavior in liquid media is depicted in Fig. 2.

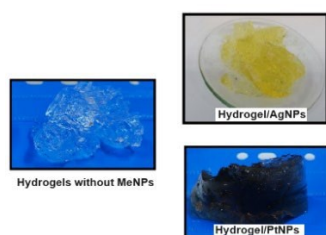


Figure 1. Formation and color change of Hydrogel/MeNPs

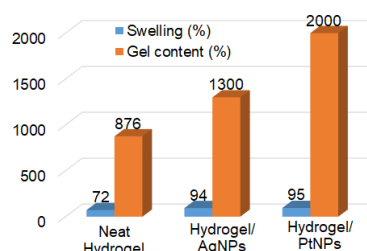


Figure 2. Hydrogel/MeNPs liquid absorption properties

Conclusions: Gamma radiation has been employed to generate PVP-CTS hybrid structures with AgNPs and PtNPs. The resulting hydrogels have demonstrated an impressive swelling capacity of up to 2000% with a gel content of up to 95%. These materials exhibit significant potential in terms of their applicability, whether as antimicrobial dressings with controlled drug release capabilities or as catalytic materials in the reduction of organic compounds in wastewater.

Acknowledgements: The financial support was provided by MCID, through contracts: 612PED/2022 and 42N/PN23140201/2023.

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RATIONAL DESIGN OF LYOTROPIC LIQUID CRYSTAL BASED CARRIERS FOR CURCUMIN TRANSDERMAL ADMINISTRATION

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Keywords: lyotropic liquid crystals; drug delivery systems; curcumin; transdermal administration

Introduction:

Surfactants present self-assembling ability and they can form a variety of colloidal systems, such as micelles, vesicles and lyotropic liquid crystals [1]. Due to their unique properties, lyotropic liquid crystals have been studied in plenty of fields, including but not limited to nanotechnology, food technology, biomedical and drug delivery [2]. They present different morphologies, such as lamellar, hexagonal and cubic and have the ability to encapsulate both hydrophilic and lipophilic active principles. [3]. Curcumin is a polyphenolic compound obtained from *Curcuma Longa* that exhibits anti-inflammatory, antioxidant, antimicrobial activity [4].

The aim of this study is to develop and characterize a lyotropic liquid crystal made of biocompatible surfactants and encapsulate it with an active principle.

Materials and methods:

Lyotropic liquid crystals (LLCs) consisting of surfactant mixtures Brij 97 - sodium cholate in water were obtained and characterized using SAXS, polarized optical microscopy (POM) and rheology and used to encapsulate an antioxidant active principle (Curcumin).

Results:

The self-assembling and adsorption behavior of the mixed surfactant systems were investigated, and the data from the surface tension isotherms reveals non-ideal mixing.

The system with minimum content of surfactants and lyotropic liquid crystal morphology was selected as carrier for the hydrophobic active principle. The encapsulation of Curcumin does not influence the nanostructure of the LLCs, as it is observed from POM and SAXS.

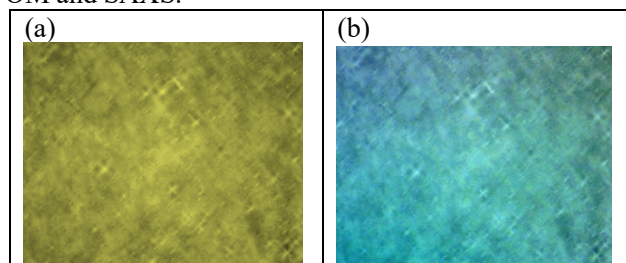


Figure 1. Polarized light microscopy images of LLCs with Brij 97, with (a) and without (b) Curcumin encapsulated.

Conclusions:

Novel LLCs were prepared, using surfactant mixtures with Brij 97 and biocompatible surfactants. The drug delivery systems show a high drug loading efficiency and the encapsulated Curcumin antioxidant activity is improved, compared to free curcumin.

The LLCs with various surfactant molar ratios exhibit a prolonged release profile of the Curcumin, proving their ability to act as transdermal drug delivery systems for sustained antioxidant therapy.

Acknowledgements: This work is supported from UB internal project, grant number UB2022

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MODIFIED ELECTRODES BASED ON ETHENE-2,1-DIYL TETRATHIOPHENE AZULENE DERIVATIVE FOR ELECTROANALYTICAL APPLICATIONS

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Keywords: ethene-2,1-diyl tetrathiophene azulene derivative, modified electrodes, quantum reactivity parameters

Introduction: This topic fits the research of azulene-based *push-pull* organic systems [1]. It's consequent objective is important due to the valuable technical properties of these derivatives, such as nonlinear optical responses, electrochemical behavior or staining properties. Some of the previously studied azulene derivatives revealed significant nonlinear optical (NLO) properties [2, 3], while others showed interesting electrochemical results [4]. Despite their large variety, most of the reported azulenic compounds are insoluble in water or in polar solvents. Generally, the structures with *push-pull* properties must exhibit good solubility in polar organic solvents for immediate technical applications. Based on the preliminary results on the electrochemical behavior of 2[(E)-2-azulen-1-ylvinyl]-thiophene as a new material for the electrode surface modification, new similar compounds exhibiting good solubility in water or in other polar solvents, have been synthesized [5]. In this work, the electrochemical properties of such ethene-2,1-diyl tetrathiophene azulene compounds have been reported, which have been selected as starting materials to obtain modified electrodes. The electrochemical study of these compounds by electrochemical methods (cyclic voltammetry, differential pulse voltammetry and rotating disc electrode) was carried out in order to determine their favorable potentials for polymeric films formation.

Materials and methods:

Electrochemical experiments were performed on the PGSTAT302N AUTOLAB potentiostat coupled to a three-compartment cell. A glassy carbon disc was used as the working electrode. The reference electrode was Ag/10 mM AgNO₃ in 0.1 M TBAP, CH₃CN. The potentials were finally referred to ferrocene/ferricinium (Fc/Fc⁺) redox couple potential (+0.07 V). The platinum wire electrode was used as the counter electrode (auxiliary electrode). All manipulations were carried out under an argon atmosphere, at 25 °C. Cyclic voltammetry (CV) curves were recorded at sweep rates of 0.05 and 0.1 V·s⁻¹. Differential pulse voltammetry (DPV) curves were recorded at 0.01 V·s⁻¹ with a pulse intensity of 0.025 V for 0.2 s. Rotating disk electrode (RDE) voltammetry experiments were performed at 0.01 V·s⁻¹ with a rotational speed of 1000 rpm.

Results:

The electrochemical investigations on the above-mentioned compound was carried out by electrochemical methods (cyclic voltammetry, differential pulse voltammetry and rotating disc electrode) to determine the most favourable potential for films's obtainment. The conditions for obtaining ethene-2,1-diyl tetrathiophene azulene modified electrodes by potential sweeping or electrolysis at controlled potential were studied, thus achieving the obtainment of electrodes modified with this ligand. The resulted modified electrodes were tested for the recognition of heavy metals (cadmium, lead, mercury, copper). In parallel, the reactivity of the ligand was also evaluated on the basis of quantum mechanics calculations, using the energies of the HOMO and LUMO frontier molecular orbitals and the electrostatic potential map.

Conclusions: Electrochemical studies showed a high electropolymerization potential for the studied ligand, experimentally confirmed by obtaining the corresponding modified electrodes. The performed density functional theory (DFT) calculations are in good agreement with the experimental behaviour revealed by the electrochemical methods.

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THE MECHANICAL, THERMAL, AND NANOMECHANICAL PROPERTIES OF COMPOSITES MADE OF BIO-BASED POLYAMIDE AND ASH POWDER

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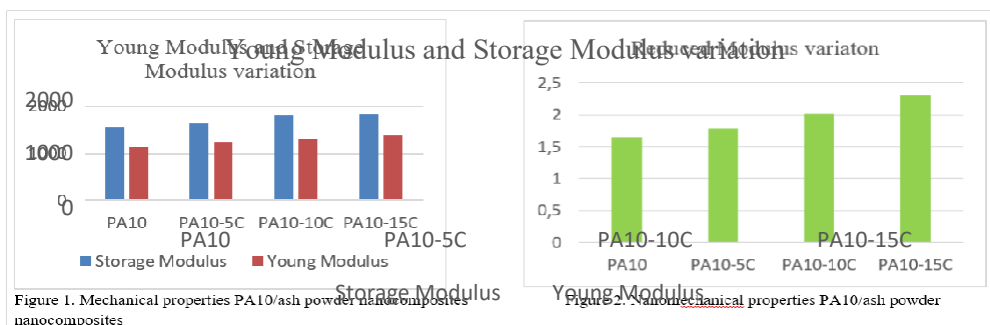
Keywords: bio-based polyamide, ash powder, mechanical properties, nanomechanical properties

Introduction: In an effort to lessen the environmental impact of plastic materials, development of biopolymers has attracted considerable attention lately. The high chemical, thermal, and mechanical properties of bio-based polyamide 10.10 (PA10), which are unique to high-performance polymers, make it a good candidate for use in a wide range of industrial applications [1-3]. However, petroleum-based polyamides like PA6 or PA6.6, which have lower cost price, are preferred. Utilizing low-cost reinforcing agents is one technique to lower the cost of PA10 while also improving some properties needed for various application fields.

The purpose of the investigation is to assess the effectiveness of ash powder as a PA10 reinforcing agent. In order to evaluate the PA10/ash powder composites, the mechanical, dynamic mechanical, and nanomechanical properties were determined.

Materials and methods: Ash powder (C) is used as a reinforcing agent in the PA10 matrix and its influence on the thermal, mechanical and nanomechanical properties is thoroughly investigated. Samples containing 5-15% C were prepared in dynamic conditions through extrusion and injection molding for physico-mechanical (tensile and impact testing, DMA), thermal (TGA, DSC) and tribological characterization (nanoindentation and nanoscratching).

Results: The addition of ash powder leads to an increase in Young modulus and storage modulus by approx. 6-16% and 8-16% respectively. Although the impact strength decreases with approx. 40% there is an increase in reduced modulus and hardness resulted from nanoindentation testing by approx. 8-29% and 3-26% respectively. The thermal stability of the composites decreases with the increase in ash concentration where the composite with 15%C has the lowest value for the temperature at the maximum rate of decomposition.



Conclusions: PA1010 represents a viable replacement for commercial synthetic polyamides that are used nowadays, presenting good mechanical and nanomechanical properties. The addition of aluminosilicates industrial waste leads to an increase in rigidity when it is mixed through melt processing methods. Further investigations are needed to evaluate the studied materials and to find applications in an industry.

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MECHANICAL, DYNAMIC-MECHANICAL AND NANOMECHANICAL PROPERTIES OF BIO-POLYAMIDE/KERATIN NANOCOMPOSITES

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Keywords: bio-polyamide, feather keratin, binary nanohybrid

Introduction: In the last 10 years, the development of biopolymers has gained a special scope in an attempt to reduce the footprint of plastic materials on the environment. Bio-Polyamide (Bio-PA) presents high chemical, thermal and mechanical properties, specific to high-performance polymers, which recommends it for applications in numerous fields of industry [1]. However, due to its high-cost price, it is still preferred to work with petroleum-based polyamides such as PA6 or PA6.6, which although have comparable mechanical performance have a 2-5 times lower cost price. One way to reduce the cost price and at the same time to improve some properties required by different fields of application is to use some reinforcing agents. Due to its many advantages, including low-cost price, thermal stability, and high mechanical properties, chicken feather keratin fibers are promising reinforcing agents in engineering polymers [2, 3]. However, in the case of polyamides, which are processed at high temperatures (over 200 °C), it is necessary to find solutions to avoid the decomposition of natural fibers.

The aim of the work is to evaluate the efficiency of keratin from chicken feathers and the nanohybrid keratin/nanoparticles as reinforcing agents of Bio-PA. The evaluation was carried out by determining the mechanical, dynamic mechanical and nanomechanical properties for the Bio-PA/reinforcing agent nanocomposites.

Materials and methods: Keratin was extracted by hydrolysis from chicken feathers. Keratin/Nanoparticles binary nanohybrids, in a ratio of 2:1, were obtained in aqueous solution, both at acidic and basic pH. Nanocomposites were obtained under dynamical conditions, through melt processing, by uniform dispersion of binary nanohybrid in a bio-polyamide 10,10 (PA) from 100% bio-based sources. The properties were determined by tensile and impact testing, by DMA and by nanoindentation and nanoscratching.

Results: **A)** the addition of keratin maintains the tensile strength of the polymer, the reduced modulus and hardness increase by 10%, but the Young modulus and the storage modulus decrease by approx. 30% and 5-10% respectively; **B)** the addition of keratin and nanoparticles slightly increase the toughness, the reduced modulus and the hardness increase by 18% and 32% respectively but the Young modulus and the storage modulus of PA decrease by only 12%; **C)** the addition of keratin/nanoparticles nanohybrid increases the toughness of PA by 20-30%, the reduced modulus and the hardness increase by 30% and 37% respectively. The best results are with the hybrid obtained at basic pH.

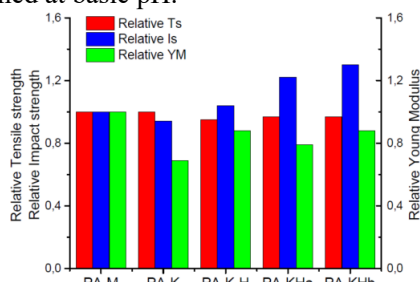


Figure 1. Mechanical properties bio-PA/Hybrid nanocomposites

Conclusions: By uniformly dispersing the binary nanohybrid in a bio-polyamide matrix, a nanocomposite with improved properties was obtained.

Applications in the automotive industry of the bio-polyamide nanocomposite are foreseen.

Acknowledgements: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PED-2021-0795, financing contract 701PED/2022.

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THE SPENDING OF WOOD SAWDUST AS POSSIBILITY TO IMPROVE THE EMBEDDING'S EFFICIENCY INTO RENEWABLE ORIGIN POLYMERIC MATRICES

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Keywords: renewable origin polymers; multiphase polymeric materials; wood sawdust

Introduction: The aim of this work was to design and get new multiphase materials with spent sawdust content embedded into thermodynamically stable matrices, based on renewable origin-polymers. The paper presents the preliminary obtained results.

Materials and methods: Finding the morpho-structural properties of un-spent and spent sawdust and its embedding possibilities into polymeric matrices. The sawdust was spent with *Pleurotus ostreatus* in one version and with *Ganoderma lucidum* in another one. Finding the sawdust concentration range possible to be embedded by melt compounding into some polar, thermodynamically stable matrices with 35-43% starch. Identification the morpho-structural characteristics of the new obtained multiphase polymeric materials and testing some possibilities to control the properties of the interface between the macromolecules of the 3 polymers from wood sawdust (cellulose, lignin, hemicellulose) and those of the starch-based matrix. The melt compounding was carried out according to some usual procedures and the characterization of the sawdust and the new obtained multi-phase materials by specific morpho-structural methods (FTIR, SEM, DSC etc.).

Results: The FTIR spectra proved that the spending was related especially to the modification of the lignin and hemicellulose and to a lesser extent to cellulose. In the case of spending of sawdust with *Pleurotus ostreatus*, not only the increasing of the kinetic independence of the specific functional groups but also the decreasing of the intensity of the absorption peaks from lignin and occurred. For the saw dust spent with *Pleurotus ostreatus* this result reveals possible some chemical reactions which had generated a new shoulder on the FTIR spectrum not existing on the un-spent saw dust or on those spent with *Ganoderma lucidum*. The SEM micrographs show that the microbiological spending changes the fibrous structure of the un-spent sawdust by creating smaller or larger voids which were also identified in the *Pleurotus ostreatus* spent saw dust but not in that spent with *Ganoderma lucidum*. According to the SEM micrographs of the multi-phase new materials, it seems that the spending makes possible to breaking of the wood fibrils under the melt compounding conditions. For these reasons the surfaces of sawdust compounds with un-spent saw dust show a fibrous appearance and as phase-in-phase type for the versions with spent sawdust with *Pleurotus ostreatus* or *Ganoderma lucidum*.

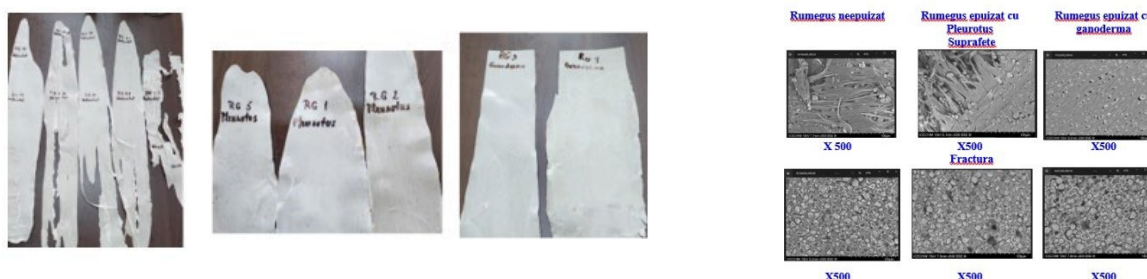


Figure 1. Images of obtained new starch based compounds with wood sawdust content and their SEM micrographs

Conclusions: Microbiological spending differently affecting the 3 polymers from sawdust, *Pleurotus ostreatus* being the one that seems to slightly affect more the three polymers from sawdust. Microbiological spending made possible the embedding about 5% spent sawdust into thermodynamically stable starch-based matrices, as opposed to 0.5-1% for the un-spent type. New works will be developed to find the ways to increase the amount of spent sawdust possible to be embedded into matrices bases on renewable origin-polymers.

Acknowledgements: This work was carried out through the PN 23.06 Core Program - ChemNewDeal within the National Plan for Research, Development and Innovation 2022-2027, developed with the support of Ministry of Research, Innovation, and Digitization, project no. PN 23.06.02.01.01- INTEGRAL

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MODULE OF A CATALYTIC OZONATION MEMBRANE REACTOR (CATOxMR) FOR WATER TREATMENT. NUMERICAL MODELING FOR PROCESS INTEGRATION

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Keywords: water treatment; numerical modeling; catalytic ozonation membrane reactor

Introduction: Drinking water treatment processes in the context of a complex pollution of water sources with hardly degradable organic compounds, inorganic nitrogen compounds and heavy metals constitute a real challenge for technology and equipment developers. The limitations imposed by real-scale applications related to: operational and energetic efficiency, reduction of the number and of the amount of reaction by-products, the sustainability of technologies, the high degree of automation as well as a reduced spatial footprint require the development of compact, multi-purpose technologies and equipment with addressability to an extended class of contaminants. The hybrid processes of advanced oxidation and membrane separation constitute an efficient and viable alternative in terms of the degradation of organic contaminants and the elimination of pathogenic organisms, as a stand-alone step or as a step in a complex water treatment process. In particular, the integration into a single functional unit of heterogeneous catalytic ozonation processes with membrane separation processes in so-called catalytic membrane ozonation reactors (CatOxMR) presents both the advantage of the optimal performance of oxidative processes, the separation of the catalyst (with its subsequent recovery) and of the reaction products from the treated water. Considering the structure of a functional model for a catalytic ozonation reactor with membranes, assembled as a single unit, with a view to subsequent integration in complex water treatment processes and to ensure the scalability of the processes, a multiphysics numerical model for a single module was developed. It was also structured a numerical model for the simulation of embedded reactor into an extended water treatment flow.

Material and methods: It is addressed, from the point of view of the numerical simulation of the processes, the configuration at the functional model level stage for a CatOxMR type reactor module and for the embedded reactor in a water treatment process. Based on the principles of CFD (Computational Fluid Dynamics) methods implemented through the finite element method (FEM), using the COMSOL Multiphysics 5.3 software package, a numerical model was developed for the reactor module, considering simultaneous processes of ozone injection and dissolution in aqueous medium (biphasic flow), catalytic ozonation processes and membrane separation processes. A scalable model was proposed for the integration of the reactor in a water treatment flow using the EPANET 2.2 software package.

Results: A new scalable multiphysics numerical model was developed for the CatOxMR type reactor module, taking into account biphasic flow processes, transfer processes of mass at the gas-liquid interface (ozone/water), transport and reaction processes. The processes of flow, transport and reaction of diluted species at the interface of porous media were modeled, in order to simulate the hybrid processes of catalytic ozonation/membrane separation. After running the model, a set of functional and dimensional parameters useful for scaling the process at the industrial scale was established. Based on these parameters, an integrated hydraulic model was developed to simulate the operation of a CatOxMR type unit in a complete water treatment flow.

Conclusion: The multiphysics numerical model developed for the reactor module (ozonation in the column/membrane separation) allows the simulation of processes and the evaluation of different scenarios considering particular sets of input parameters, depending on the individualization of the process (geometrical, hydraulic and pneumatical parameters that determine biphasic flow pattern, global coefficient of gas/liquid transfer, porosity and permeability of membrane layers) in order to obtain sets of values necessary for scaling the reactor at the functional model stage.

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PREPARATION AND FUNCTIONALIZATION OF NANOCELLULOSE USING LACTIC ACID: MORPHO-STRUCTURAL CHARACTERIZATION AND EMULSIFYING CAPACITY

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Keywords: nanocellulose; chemical modification; Pickering emulsions

Introduction: Pickering emulsions have gained much interest in the last few years, finding applications in biomedicine, food, cosmetics, catalysis, fine chemical synthesis, paints, etc. Differing from classic emulsions by the fact that they do not use oil-based small molecular surfactants or macromolecular emulsifiers as stabilizers, but solid particles, mostly of natural origin, Pickering emulsions present unique advantages such as higher sustainability, lower costs, superior stability against coalescence, and non-toxicity [1]. An attractive candidate for the stabilization of Pickering emulsions is nanocellulose (NC) due to its attractive characteristics such as the possibility of isolation from renewable resources or biomass residues, large surface area, biocompatibility, biodegradability, excellent mechanical strength, high surface reactivity, and, above all, an amphiphilic character that allows wetting by both the aqueous and the oily phase of an emulsion. However, the predominantly hydrophilic and less pronounced hydrophobic character of NC does not allow for an equally good wetting of NC by both the aqueous and the oily phase of the emulsion which restricts the stabilizing capacity of NC [2]. In this work, NC was chemically modified with lactic acid (LA) to tailor its surface hydrophobicity, and the behavior of the modified cellulose (NCLA) as an emulsifier was thoroughly studied and discussed.

Materials and methods: NCLA was obtained by the chemical treatment of microcrystalline cellulose (MCC) with lactic acid followed by mechanical defibrillation by microfluidization. NCLA was characterized in terms of chemical structure, thermal stability, and morphology by *Fourier-transform infrared (FTIR) spectroscopy*, *thermogravimetric analysis (TGA)*, and *scanning electron microscopy (SEM)*. A control sample was prepared by the chemical treatment of MCC with HCl followed by microfluidization. The emulsions stabilized by NC and NCLA, respectively, were obtained by ultrasonication from water and a vegetable oil and investigated by optical microscopy (OM).

Results: The *FTIR spectroscopy* confirmed the successful esterification of NC with LA by the presence of a new peak characteristic to the C=O bonds in esters in the spectrum of NCLA. The TGA results indicated a better thermal stability for the NCLA as compared to the NC, while the SEM images showed that the diameters of both NC and NCLA reside within the nanometric domain. As revealed by the OM images recorded on the prepared emulsions, more efficient as stabilizer for the oil/water emulsions was the esterified NC, while the poorest results were obtained for the control sample prepared by the acid hydrolysis of MCC with HCl.

Conclusions: The chemical modification of cellulose with LA allowed us to tailor the surface properties of NC, balance its hydrophilic-hydrophobic character, and intensify its amphiphilicity, which increased the capacity of NC to act as a stabilizing agent for Pickering-type emulsions.

Acknowledgements: This work was financially supported by the Ministry of Research, Innovation and Digitization through the project PN 23.06.02.01/2022 *InteGral*, within PN 23.06 Core Program-*ChemNewDeal*, the project 15PFE/2021 *NeXT-Bexcel* within Subprogram 1.2-Institutional performance-Projects to finance excellence in RDI, and through the project PN-III-P4-PCE2021-0435 (*CELGAS*) Contract 77PCE/2022.

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ENCAPSULATION OF POLYPHENOLIC EXTRACTS FROM *VACCINIUM MYRTILLUS* IN FUNCTIONALIZED MESOPOROUS SILICA WITH ANTI-INFLAMMATORY ACTIVITY

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Keywords: bilberry; polyphenolic extract; mesoporous silica; anti-inflammatory.

Introduction: In recent years, many studies have shown that the bilberry (*Vaccinium myrtillus*) fruit extracts possess various beneficial effects on human health, such as reducing blood sugar and lipid, antioxidant, anti-inflammatory, and anti-cancer activities [1]. The radical scavenger activity is due to the presence of anthocyanins, procyanidins, and flavonoid compounds [2]. Anthocyanins are prone to degradation having a short life inside the human organism. To enhance their stability and thus to preserve their benefits, the extracts can be encapsulated in various supports (e.g., mesoporous silica, polymers, liposomes, etc.) [3].

Materials and methods: Pristine, functionalized with organic moieties (mercaptopropyl and propionic acid), or coated with natural polymer (fucoidan) mesoporous silica were employed as supports for encapsulation of polyphenols. The extracts were obtained in ethanol acidified with citric acid through conventional method or in inert atmosphere. The chemical profile of the extracts was determined by spectrophotometric quantification methods and high-performance liquid chromatography. The supports were characterized by X-ray diffraction, FTIR spectroscopy, N₂ adsorption/desorption isotherms recorded at 77 K, thermal analysis, and scanning electron microscopy. The cytotoxicity and anti-inflammatory activity (NO and COX enzyme inhibition assays) of free and embedded extracts were assessed on mouse macrophage RAW264.7 cell line.

Results: Up to eight bioactive compounds were identified in the polyphenolic extracts, the most abundant being delphinidin chloride, rutin hydrate and chlorogenic acid (Figure 1). Pristine and functionalized MCM-41 silica showed high pore volume (0.47-1.15 cm³/g), being able to accommodate high amount of polyphenols (20-39 %wt), and good biocompatibility.

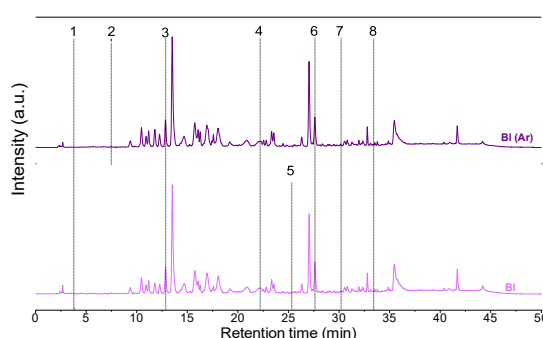


Figure 1. HPLC-PDA chromatogram for bilberry extracts recorded at 326 nm (1-gallic acid, 2-protocatechuic acid, 3-chlorogenic acid, 4-delphinidin chloride, 5-cyanidin chloride, 6-rutin hydrate, 7-myricetin, 8-*trans*-resveratrol)

Conclusions: Free and encapsulated extract presented good antioxidant potential and no cytotoxicity at the tested concentrations (up to 100 µg/mL). They showed a good therapeutic potential as anti-inflammatory agents that were more selective to COX-2 than COX-1.

Acknowledgements: The financial support from UEFISCDI through project PCE no 117/2022 is highly appreciated.

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DEVELOPMENT OF NANOCOMPOSITE BASED ELECTROCHEMICAL BIOSENSORS FOR THE MONITORING OF CLINICALLY RELEVANT ANALYTES

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Keywords: nanocomposites; fullereneol; hydrogels; glucose; lactate;

Introduction: The monitoring of clinically relevant analytes, such as hydrogen peroxide, glucose, lactate, and cortisol is of great importance for healthcare applications and diagnostics. Some of these compounds represent markers for various medical disorders and diseases, such as inflammation, diabetes, and sepsis. Among the sensing methods used for the detection of such compounds, (bio)sensors and the advance of nanotechnology offer the advantages of miniaturization and integration into portable electronic bioanalytical tools, with low costs for health evaluation and clinical applications [1]. Electrochemical (bio)sensors were designed and developed based on hydrated agarose-based polymer network and conductive carbon-based nanomaterials (e.g., carbon nanotubes, polyhydroxylated fullerene, etc.), allowing the entrapment of specific bioreceptors [2].

Materials and methods: Electrochemical (bio)sensors were prepared by deposition on the surface of the commercial carbon paste screen-printed electrodes (SPE) of composite nanomaterials based on single-walled carbon nanotubes (SWCNT), polyhydroxylated fullerenes (FL), metal nanoparticles (e.g., PtNP, AgNP), and agarose-polyaniline based hydrogels (HG). The redox mediator Prussian Blue was used in combination with the nanomaterials to increase the electron transfer rate at the sensor surface and to decrease the overpotential used for bioanalytes detection. The enzymatic bioreceptors, glucose oxidase (GOx) and respectively, lactate oxidase (LOx) were entrapped in hydrogel network (HG), orin sol-gel (SG) and chitosan (CS) matrices for the sensitive and selective detection of the biological analytes glucose and lactate, respectively. The electrocatalytic properties of the nanocomposite materials were studied by cyclic voltammetry (CV), amperometry and electrochemical impedance spectroscopy (EIS). To confirm the formation of the nanomaterial layers and the entrapment of the bioreceptors, the obtained bio-composite films were characterized by FTIR spectroscopy and SEM analysis.

Results: In order to obtain the hydrogel network, the conditions of the polymerization (pH medium, temperature, time), the reticulation and swelling degrees were optimized. CV studies revealed that the sensors based on PB-FL-HG nanocomposite exhibit an enhanced electrocatalytic effect for the reduction of H₂O₂ compared with the sensors based on SWCNT-PB. The PB-FL-HG/SPE sensors were used for the amperometric detection of H₂O₂ with a specific sensitivity of 177.86 mA·M⁻¹·cm², within a range of concentration extended up to 900 μM, and with a detection limit of 2.0 μM. The sensor also has the advantage of carrying out H₂O₂ detection without the need of a specific bioreceptor. Glucose detection was achieved using the biosensor based on GOx entrapped in the CS matrix deposited on a FL-PB/SPE based sensor, with a specific sensitivity of 8.67 mA·M⁻¹·cm², in a linear range of concentrations up to 2.3 mM, and with a detection limit of 55 μM. The lactate determination was possible by using the biosensor developed through immobilization onto the SWCNT-PB/SPE sensors of the LOx entrapped in the SG matrix. The specific sensitivity of LOx-SG/SWCNT-PB/SPE biosensors for lactate detection was 28.58 mA·M⁻¹·cm², in a linear concentration range up to 2.2 mM, and the detection limit was 25 μM.

Conclusions: The performance of the developed biosensors for the detection of analytes, such as hydrogen peroxide, glucose and lactate, showed a synergistic combination of the advantages offered by the carbon nanomaterials, redox mediator and hydrogel network, and those of the specific bioreceptors.

Acknowledgements: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project M-ERANET-3-FULSENS-GEL within PNCDI III, Contract no. 318/2022 and with the PN 23.06 Core Program - ChemNewDeal within the National Plan for Research, Development and Innovation 2022-2027, developed with the support of Ministry of Research, Innovation, and Digitization, project no. PN 23.06.01.01.

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ASSESSMENT OF BIOGENIC AMINES IN FOOD PRODUCTS AND THEIR DETECTION USING NANOCOMPOSITES BASED ELECTROCHEMICAL BIOSENSORS

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Keywords: biogenic amines, Enterobacteriaceae, nanocomposites, chitosan, sol-gel

Introduction: Biogenic amines (BAs) are composed of low-molecular-weight organic nitrogenous compounds which can be present in foods. They are generally produced by microbial decarboxylation of amino acids in food products. BAs can be synthesized by Gram-positive and Gram-negative bacteria and also fungi (molds, yeast). A moderate amount of BAs can promote normal physiological activities of the human body, but excessive accumulation in food can be toxic to living organisms. BAs are also used to evaluate the hygienic quality and safety of different foods [1-3]. This study investigated the biogenic amine synthesis abilities of 15 strains of enteric bacteria and yeasts isolated from different samples of food, such as cheese, meat (chicken), fish (gilt-head bream - *Sparus aurata*), sliced ham, salami, beer, white and red wine.

Materials and methods: For microbiological analysis, the food samples were crushed and homogenized with buffered peptone water. The mixtures were incubated at 140 rpm, followed by inoculation on specific media. Colonies grown on selective agar media were selected, purified and identified to species level by MALDI-TOF mass spectrometry. The detection of amine-forming capacity of microbial strains was evaluated using amperometric biosensors, developed through the entrapment of the enzymes diamine oxidase (DAO) and monoamine oxidase (MAO) in sol-gel and chitosan-based polymeric matrices for the detection of putrescine and histamine, respectively. The enzymes were immobilized on screen-printed electrodes (SPEs) modified with a nanocomposite material based on direct precipitation of redox mediator Prussian blue (PB) onto single-walled carbon nanotubes (SWCNT).

Results: The main microbial group identified and involved in BAs production in food samples was represented by Gram negative bacteria from the *Enterobacteriaceae* family such as *Citrobacter*, *Enterobacter*, *Escherichia*, *Klebsiella*, *Proteus*, *Kluyvera*. Gram positive bacteria such as *Enterococcus faecalis* and yeasts such as *Candida lusitanae* and *Candida guilliermondii* have also been identified. The most microbial strains were detected in fish samples, followed by cheese, salami, chicken, ham and beer. The developed biosensors based on entrapment of DAO and MAO in sol-gel and polymeric matrices were characterized by specific sensitivities of 6.25 mA M⁻¹cm⁻² for histamine and respectively 153.7 mA M⁻¹cm⁻² for putrescine, and detection limits of 57 μM for histamine and 4.7 μM for putrescine. The working applied potential was -0.05 V vs. Ag/AgCl which ensures an increased selectivity for putrescine and histamine detection.

Conclusions: BA-producing microorganism were isolated and identified from food samples. The amperometric biosensors based on SWCNT-PB nanocomposite material and DAO/MAO enzymes entrapped in sol-gel and chitosan matrices were used for the sensitive detection of histamine and putrescine in food samples.

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COMPARATIVE ASSESSMENT OF MARBLE AND GRANITE SPECIMENS EXPOSED TO CLIMATIC CYCLES

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Keywords: *marble, granite, climate cycles, gloss, aesthetic parameters*

Introduction: Marble and granite are widely used building materials, although they are mostly used for buildings facades, decorations and aesthetic elements their use is not limited to those examples. As all materials exposed to the environmental conditions, they are prone to different degrees of weathering, depending on their exposure, climate, composition, anchoring systems, etc. Marble composition consists of calcite (major component) and various impurities, which induce a high resistance in time. However, marble surfaces exposed to weathering will support considerable decay consisting in decohesion and bowing [1]. By comparison, granite is composed of 20-60% quartz with variable proportions of alkali feldspar and plagioclase, and has a natural and textured appearance compared to the polished look of marble. It is available in a variety of colors and patterns and textures, offering a more earthy and rugged aesthetic, and by comparison with marble is considered more resistant to weathering, at different climate, exposure, composition, pollution, etc., [2]. In this work the aesthetic properties of three different types of marble and three different types of granite were investigated before and after freeze thaw cycles and artificial weathering in a climatic chamber.

Materials and methods: The samples were obtained by cutting pieces of marble with a diamond blade. They were exposed to 20 freeze-thaw cycles according to ASTM STP 169C and 20 thermal cycles in climatic chamber which simulates day-night cycle using a climatic chamber KK POL-EKO 115 SMART PRO. The analyzed samples are black and white Carrara marble (CBWM), pink Ruschita marble (RPM) and white Albesti marble (AWM) and granite, Rosa Aswan (RA), Gray Granite (GT) and Beige Granite (BG). The samples were analyzed by visual and stereoscopic analysis with (Euromex Binocular Stereomicroscope), by chromatic analysis (with a Konica Minolta CR-410 Chromometer) and by glossmetry (with Glossmetr HG268, gloss was measured at an angle of 60 degrees).

Results: As expected, both freeze-thaw cycles and artificial weathering caused a slight decrease in the marble samples gloss and small color change $\Delta E < 5$, which cannot be observed with naked eye, in good agreement with previous results [3]. The change in gloss and color for the granite sample were not significant, which may be explained by their low porosity and their composition (around 60% quartz) material that does not show the anisotropic thermal expansion of calcite or quartz crystals. The analysis done via stereo microscopy revealed small microcracks at the surface exposed to temperatures and UV lamps, more accentuated for marble than for granite.

Conclusions: Based of results obtained could be concluded that the most stable type of marble is Ruschita marble (RPM) followed by Carrara marble and by Albesti marble. While the most stable granite type is Gray Granite (GT), followed by Beige Granite (BG) and Rosa Aswan (RA). The granite samples show less degradation during freeze-thaw cycles as well as artificial weathering at least over the 20 cycles studied.

Acknowledgements: This work was supported by the project PN-III-P2-2.1-PED-2021-3885 (687PED/2022) from UEFISCDI-MCID, within PNCDI III, Project PFE 15PFE/2021 - ID 583 and the project PN 23.06 Core Program - ChemNewDeal, project no. PN 23.06.02.01 - InteGral.

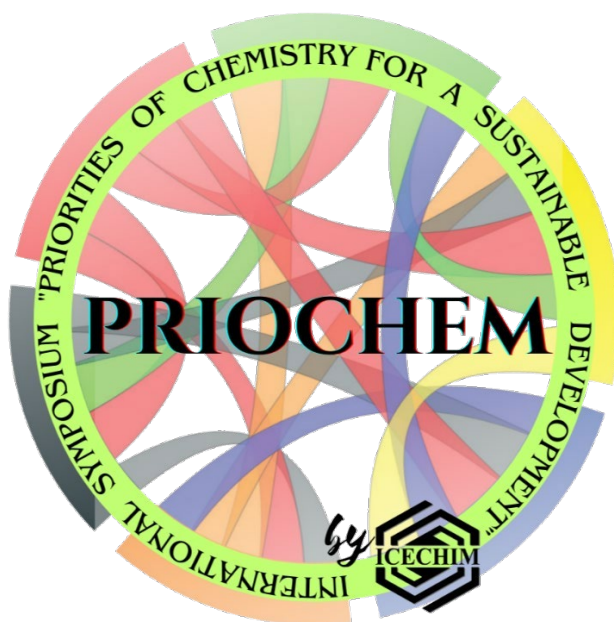
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SCIENTIFIC CONTRIBUTIONS

Section 2 – BBB

Bioresources, biotechnologies
and biorefining



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DIFFUSION-BASED METASTABLE LIQUID-LIQUID EXTRACTION METHOD

ASSESSMENT OF DRINKING WATER QUALITY AND POTENTIAL RISK TO HUMAN HEALTH

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Keywords: drinking water; health risk; carcinogenic risk

Introduction: Drinking water is the primary source of toxic metals intake by humans. In Romania, the water pipes (majority of them) are made of iron/lead based alloys and are outdated and degraded. On the other side, the wells or surface waters - used as the main resource for drinking water - are affected by environmental pollution. This study aimed to determine the toxic metals concentrations in drinking water and assess non-carcinogenic/carcinogenic health risks via daily human intake. Seventeen water samples (from local networks or wells) from the South and South-Eastern parts of Romania were collected during the spring season.

Materials and methods: The nitrites, nitrates and ammonium content were evaluated using spectrophotometric methods. Total organic carbon and total nitrogen were performed using a Multi N/C Analyzer (Analytik Jena). The toxic metals content was determined by inductively coupled plasma mass spectrometry (ICP-MS) using iCAP Qc spectrometer (Thermo Scientific). Estimated daily intake (EDI) and health risk index (HRI) were calculated in order to assess the potential risk to human health - adults and children.

Results: The values of ammonium determined in the 17 water samples varied between 0.02 (P3) and 0.14 (I4) (Figure 1). According to Law No. 458/2002 of 08.07.2002 regarding the quality of drinking water, the ammonium content is 0.50 mg/L, thus, the water samples subjected to analysis are within the optimal parameters. Although ammonium is not harmful to human health, its presence in water can be a sign of contamination. Excess ammonium in raw water is undesirable in water supply systems because it can lead to problems including off-flavors, microbiological growth in the water distribution system, reduced chlorine disinfection efficiency, and increased chlorine usage [1]. The health risk index (HRI), calculated for adults and children (Table 1), exceeds the maximum allowed limit (1) for Cr in all samples for both categories (i.e., adults and children). At the same time, the HRI for Pb has recorded high values, which highlight the necessity to change the damaged/aged water pipes.

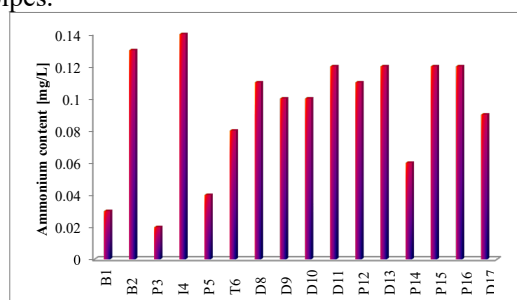


Figure 1. Ammonium content in analyzed samples.

Table 1. Health risk index for adults and children.

HRI		Cr	Mn	Ni	Cu	Zn	Cd	Pb
Adults	min	1.099	0.003	0.011	0.022	0.002	0.054	0.545
	max	1.437	0.141	0.100	0.321	0.019	0.143	5.005
Children	min	4.123	0.010	0.042	0.084	0.006	0.203	2.044
	max	5.390	0.528	0.376	1.204	0.070	0.538	18.771

Conclusions: This study presents a series of investigations conducted by the authors, and it is certainly the most comprehensive research regarding drinking water quality for this geographical area of Romania. In this respect, the present data are focused on the adult and children's health risks induced by the water consumption.

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THE PROPERTIES OF BIOPRODUCTS FROM STREAMLINED ULTRASONIC LYSIS OF SPENT BREWER'S YEAST CELLS ARE HIGHLY INFLUENCED BY LYSIS PARAMETERS

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Keywords: ultrasonic parameter variation, yeast bio-compounds, cell walls, extract, antioxidant activity

Introduction: Sustainable waste management and enhanced food quality have become general priorities as their great influence on today living standards has been invariably acknowledged. The massive quantities of industrial by-products and the health-promoting benefits of yeast-based products reveal the opportunity of upcycling spent brewer's yeast (SBY) as a functional ingredient [1-4]. This study presents a facile and streamlined method of SBY cell lysis through ultrasonication, while highlighting the parameter influence on the composition and antioxidant activity of the resulted SBY derivatives, specifically spent brewer's yeast extracts (SBYE) and spent brewer's yeast cell walls (SBYCW).

Materials and methods: A streamlined ultrasonication SBY cell lysis method was developed by optimization of various processing parameters, i.e., sample concentration, ultrasonication temperature and duty cycle (DC). The influence of these parameters on the lysis efficiency was evaluated through quantification by Biuret assay of the released intracellular proteins and gravimetrically. Optical and scanning electron microscopy (SEM) were used to observe SBY cell lysis. The antioxidant activities (AOA) of the two SBY derivatives, SBYE and SBYCW were assessed by radical scavenging activity – DPPH and potassium ferricyanide reduction – PFRAP methods. SBYCW were also characterized by attenuated total reflectance (ATR)-Fourier transform infrared spectroscopy (ATR-FTIR) and β -glucan content.

Results: Ultrasonication of highly diluted samples, at 40°C and 33.33% DC were identified as optimal parameters for efficient lysis. The efficiency of the optimum parameters in yeast cell lysis was confirmed by an elevated release of intracellular proteins. Optical microscopy and SEM also confirmed the release of the intracellular content, as well as the isolation of SBYCW. The FT-IR spectra revealed structural changes related to proteins, polysaccharides and chitin. High β -glucan content of the solid yeast derivatives indicated the presence of yeast cell walls. Temperature and DC affected differently AOA. The protein content was positively correlated with AOA.

Conclusions: The lysis parameters had a significant impact on the lysis efficiency and derivative properties. Our results confirm that the proposed ultrasonication method provides an efficient lysis for SBY cells. Moreover, the resulted SBY derivatives emerge as products with great nutraceutical value and elevated content of bioactive compounds, such as proteins, polysaccharides and antioxidants.

Acknowledgements: This work was supported by Ministry of Research, Innovation and Digitization, CNCS/CCCDI—UEFISCDI, contract number 67PTE/2022 - FortiFol, within PNCDI III and by the Romanian Ministry of Agriculture and Rural Development, project Research regarding development of sustainable technologies for obtaining and valorizing innovative ingredients and foods, for nutritional equilibration of modern consumer diet - ADER 17.1.2.

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ANALYTIC FINGERPRINTS OF Se-STIMULATED CABBAGE BIOFORTIFICATION

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Keywords: molecular fingerprints; selenium foliar biostimulant; vinasse; betaine; drought.

Introduction: Plants are evolving since 3.7 billion years ago in a continuous optimization of biosynthesis mechanisms and adaptation to environmental conditions. Plant physiology studies developed exponentially in the last century, together with the global technology and towards molecular and bionanotechnologies usage for a better understanding of the green world [1]. This study aims to highlight and discuss particular aspects of the biostimulant effects of a selenium-betaine nanoformulation (Se-BNF) on cabbage growth in drought conditions [2], concentrating on particular physical-chemical fingerprints of plant cell wall response to foliar fertilization.

Materials and methods: Infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetry (TGA), and fiber content were used to compare the inner and outer leaves of Se-biostimulant treated cabbage cultivars.

Results: FTIR analyses presented in Fig. 1.a) evidenced the particular absorption bands of cellulose I α , pectin and lignin that are further found convoluted in the cabbage spectrum. The free -OH bands around 3740 cm⁻¹ are reduced in the cultivars treated with Se-BNF, while the bound -OH band around 3300 cm⁻¹ increased, suggesting a tighter-packed, or biofortified, molecular structure by chelation of Se, minerals, glycine-betaine and other biocompounds. Secondly, the intense C-H bands around 2918 and 2852 cm⁻¹ for Se-BNF-treated cultivars may indicate the development of aliphatic (seleno)glucosinolates and lipids. A third FTIR fingerprint is linked to the pectin bands around 1738 cm⁻¹ and 1612 cm⁻¹, specific for esterified, respectively unesterified carboxyl groups, the ratio inversion after Se-BNF treatments suggesting a stabilization of pectins in unesterified form. The fourth FTIR fingerprint is the absorption region of carbohydrates around 1030±100 cm⁻¹, which suggests the development of polysaccharides, especially cellulose I α , as confirmed by XRD in Fig. 1.b).

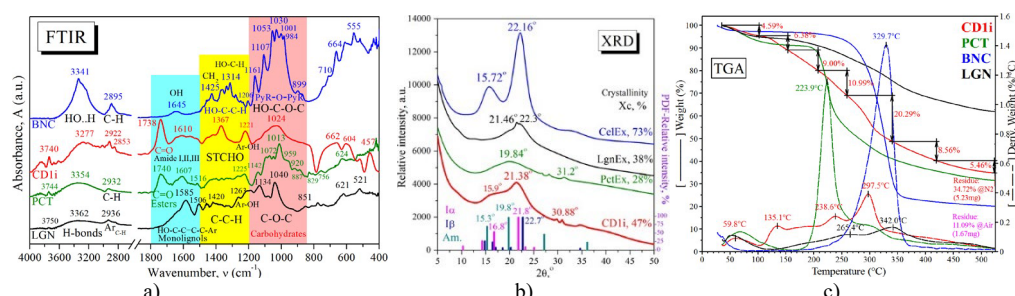


Figure 1. a) FTIR spectra of cellulose I α -rich bacterial nanocellulose (BNC), cabbage treated with dose D1i (CD1i), pectin (PCT), and lignin (LGN); b) XRD analyses of CD1i, extracted pectin (PctEx), cellulose (CelEx) and lignin (LgnEx); c) TGA and DTG analyses of CD1i, PCT, BNC and LGN.

The TGA and derivative DTG curves presented in Fig. 1.c) suggested the splitting of the temperature range 25–525°C into 7 specific thermo-regions with 2 additional regions for N₂ and air residues. The corresponding weight losses evidenced that the foliar Se-biostimulant induced an accelerated biomass accumulation in the pectin and cellulose thermo-regions, together with an increased mineral content in the ash.

Conclusions: The applied analytical methods evidenced a cellulose I α -pectin structure of cabbage, together with lignin as a molecular and structural binder. FTIR evidenced more hydrogen bridges than free OH and a low esterification of pectins induced by the Se-biostimulant. All techniques suggested the accumulation of carbohydrates in the cell walls upon Se-BNF treatment.

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PHOTOPROTECTIVE COSMETIC PRODUCTS WITH POLYPHENOLIC EXTRACT FROM GRAPE MARC

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Keywords: sunscreen, grape marc, polyphenols, antioxidants, photoprotection

Introduction: Chemical sunscreens contain aromatic organic compounds conjugated with a carbonyl group. They are designed to absorb high-intensity UV radiation, pass into an excited state of higher energy, and, upon returning to the ground state, convert the absorbed energy into radiation of longer wavelength but lower energy [1]. Currently, to optimize sun protection and photostability, sunscreens use natural antioxidant compositions [2,3]. Polyphenols are molecules that help prevent oxidative stress caused by reactive oxygen species. In addition to their antioxidant properties, polyphenols can also act as enzyme inhibitors or activators, impacting anti-inflammatory pathways. Skin areas that were treated with natural polyphenolic extracts prior to UV exposure developed less erythema and were found, on microscopic examination, to present less sunburn [4]. The paper presents alternatives for the extraction of polyphenolic compounds from grape pomace of several varieties, their characterization and testing to obtain cosmetic products with a potential photoprotective effect.

Materials and methods: The polyphenolic extracts were obtained from grape marc (production 2022) resulted as a by-product of the Merlot variety grapes vinification. The compounds extraction was carried out by classical procedures using 70% ethanol. The solid:solvent extraction ratio was 1:10 (g/mL), the extraction time was 2 hours at a temperature of 40°C. Finally, the solid mass was separated by centrifugation and the supernatant was analyzed in order to determine the total content of polyphenolic compounds (through the D280 index and the Folin-Ciocalteu method) and the antioxidant activity (CUPRAC method). The lotions were obtained by mixing the resulted extracts (as aqueous or ethanolic solutions) with a commercial lotion base (Lotion Base Organic) purchased from Elemental SRL Oradea. The prepared creams were evaluated in terms of stability by visual examination at 24 and 48 hours and in terms of the in vitro photoprotective effect using the COLIPA method [5].

Results: The extraction with 70% ethanol of the Merlot grape marc leads to obtaining a high concentration of polyphenolic compounds with important absorbance in the UV range (290-400 nm) and high antioxidant activity. The analysis of the results obtained through the in vitro determinations based on the COLIPA method shows a potential photoprotective effect for the polyphenolic compounds extracted from grape pomace. The compatibility of the polyphenolic extracts with the lotion base used in this stage is very good when an aqueous solution is used and good for the extracts in an alcoholic solution. The method of obtaining the creams tested at this stage allows the addition of up to 50% aqueous extract solution and up to 40% alcoholic extract solution, indicating an in vitro sun protection factor (SPF) of about 10-15.

Conclusions: Polyphenols can be an effective source of skin protection against the effects of UV radiation (UVA and UVB). The 70% ethanol extraction of grape marc represents a viable alternative to obtain a high concentration of polyphenols with important antioxidant activity and high absorption in the UV range. In vitro testing of sunscreens with polyphenolic extracts shows values of the SPF factor in vitro of 10-15. Combining polyphenolic extracts with other UV protectors, either physical or chemical, can represent a viable alternative for obtaining sun creams with commercial potential.

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Research, Innovation and Digitization, CCCDI – UEFISCDI, project number number PN-III-P2-2.1-PED- 2021-0273, within PNCDI III”.

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BIO-ADSORBANT BASED ON CARBON DECORATED SILVER NANOPARTICLE FOR METHYLENE BLUE ADSORPTION

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Keywords: silver nanoparticles, silver nanoparticles decorated carbon, methylene blue adsorption

Introduction: This study presents the preliminary results obtained by a bio-adsorbent based on carbon materials decorated with silver nanoparticles for the adsorption of methylene blue. The bio-adsorbent was obtained by an ecological, economical, sustainable process using food waste as raw material [1]. The decoration of carbon materials with silver nanoparticles was done by nuclear techniques [2,3].

Materials and methods: The *morphostructural* characteristics of bio-adsorbent based on carbon material are investigated by UV-Vis and FTIR Spectroscopy, Differential Scanning Calorimetry (DSC), and Scanning Electron Microscopy (SEM).

Results: The qualitative and quantitative effect was provided by methylene blue index. The UV-Vis spectra are presented in the picture 1.

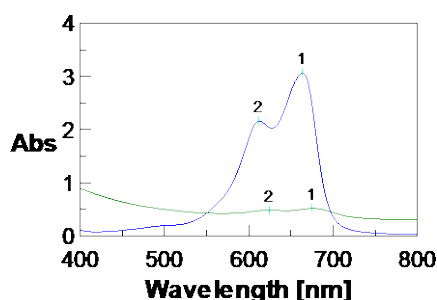


Figure 1. Green line – present the UV –Vis spectra of bio-adsorbent in solution after 24 hours and blue line etalon solution of methylene blue.

Conclusions: The synthesized bio-adsorbent based on carbon materials decorated with silver nanoparticles exhibited excellent adsorption performance of methylene blue.

Acknowledgements: The financial support was provided by MCID, through contract 42N/PN23140201/2023.

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ANTIMICROBIAL ACTIVITY OF MUSHROOMS EXTRACTS

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Introduction: As a result of the multitude of infectious diseases, new therapeutic agents with antimicrobial potential are currently being identified [1].

Mushrooms have considerable nutritional properties due to their content in carbohydrates, proteins, free amino acids and vitamins, as well as various essential minerals and trace elements. They also contain secondary, bioactive metabolites with a significant therapeutic value such as lectins, polysaccharides, phenols and polyphenols, terpenoids, ergosterols and volatile organic compounds. Mushroom extracts have therapeutic applications for immunomodulatory, antitumor/anticancer, anti-inflammatory, antibacterial and antiviral, antioxidant and hypoglycemic actions [2, 3].

While numerous studies have been conducted on antibacterial activities of hot water, cold water, ethanol, chloroform and acetone extracts of fresh mushrooms [4], our study used dried body fruits ethyl acetate extracts, obtained at boiling temperature of the solvent. This study evaluated the potential of studied mushrooms as antibacterial agents, emphasizing as extraction solvent ethyl acetate (that can dissolve both lipophilic and hydrophilic compounds)

Materials and methods: This study has investigated the antimicrobial activity of some extracts of mushrooms (dried body fruits) against gram negative (*Escherichia coli* ATCC 8739) and gram positive (*Staphylococcus aureus* ATCC 6538) bacteria. For ethyl acetate extracts, obtained from 5 species of mushrooms (*Agaricus bisporus* white, *Agaricus bisporus* brown, *Lentinus edodes*, *Pleurotus ostreatus* and *Agaricus campestris*), the antimicrobial potential was evaluated by the agar disk diffusion method. Activities were classified according to the inhibition zones: where diam. <10 mm means no activity, diam. 10–15 mm means weak activity, diam. 16–20 mm means moderate activity, and diam. >20 mm means certain activity.

Results: The obtained results suggest that the extract of white *Agaricus bisporus* do not have antibacterial activity against the 2 bacterial strains studied; the *Pleurotus ostreatus* extract is inactive against *Escherichia coli*, and *Agaricus bisporus* brown against *Staphylococcus aureus*. At the opposite pole is the *Agaricus campestris* extract, which shows strong antibacterial activity against both gram-negative and gram-positive strains, being the sample with the highest antibacterial potential. The extract obtained from the species *Lentinus edodes* possesses moderate antibacterial activity.

Conclusions: The present study has shown that extracts of *Agaricus campestris*, *Lentinus edodes* have shown promising antimicrobial activities against the tested organisms. Further investigation is needed to evaluate isolate, identify, and explain the mode of action of the bioactive compounds responsible for the antimicrobial activities and confirm the activity of the extracts against other human pathogenic microorganisms.

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EVALUATION OF PHYTOCHEMICAL COMPOUNDS AND ANTIOXIDANT ACTIVITY OF *MURRAYA KOENIGII* L. FLOWERS

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Keywords: antioxidant activity, phytochemical properties, UV-VIS, TOF LC/MS

Introduction: *Murraya koenigii* L., known as curry leaf tree, belongs to the *Rutaceae* family and it is a tropical-subtropical plant [1]. The bio-compounds of *Murraya koenigii* have high therapeutic properties, being used for treating various ailments, to prepare specific dishes and cosmetic products, as well [2]. The main bioactive compounds of curry leaf tree's flowers (Figure1) were analyzed and described in the present study.



Fig. 1. Flowering plants of *Murraya koenigii* L. cultivated at ICDIMP Horting

Materials and methods: *Murraya koenigii* L. was cultivated in 2018 by seedlings at ICDIMP Horting, representing Avant-guard research in our country [3]. Approximately 20 grams of flowers were extracted in 70% (v/v) ethanolic solvent (Merck), ultrasonicated 90 min at room temperature, then concentrated up to 20 % (v/v) at rotavapor (VV Micro Heildoph). The TOF LC/MS (6224 Agilent Technologies) was applied for compounds identification; thru UV–VIS technique (Cintra 202) it was determinate total polyphenols content ($\lambda=765$ nm), total flavonoids content ($\lambda=510$ nm), and antioxidant activity ($\lambda=517$ nm, DPPH method).

Results: In *Murraya koenigii* L. flowers extract, the compounds identified by TOF LC/MS were: proline, 1-methyl-pyrrolidine-2-carboxylic acid, phebalosin, 2'-O-ethylmurrangatin [4]. The total phenolic content-TPC was of 1.16% (g gallic acid equivalent/100 g) and total flavonoid content-TFC was of 0.98 % (g catechin equivalent/100 g) [5]. The antioxidant activity of *Murraya koenigii* was of 84.4%, demonstrating a good scavenging capacity for free radicals [6]. The values obtained were comparable with those mentioned in the various studies [4-6].

Conclusions: The results of this study indicate that *Murraya koenigii* L. flowers are an important source of bio-compounds with great antioxidant activity and high values of total polyphenols and flavonoids content.

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DESALTING OF SODIUM LIGNOSULFONATE FROM THE SPENT SULFITE LIQUOR USING A DIFFUSION-BASED METASTABLE LIQUID-LIQUID EXTRACTION METHOD

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Keywords: sodium lignosulfonate, liquid-liquid extraction, ultrafiltration

Introduction: The sodium sulfite process is a one of the first methods to be applied industrially to obtain cellulose destined to be turned to cardboard or paper products. Apart from its general success over the years, nowadays this process needs to be improved and adapted to also recover a purified stream of sodium lignosulfonate which has been shown to be a high-value product in several applications [1]. While a simple recovery of sodium lignosulfonate is possible by precipitating it with calcium oxide according to Howard method [2], it does not lead to a recovery of useful salts such as sodium sulfite. In this work, we propose a milder alternative that takes advantage of both the liquid density differences between the spent sulfite liquor and water acting as an extracting liquid and the different diffusion rates between the sodium sulfite and the sodium lignosulfonate into water. The main requirement of this operation is to contact the spent sulfite liquor and the extracting liquid in a low shear situation. Process intensification methods are also investigated.

Materials and methods: Spent sulfite liquor was recovered directly from the sulfite process at CCH Drobeta Turnu-Severin. The first step was to prefilter it on a 5 µm T1-70 ceramic membrane using a Pall XLab 5 testing system to remove any micronic or larger cellulose contaminants and other small insoluble debris. The filtration was performed at a low pump rotation speed (setting 3) which led to an important flux reduction compensated by a frequent backpulse operation (30 sec). These mild hydrodynamic conditions were employed to reduce chances to break the sodium lignosulfonate aggregates. The permeate was recovered and concentrated at 40 °C in a well-ventilated dryer to obtain 3 concentrated streams (concentration factors: 2, 3 and 4). The volumetric density was measured. The diffusion experiments were performed in either stagnant or reduced flow conditions by adding the sodium lignosulfonate streams under a known volume of bidistilled water. Diffusion of sodium sulfite salt was measured using a conductometer. The concentration of sodium lignosulfonate was estimated by measuring its absorbance at 280 nm with a UV-Vis spectrophotometer.

Results: The diffusion kinetics were evaluated in several situations and several parameters were estimated by regression of diffusion models applied to the experimental data. With the found characteristics in terms of viscosity, liquid density and salt and lignosulfonate diffusion, a liquid-liquid extractor could be predimensioned to show the possibility of using this kind of low-energy separation operation to simultaneously recover the sodium sulfite salt and a purified sodium lignosulfonate.

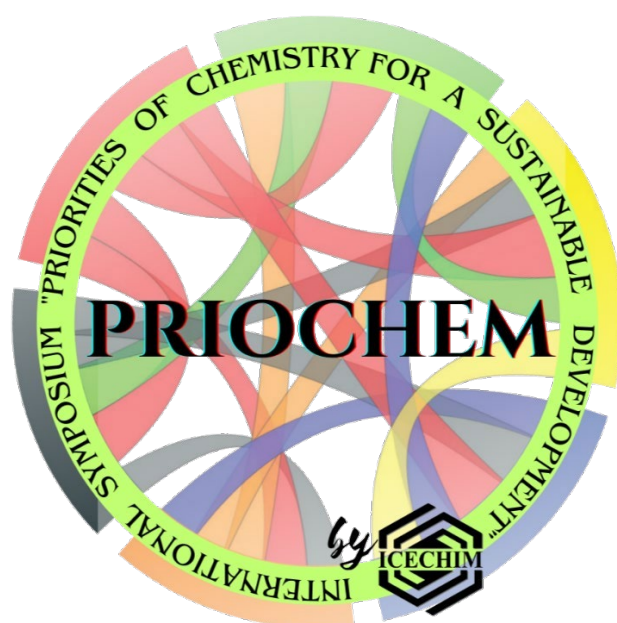
Conclusions: In this work, a novel operation is proposed for the simultaneous recovery of sodium sulfite and sodium lignosulfonate from a spent sulfite liquor. This operation takes advantage of diffusion processes that are further enhanced when the sodium lignosulfonate stream has a higher concentration which enhances the aggregation of sodium lignosulfonate. The process has to be done in a low shear rate manner which takes advantage of the high liquid density of the sodium lignosulfonate compared to water. The results show that this approach could be a cost effective way of separating the sodium lignosulfonate from the sodium sulfite with a low energy input.

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DEVELOPMENT OF PROTECTIVE COSMETIC PRODUCTS THROUGH BIOECONOMY APPROACHES

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Keywords: water depollution, nanosensors, nanomaterials, sol-gel materials, (photo)catalytic materials

Chronic exposure of human skin to solar UV radiation is widely recognized as the key factor responsible for photo-ageing. For these reasons, the role of photoprotection is critical to avoid skin cancer and others undesired effects. The grape industry, especially the wine industry, generates nutrient-rich by-products that are underutilized and often end up polluting the environment. After the extraction of grape juice, the remaining materials are currently not valued as highly profitable waste, being mainly dumped in open spaces, thus causing environmental problems.

The **goal of the project *BioProtect*** is to propose the use of nanomaterials both as active ingredient and delivery system of bioactive compounds (mixtures of phenolic compounds – rutin and quercetin) recovered from grape by-products for development of UV blocking cosmetic products.

The ***BioProtect*** project proposes the use of nanomaterials both as active ingredient and delivery system of bioactive compounds (mixtures of phenolic compounds – rutin and quercetin) recovered from grape by-products for development of UV blocking cosmetic products. Target molecules obtained through green technologies from grapes by-products can be used as potential active UV blockers in cosmetic formulations being delivered by apatitic materials.

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PHYTOSYNTHESIS - SYNTHESIS OF THE FUTURE. THE BIOECONOMY APPROACH

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Keywords: *photosynthesis, bioeconomy, sensing platforms*

Nanomaterials are now regarded as a key tool in a variety of industries, including textiles, energy, the environment, electronics, photonics, food, agriculture, biomedicine, and health care. The use of nanoparticles for creating control systems to assure food quality and safety has recently come to light thanks to advancements in the field of nanotechnology. While being utilized in (bio)detection systems, nanomaterials have proven to be incredibly beneficial in enhancing the analytical performance of traditional/laboratory procedures and advancing biosensing technologies. The widespread adoption of nanomaterials over the past few years is mainly due to the significant advantages they provide in the production of theoretically novel biosensors or the enhancement of already existing ones. Appropriate preparation techniques are required to use nanoparticles in chemical reactions. New ways for preparing nanoparticles emerged in recent years by substituting plant extracts acquired under various conditions for the traditional chemicals. The scientific term for this process is phytosynthesis or "green synthesis".

In the context of "synthesis of the future", this method has garnered interest because it is eco-friendly, cost-effective, and provides a sustainable approach to nanoparticle synthesis. In essence, the phytosynthesis of nanoparticles is just one of the many innovative approaches that fit into the bioeconomy paradigm. As our global society continues to prioritize sustainability, such methods will likely gain more traction and importance.

Bioeconomy encompasses the production of renewable biological resources and the conversion of these resources, residues, by-products, and side streams into value-added products, such as food, feed, bio-based products, and bioenergy. The phytosynthesis or green synthesis of nanoparticles, as described earlier, fits within the broader framework of bioeconomy. One of the fundamental principles of bioeconomy is the sustainable production and utilization of biological resources. Using plants to synthesize nanoparticles is a perfect example, as it typically uses renewable plant resources and minimizes the need for non-renewable or toxic materials.

Bioeconomy often emphasizes adding value to biological materials. For instance, certain plant extracts might have limited economic value on their own. Still, when they are used to produce valuable nanoparticles, they suddenly become part of a high-value production chain. Many bioeconomy strategies focus on using waste streams or by-products. In the context of nanoparticle synthesis, one could imagine using waste plant materials or by-products from other processes as sources for nanoparticle production. The move towards the bioeconomy is often driven by innovations that replace traditionally produced materials with bio-based alternatives. Nanoparticles produced via phytosynthesis can replace those produced through conventional methods, which often involve harsh chemicals and energy-intensive processes. Bioeconomy strategies are often linked to larger societal goals, like mitigating climate change, preserving biodiversity, and reducing pollution. Phytosynthesis of nanoparticles aligns with these goals by offering a cleaner, more environmentally friendly method of production.

Phytosynthesized nanoparticles have potential applications in various fields like drug delivery systems and as antimicrobial agents; water purification and as sensors; as pesticides and growth-promoting agents; in the manufacturing of electronic devices and to speed up chemical reactions.

It should be noted that while the green synthesis of nanoparticles offers several benefits, it's essential to carefully choose plant materials based on their availability, cost, and the types and concentrations of phytochemicals they contain. Also, for some advanced applications, it might be necessary to further modify or functionalize the surface of these nanoparticles.

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FUNDING OPPORTUNITIES FOR INNOVATION AND TECHNOLOGY TRANSFER

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In today's rapidly evolving technological landscape, the symbiosis between academic research and industrial applications is critical for fostering innovation and economic development. However, significant barriers still impede the seamless transition of research results to the marketplace. One of the most pressing challenges in this technology transfer process is securing appropriate funding that serves the interests of both academia/research and industry.

This workshop presents several funding opportunities available at the European, national, and private levels. These range from traditional research grants and public-private partnerships to venture capital, equity financing, and novel financial instruments tailored specifically for technology transfer. The presentation also emphasizes the role of intermediary organizations, such as Technology Transfer Offices (TTOs) and industry liaison offices, in facilitating this complex process. We discuss how these entities can assist in intellectual property management, commercial feasibility assessments, and establishing mutually beneficial relationships between researchers and industry partners.

Furthermore, we explore regional and sector-specific funding schemes available in Romania and within the European Union, illustrating how these opportunities can be leveraged for maximized impact. Special attention is given to Horizon Europe, Eureka Network, and national technology transfer initiatives, providing an overview of the main characteristics of the funding instruments.

SHORT PRESENTATION OF THE BIOPLASM PROJECT

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Keywords: nanocellulose, plasma treatment, antibacterial

BIOPLASM project is focused on the development of new wound dressings based on nanocellulose and cold plasma processing. Currently, the clinical management of chronic wounds is difficult due to the increasing risk of infection with antibiotic-resistant bacteria and the shortcomings of current therapies. Therefore, the development of effective dressings for the treatment of infected wounds is of utmost importance. In the frame of BIOPLASM this problem will be managed by developing a novel technology for the production of antibacterial nanocellulose nanocarriers deposited on a biopolymer substrate.

The use of cold plasma for nanocellulose and biopolymers processing in view of medical applications is an effervescent field, with important benefits related to eco-friendliness, lack of secondary or waste products, sterilization, and large functionalization capabilities. Cold plasma treatment of the liquid suspensions of nanocellulose is a concept developed by ICECHIM and INFLPR in a previous project (CELAB-SLP). This served as a starting point for building a new technological approach to fabricate wound dressings in the frame of BIOPLASM. The project is implemented by a group of researchers from ICECHIM, INFLPR and, Cantacuzino Institute.

For achieving the objectives of the project, several stages have been or are underway:

- Designing new nanocarriers based on nanocellulose;
- Synthesis of nanocellulose carrying different antibacterial agents;
- Testing new technological routes for the deposition of nanocarriers on plasma activated biopolymer substrate;
- Characterizing in terms of structure, morphology, thermal, and mechanical properties of the obtained structures;
- Characterizing the *in vitro* cytotoxicity and antimicrobial activity of the nanocellulose carriers and wound dressings;
- Selecting the optimal technological solution.

The strong research background of the partners, ICECHIM, INFLPR, and Cantacuzino Institute, the human resources and infrastructure of the partners have made the objectives of the project to be successfully achieved up to this point.

The research work carried out so far have been disseminated through 2 published articles (Journal of Polymers and the Environment 2023, 31, 1584–1597; International Journal of Molecular Sciences 2023, 24(14), 11871), 2 oral communications (21th International Balkan Workshop on Applied Physics and Materials Science, IBWAP23, 11-14 July 2023, Constanta; Exploratory Workshop NeXT-Chem 22-23 May 2023), and 2 posters (The 7th International Colloquium on “Physics of Materials”, PM-7, 10.11 - 11.11.2022, Bucharest; 22nd Romanian International Conference on Chemistry and Chemical Engineering, RICCE22, 7.09 -9.09.2022, Sinaia).

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TREATMENT OF NANOCELLULOSE BY ANTIBACTERIAL AGENTS OF NATURAL ORIGIN

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Keywords: nanocellulose, natural extracts, antibacterial

Nanocellulose is a valuable material in tissue engineering, wound dressing, and drug delivery applications due to its low toxicity, biodegradability, biocompatibility, high surface area, and the capacity to undergo extensive physical and chemical modifications that enhance its properties. The lack of antibacterial activity is a major drawback of the otherwise successful nanocellulose in biomedical applications. Fortunately, natural compounds, which combine a low toxicity with biodegradability and biocompatibility, give us endless opportunities to imprint antibacterial activity to the nanocellulose. In the frame of the BIOPLASM project, nanocellulose was modified with several plant extracts such as basil ethanolic extract, basil seed mucilage, curcumin extracts, and propolis ethanolic extract with the aim to obtain nanocellulose showing antibacterial activity. As a result of the experimental work done so far, a facile and environmentally friendly method was developed for obtaining nanocellulose sponges containing plant extracts. It was observed that the antibacterial plant extracts did not change the opened-cell structure and nanofibrillar morphology of nanocellulose sponges. Moreover, the obtained sponges showed thermal properties comparable to those of the unmodified nanocellulose sponges but better mechanical properties and antibacterial activity against *Staphylococcus aureus* and in some cases also against methicillin-resistant clinical strains.

The nanocellulose/plant extracts sponges are intended for wound healing applications as such, or as antibacterial nanocarriers deposited on plasma-activated biopolymer substrates.

Part of this work was disseminated through the publication of an article in the International Journal of Molecular Sciences (2023, 24(14), 11871) and three communications.

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BIOPOLYMER FILMS AND NANOCELLULOSE MODIFICATION BY PLASMA TREATMENTS

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Keywords: nanocellulose, plasma treatments, biopolymer film

Plasma treatment was intensively studied for improving the surface properties of cellulose-based textiles but only recently nanocellulose suspensions in water were plasma-treated for surface modification. Moreover, biopolymer composite films were plasma-treated to improve their antibacterial activity. These procedures are environmentally friendly, relatively simple due to the absence of vacuum components, use low temperatures during the treatments, and have low operating costs.

INFLPR by its Plasma Processes, Materials and Surfaces (PPMS) group has extensive activity in the field of plasma treatments of different materials including polymers, synthesis of carbon nanostructures and composites, plasma polymerization, and development of plasma sources at low, atmospheric pressure, and under liquid discharge. In the frame of BIOPLASM, plasma treatments were used to obtain new antibacterial patches. Various plasma treatments were tested on biopolymer blends by using atmospheric pressure plasma to modify their surface characteristics in the sense of increased hydrophilicity and biocompatibility with the antibacterial layer. Dielectric barrier discharge (DBD) plasma sources working at atmospheric pressure in various gases such as Ar, Ar/O₂, or Ar/N₂ mixtures and water vapors were used to scan the biopolymers surface for modifying their wettability, surface chemistry, and even their morphology.

Moreover, plasma treatment of cellulose suspensions containing different oxidizing agents was applied for imprinting bactericidal activity to the cellulose. By combining the action of chemical agents and plasma, a noticeable oxidation of cellulose was obtained. Thus, the presence of oxidizing agents amplified the oxidizing effect of plasma. The X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy proved the surface modification of cellulose.

Part of this work was disseminated through the publication of an article in Diamond and Related Materials and by three communications.

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TESTING THE ANTIBACTERIAL ACTIVITY OF CELLULOSE-BASED MATERIALS

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Keywords: nanocellulose, antibacterial agents, wound healing

For more than 10 years, one of the research concerns of the Nosocomial and Antibiotic Resistant Infections laboratory of the Cantacuzino Institute has been testing the antibacterial activity of various natural substances such as essential oils, copper- or silver containing surface coatings, and modified biopolymers. In the frame of the BIOPLASM project, the main activity of Nosocomial and Antibiotic Resistant Infections laboratory was the evaluation of the antimicrobial activity of nanocellulose treated with natural extracts. The screening of the antimicrobial activity was performed using the disc diffusion method against various Gram-positive and Gram-negative bacterial species, including clinical isolates. For example, in the case of basil extract-treated nanocellulose sponges, the most important antibacterial activity was observed against *Staphylococcus aureus* ATCC 29213. In the case of propolis-treated cellulose samples, growth inhibitions were noticed against *S. aureus* ATCC 29213 and MRSA (Methicillin-resistant *Staphylococcus aureus*) clinical strain.

The results obtained so far are promising showing that the use of natural extracts in nanocellulose alone, or in combination with standard antibiotic therapy may improve the treatment of bacterial infections.

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REMOVAL OF HEAVY METALS AND ARSENIC FROM WATER MATRICES USING ADSORBENT NANOMATERIALS

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Keywords: *nanomaterials, heavy metal adsorption, arsenium*

At present, there are no integrated, efficient, operational and investment-integrated industrial technologies for the removal of As from water (found in combination with heavy metals, nitrogen compounds and the natural organic water matrix), without the generation of toxic by-products and residues, neither at national nor at international level.

The project goal is the transfer and development of a technology for the depollution of water containing heavy metal and arsenic, found in a complex polluting matrix, to an economic agent with important activity in the development, implementation of technologies and production of water treatment systems (ICPE Bistrița), in order to increase its economic competitiveness, as well as the implementation of the technology at an economic operator with important activity in the treatment and distribution of drinking water (Aquatim S.A.).

The specific objectives of the project are:

- Documenting the industrial scale transfer of validated laboratory technology and identifying the possibilities for optimizing the proposed technology (functional, operational and energy) by aligning with the latest scientific discoveries in the field, to ensure the success of the transfer;
- Transfer and optimization in the industrial environment of the proposed technology;
- Validation of technology efficiency by independent entities;
- Demonstrating the efficiency of the technology implemented in the industrial environment.

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PORTABLE MINIATURIZED OPTO-ELECTROCHEMICAL SYSTEMS FOR IN-FIELD MEASUREMENTS

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This workshop will address the need of portable and cost-effective systems for in-field monitoring of the pollutants, but also for fast real-time monitoring of health conditions, food quality and contaminants/pathogens detections, increasing in this way the quality of life. The design and development of miniaturized opto-electrochemical bioanalytical tools based on the advance in nanomaterial technology allow the achievement of unique features and diverse functionalities for various promising fields of applications: wearable, flexible and point-of-care sensors for clinical diagnostic, food quality control, environmental monitoring, flexible energy storage device, human-machine interfaces and intelligent sensors, based on self-healing and self-adhesive nanomaterial.

Although nanomaterials are already found in many quotidian products, such as sports equipment, cosmetics, coatings, new nanomaterials with enhanced opto-electrochemical properties are still emerging, and their uses are frequently appearing in innovative applications such as catalysts, electronics, solar panels, batteries and biomedical applications including diagnostic devices and tumor therapies. It further creates innovation opportunities for new products and processes, such as energy and environmental technologies, medical and optical techniques, chip development and manufacturing, technical data protection, construction industry, as well as paints, drugs and medical technique. The benefits of nanomaterials vary from saving lives, to advance in new applications or reducing environmental impacts, up to improving the functions of products used daily.

The target audience mainly consists of electronic manufacturers, health and care clinics/laboratories, other agriculture companies affected by food safety regulation, and also education and R&D customers.

BRIEF PRESENTATION OF THE PARTNERSHIP INVOLVED IN ACHIEVING THE SPECIFIC OBJECTIVES OF THE 701PED/2022 - ECONANO4AUTO-PROJECT

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The partnership for this project involves 2 R&D National Institutes competent in the project field and with scientific and technical potential for development and characterization the new technologies for obtaining bio-polymer nanocomposites.

The project coagulates two directions of expertise, that of INCDCP-ICECHIM in the field of development of polymer composites and nanocomposites for auto parts and that of INCDTIM in spectral and morpho-structural characterisation of the nanocomposites and also in nanotoxicology. Both partners involved in this project are R&D organizations well known in Romania and abroad, with important achievements in this field. *The knowledge and the results* achieved in previous national/international projects will *lead to the basic concept of the project*. In the period 2018-2021, the two research teams have been involved in a joint research project (<http://icechim-rezultate.ro/proiect.php?id=49>) which provides additional favourable premises for good relationship in the consortium dedicated to carry out this new project.

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KERATIN/NANOPARTICLE HYBRIDS FOR BIO-PA NANOCOMPOSITES

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Thanks to their high strength-to-weight and stiffness-to-weight ratios, as well as their high energy-absorption qualities, plastic has become one of the key materials required for the structure, performance, and safety of automobiles. Fibre-reinforced polymeric composites are the solution for light construction materials due to their flexibility, functionality and formability in complicated design parts. Typically, glassfibres are used as reinforcing agents for polymeric materials. Emerging trends in the development of lightweight materials are to develop automotive composites with reduced environmental footprint of plastic by developing new polymers with bio resources and recyclable materials reinforced with performing but cheaper and more eco-friendly reinforcement agents.

Keratin fibres from chicken feathers are promising reinforcing agents in engineering polymers contributing at the same time to diminishing the natural wastes and rational valorisation of them. Chicken feather fibres have many advantages including low cost, low density, good thermal stability and high specific mechanical properties. Furthermore, are biodegradable, nonabrasive and a continuously renewable resource of keratin.

Bio-polyamide 10,10 (PA10,10) from 100% bio-based sources, is a high-performance plastic, with higher mechanical properties, higher chemical and/or higher heat stability, but 2-5 times more expensive than polyamides 6 (PA6) or 6,6 (PA6,6), the most widely used grades. A way to reduce the cost of bio-PA and to maintain its quality as a „green material” is to replace some of the bio-polyamide with bio-based fillers, but with maintaining or even improving its properties.

The main problem with natural fibres, which limit their use as reinforcement in PA, is the poor thermal stability at the processing temperatures of PA (and engineering thermoplastic in general). Bio-PA 10,10, has a melting temperature below 200 °C (~185 °C), which can be processed at temperatures below the degradation temperature of natural fibres.

The scope of the project is the obtaining of bio-polymer nanocomposites with improved properties, recyclable, reusable and bio-integrable at the end-of-life cycle, based on bio-PA and keratin from chicken feathers.

The new bio-polymer nanocomposite will be specially tailored using the advanced material bio-PA in which a special nanohybrid, from feather keratin and special nanoparticles, will be added. The nanoparticles will contribute to the increase of the keratin strength and heat resistance.

The keratin from feather was obtained using more environmentally friendly methods, as much as possible without or with minimal usage of chemicals (i.e., extraction with ionic liquids; thermal/alkaline hydrolysis). Keratin/nanoparticle hybrids were obtained in aqueous solution, at different pHs and ratios between components.

The properties of the extracted keratin and the keratin/nanoparticle hybrids were investigated by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

Under dynamic conditions, by melt processing, nanocomposite samples based on bio-PA and different keratin/nanoparticle hybrid ratios were obtained. The thermal and mechanical properties of the obtained nanocomposites were analysed and the optimum composition was selected.

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MORPHOLOGICAL AND TOXICOLOGICAL ASSESSMENT OF NANOPARTICLES AND KERATIN/NANOPARTICLE HYBRIDS

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The purpose of the project is to obtain recyclable, reusable and bio-integrable bio-polymer/nanocomposites based on bio-PA and keratin from chicken feathers. At different stages of implementation morpho-structural characterizations of the nanocomposites as well as chemical compound characterizations are crucial for tailoring of and synthesis of the new keratin/nanoparticle hybrids. Additionally, the behavior of the cells after exposure to various types of nanoparticles, (such as nanosilicates and nanosilica) and/or to newly synthesized keratin/nanoparticle hybrids must be carefully assessed. This behavior comprises at least 2 levels of understanding, such as morphological and functional. In order to achieve all these goals the INCDTIM team focused on three main research directions: i) Morpho-structural characterization of the involved nanoparticle/nanocomposites, ii) Risk analysis of nanoparticle use and work methods to mitigate safety and health impacts and iii) Toxicological studies on the effect of nanoparticles, such as nanosilicates and nanosilica, on epidermal cell lines.

The obtained results can be summarized as follows:

- i) To determine the morphology of halloysite and aerosil nanomaterials, the transmission electron microscopy (TEM) technique was used. The equipment used was TEM Hitachi HD2700, operated at 200 kV, cold field emission. The Halloysite type nanomaterial has a nanotube structure and the Aerosil type nanomaterial has a nanoparticle structure, with dimensions below 10 nm;
- ii) Methodological guide on the prevention of risks related to working with nanoparticles. Silica-based nanoparticles have extensive applications in biomedicine and are known for their low cytotoxicity to organisms. However, a lot of recent studies are focused on a deeper understanding of the adverse effects that this type of nanoparticles could have. As a conclusion it can be stated that the toxicity of nanoparticles depends on factors such as size, functionalization or the material from which they are made. By controlling these parameters, it is possible to obtain nanoparticles with reduced adverse effects and which constitute a safe basis for obtaining devices with applications in medicine.
- iii) The cytotoxic effect of nanosilicates and nanosilica nanomaterials was first analyzed on human HaCaT (skin keratinocytes, normal, non-cancerous) cell lines. Depending on these preliminary results, it will be decided whether additional tests will be needed on other types of epithelial cells.
 - a. **MTT Viability Assay:** this analysis was carried out on 10 different concentrations of silica and silicate nanoparticles to determine the concentration at which 50% of cells (IC₅₀) are affected. Based on these results, the IC₅₀ value could be found: 92 µg/mL for halloysite and 1.7 mg/mL for aerosil.
 - b. **Morphology of HaCaT cells treated with nanosilica and nanosilicates:** a reduction in the number of cells attached to the plaque can be seen compared to untreated cells, but the morphology does not appear to be altered
 - c. **Biochemistry of HaCaT cells treated with nanosilica and nanosilicates:** the exposure of HaCaT cells to halloysite nanoparticles does not cause any significant changes in the biochemical behavior of the cells.

After determining the morpho-structural characteristics of Halloysite and Aerosil nanomaterials, they were tested on human keratinocyte cell lines. This type of cells was chosen because it represents an organ with a very large extent (the skin), and if these nanomaterials were to have cytotoxicity at this level, then it is possible that they could also affect the deeper layers. The carried out toxicity tests (biochemical and morphological) show that the nanomaterials used do not present a threat to the keratinocyte cell line. However, in the next steps the effects on other types of epithelial cells will also be investigated, to determine what can happen if the nanomaterials are inhaled and reach the body.

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NANOTECHNOLOGY AND NANOMATERIALS FOR DENTAL APPLICATIONS

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Keywords: *nanomaterials, nanotechnology, dental restoration materials*

The main goal of the project is to propose a potential dental restorative material with simultaneous antibacterial properties and enhanced mechanical strength, based on substituted apatitic nanomaterials (decorated with metallic nanoparticles) and natural compounds, applicable in cement base (glass-ionomer cements). The degree of novelty of the proposed project emerges from the properties of the proposed material related with potential final application: simultaneous antibacterial and enhanced mechanical strength of the developed nanomaterials-based structures, applicable in the cement base (glass-ionomer cements).

The solution developed in the research project will lead to a completion of the teeth treatment through the possibility of having antibacterial properties and slow release after the cavity is closed, with enhanced mechanical properties.

The scientific concept of the project is based on some specific logical steps:

- S1. Synthesis of modified apatitic nanomaterials (MAN), substituted with different metals such as zinc, silver, titanium etc., and further decorated with mono or bimetallic phytosynthesized nanoparticles and metallic oxides nanoparticles (such as silver and silver oxide nanoparticles, zinc and zinc oxides nanoparticles, silver/zinc bimetallic nanoparticles, etc.), with controlled morphologies and properties;
- S2. Demonstration of their enhanced properties;
- S3. Enriching the MAN with natural compounds (commercially available polyphenols, such as eugenol, gallic acid, or catechin, for example) – NNC;
- S4. Obtaining nanoparticle-based platforms (incorporation of apatitic materials enhanced with natural compounds in glass-ionomer cements – NGI);
- S5. Demonstration of the enhanced properties of the obtained nanoparticle-based platforms (NGI);
- S6. Demonstration of their efficiency in the laboratory model (simulated conditions);
- S7. Validation of the proposed solution.

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MULTIFUNCTIONAL COMPOSITES FOR THE PROTECTION OF CULTURAL HERITAGE OBJECTS: INHERITAGE PROJECT

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Keywords: *cultural heritage protection, coatings, multifunctional composites*

As the degradation processes of cultural heritage objects remain inevitable, the continuous development of advanced materials able to counteract specific degradation processes is also necessary. Thus, are needed thorough scientific studies in order to develop tailored formulation, in order to protect, preserve, and restore cultural heritage objects, and this represents a continuous challenge for the scientists, aiming to replace the current rather serendipitous approaches in restoration.

The InHeritage project aims to develop novel multi-layer composite materials with multiple functions (consolidation, self-cleaning and anti-microbial effect), applicable for the conservation of different inorganic substrates. The solutions developed in this project will represent not only an alignment to the international level of research, but also a very important technical solution, innovative at national level, that will contribute to the project sustainability after the implementation period.

The main goal of the project is to develop novel multi-layer composite materials with multiple functions (consolidation, self-cleaning and anti-microbial) applicable for the conservation of different inorganic substrates.

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**NEW MATERIALS FOR AN INTEGRATED APPROACH OF THE WATER
RESOURCES PROTECTION.
THE AQUAMAT PROJECT: ICECHIM'S VISION ON WATER PROTECTION**

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Keywords: *water depollution, nanosensors, nanomaterials, sol-gel materials, (photo)catalytic materials*

The integrated approach proposed within the AquaMat project, starting from the construction of very sensitive miniaturized bioanalytical systems for the rapid screening of the presence of pollutants in the environment, combining the advantages of adsorption processes with those of advanced oxidation processes and nanoporous membrane systems for the advanced purification of sources of water, reducing the disadvantages specific to each type of process, will contribute both to scientific progress and to an important technological advance, constituting an absolutely original approach.

The main goal of the project is to develop an integrated approach to the monitoring and treatment of (potentially) contaminated water sources, building on ICECHIM's demonstrated experience of developing new materials and technologies for the protection/remediation of water sources. This approach will materialize in a modular technology for the monitoring and treatment of deep and surface water, adapted to various types of water sources, its components to be developed by achieving the specific objectives of the project.

The system in which the project is designed allows its approach by fulfilling 5 specific objectives, with a single final application, namely the improvement of water quality through organic and inorganic pollutant removal treatments, these directions having a solid interconnection.

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