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FOREWORD

Making complex scientific topics accessible to wider audiences while maintaining scientific accuracy requires placing science and research in a larger narrative context, obliging Open Science conventions. It is only by observing the forward tendencies and communicating the social role of science with honesty, impartiality and to high professional standards will specialists manage to relate to the broader public at a fundamental, accountable level. Society has become more and more dependent on the scientific work and experts ought be aware of their social role. Whenever scientists succeed at communicating effectively beyond their peers to broader, non-scientist audiences, it builds support for science, promotes understanding of its wider relevance to society and encourages more informed decision-making at all levels, from government to communities to individuals. In a period marked by many policy changes, PRIOCHEM 2022 is an hallmark memento for INCDCP – ICECHIM Bucharest, which continues to grow and adapt, remaining permanently driven, focused and open to new ideas, making sure that Romanian research and academic institutions continue to be part of the global research elite.

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Lectures

"I have suggested that scientific progress requires a favorable environment."

Ernest Lawrence

USING MICROWAVES TO EXTRACT AND MAKE FUNCTIONAL NATURAL OR BIO-SOURCED MACROMOLECULES

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Keywords: microwaves, saponin, extraction, polysaccharide, chemical modification

Introduction: Microwave irradiation is a way to quickly introduce energy within a chemical system differing from conventional heating techniques. Besides this energy input, this process allows reducing the quantity of organic solvent necessary for reactions, substituting an aqueous medium, bio-sourced or renewable solvents, introducing atoms economy. We present two examples in using microwaves irradiation with bio-sourced materials: the extraction of saponins from soapnuts, and the chemical modification of a polysaccharide, chitosan.

Synthetic surfactants are widely used in emulsion polymerization, but it is increasingly desirable to replace them with naturally derived molecules with a reduced environmental burden. Saponins were used as biodegradable and renewable surfactants for emulsion polymerization.

Chitosan is a well known biosourced macromolecule obtained from chitin. However its chemical structure needs modifications to extend its domain of applications as thickening or chelating polymer as examples.

Materials and methods: Saponins were extracted from crude *Sapindus Mukorossi* soapnuts. Crude microwave-assisted extracts of saponins have been employed at various concentration to carry out an emulsion polymerization of styrene in classical way in terms of monomer content (20 wt-% *vs.* water), initiator ratio (3,7 wt-% *vs.* monomer), at 70°C under magnetic stirring.

The alkylated chitosan derivatives were obtained by reductive amination. Two types of process have been used to keep the temperature constant: the conventional heating using a jacketed reactor or microwave irradiation. In all the cases the reaction was carried out in a 100 mL one-necked round bottom flask capped with a rubber septum.

Results: Saponin has been extracted from soapnuts by microwave assisted extraction and characterized in terms of surfactant properties prior to emulsion polymerization. The results in terms of particle size distribution and morphology control have been compared to those obtained with classical nonionic (NP40) or anionic (SDS) industrial surfactants. Microwave extracted saponins were able to lead to latexes as stable as standard PS latex as showed by the Critical Micellar and Critical Coagulation Concentration measurements.

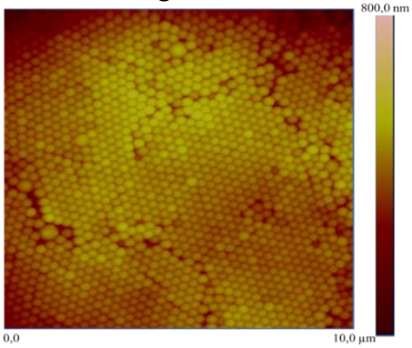

Figure 1. Polystyrene particles obtained with 4wt-% of saponins vs. monomer (AFM image)

Conventional heating and microwave irradiation have been compared for the synthesis of chitosans grafted with alkyl chains. Reaction time, temperature and chitosan molar mass have been studied onto the yield of alkylation. Rheological behaviour and interface properties were studied as a function of the yield of alkylation.

Conclusions:

Saponins represent a new sustainable and renewable surfactant with a very low CMC, insignificant salt-sensitivity and low pH-sensitivity. Lastly, such a sustainable surfactant offers the advantage of avoiding the toxicity associated with common synthetic non-ionic surfactants containing phenol groups. Monomodal, monodispersed and stable particles of polystyrene have been obtained with saponins and the results demonstrate the great potential of this “green” surfactant.

All the results tend to prove that microwave assisted synthesis is a powerful method to obtain modified chitosan under extremely low reaction time without any degradation and/or property modifications.When compared to modified chitosan obtained under conventional heating, the results showed that the irradiated chitosan exhibits the same properties in terms of viscosity and surface tension.

AEROGEL-BASED SYSTEMS: PREPARATION AND APPLICATIONS

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Silica aerogels are solid amorphous materials consisting of interconnected particles, which form an open 3-D network structure. They are obtained by the sol-gel technology and exhibit unique properties, namely low thermal conductivity (< 20 mW m-1 K-1), low density (< 50 kg m-3), high porosity (80-99.8 %), and high surface area (500-1200 m2 g-1) [1],[2]. Additional properties, like non-flammable character, low refractive index and low thermal expansion coefficient, make them excellent candidates for a wide range of applications in thermal insulation, battery electrodes, catalysts, humidity sensors, adsorbents for pollutants, as well as optical, acoustic and dielectric applications [1],[2].

Despite these exceptional properties, pure silica aerogels present also some drawbacks, like fragility and hydrophilic behaviour, which limit their application on a large-scale. Nevertheless, silica aerogels present high versatility for surface modification and allow easy incorporation in their structure of various compounds, such fibres, particles and polymers, for improving their mechanical, optical and thermal properties [1],[3]. Additionally, the proper selection of silica precursors permits also to obtain more durable aerogels with higher strength and stiffness. The continuous expansion of the application range of the aerogel-like materials can be easily explained considering that by tailoring these materials it is possible to obtain novel systems with improved structural and functional properties [4],[5].

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NATURAL PRODUCTS ALTER COMMON METABOLIC PATHWAYS IN MYCOBACTERIA

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The known bacterial cellular processes targeted by antibiotics are grouped into: cell envelope biogenesis; DNA replication; transcription; and protein biosynthesis[1]. Studies on slow growing *Mycobacterium tuberculosis* have revealed important insights into the antibiotic-induced metabolic dysregulations that contribute to bacterial cell death or stasis[1]. Intracellular accumulation of reactive free radical species is for example a downstream metabolic by-product of bactericidal antibiotics[2],[3]. Also, extensive metabolome remodelling was observed as a compensation mechanism for intracellular ATP depletion after bedaquiline treatment in mycobacteria[4]. Similar observations were described for rapidly growing model organisms showing the metabolome remodelling characterized by an increase in abundance of central carbon metabolites and a decrease in concentrations of free lipids and nucleotide pools as a response to antibiotics[5]. Finally, bactericidal action of antibiotics was linked with increased respiratory activity, whereas growth inhibition from bacteriostatic antibiotics was associated with suppressed cellular respiration[6].

Little information is available about the detailed antimycobacterial mechanism of action of natural products. Therefore, the application of metabolomics and transcriptomics was used to characterize metabolic pathways altered by natural products in *Mycobacterium tuberculosis*. The main metabolic consequences observed after bacteria exposure to different natural compounds were related to maintenance of outer membrane stability, redirection of carbon flow, activation of detoxification mechanisms, launching of intracellular energy resources and alteration of redox balance. Some of these mechanisms were common, while other compound-specific.

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LAYERED DOUBLE HYDROXIDE-DERIVED TRANSITION-METAL-BASED MIXED OXIDES, PROMISING CATALYSTS FOR VOLATILE ORGANIC COMPOUNDS ABATEMENT

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Keywords: catalytic materials; layered double hydroxides; mixed oxides; volatile organic compounds; total oxidation.

Volatile organic compounds (VOC) recovery from the residual gaseous effluents occurring in different industrial processes is economically disadvantageous due to their very low concentrations and, therefore, their destruction is the only viable alternative, the process of choice for this being the catalytic combustion [1]. Due to its high stability, methane is often used as a test molecule for the catalytic combustion of VOC. Promising catalytic materials for this process were shown to be the transition-metal-containing mixed oxides obtained by controlled thermal decomposition of layered double hydroxides (LDH) precursors [2].

Layered double hydroxides or hydrotalcite-like compounds are lamellar anionic clays with the general formula $M^{2+}_{1-x}M^{3+}_{x}(OH)_2A^{n-}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are bivalent and trivalent cations, respectively, with ionic radii not too different from that of Mg^{2+}, and x is the molar fraction of trivalent cation, usually comprised between 0.2 and 0.4 [3]. The cations are hexa-coordinated to hydroxyl groups and such edge-sharing octahedra form infinite sheets which stack to create a layered structure similar to that of brucite, $Mg(OH)_2$. A large variety of inorganic and organic counter-anions A^{n-} can be intercalated in the inter-layer space also containing water molecules, to compensate the positive charge introduced by the M^{3+} cations that isomorphically replace the M^{2+} cations in the brucite-like sheets. Two or more cations can enter simultaneously the brucite-like layers where they are homogeneously distributed and intimately mixed together. Notably, the LDH can be easily synthesized by several methods, the most frequently used being the co-precipitation, which is simple, reliable and usually produces good results in the case of multicationic LDH [2]. Due to their structure and compositional flexibility, the LDH possess versatile physicochemical properties, which make them excellent candidates as multifunctional nanostructured catalysts and catalyst precursors [4], [5]. Indeed, they can be used as such, particularly in low-temperature catalytic processes, or as mixed oxides obtained by their controlled thermal decomposition, in high-temperature gas-phase catalytic processes, including selective oxidation, oxidative dehydrogenation and total oxidation [2].

Highly homogeneous mixed oxide structures with high specific surface areas, good thermal stabilities and tunable acid-base and redox properties can be obtained from LDH precursors. Due to these properties, the ex-LDH transition-metal-containing mixed oxides have been recognized as very promising catalysts for different processes, including the complete oxidation as a valuable technology for the destruction of volatile organic compounds [2].

Through selected examples from our own research work, the high potential of the ex-LDH transition-metal-based catalytic materials for the total oxidation of methane will clearly be demonstrated through the correlation preparation method – physicochemical characteristics – catalytic performance.

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CULTURAL HERITAGE CONSERVATION: FROM NANOMATERIALS TO PORTABLE WIRELESS DEVICES FOR THE AIR QUALITY MONITORING

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Keywords: Nanomaterials; Green Chemistry Nanoparticles; stones; sandstones; ancient manuscripts; nano collagen

Introduction: In the header of the document please insert the Section code:

- MTCH - Multifunctional materials, nanocomposites, innovative technologies and cultural heritage protection

Nanomaterials, synthesized by a new Green Chemistry based Eco-friendly approach is presented and discussed here. Especially, its application in conservation and restoration of damaged historical surfaces and Art-Work objects is widely reported. Several cases of study are discussed here, ranging from the stones (as marble, Pietraforte [1], Pietra Serena[2], Bugnato, sandstones, limestone, etc.;) to the paper manuscripts, parchment and ancient leather books. In this study, a synergistic approach is presented, concerning the innovative strategies for restoration and conservation of historical surfaces and (at the same time) the environmental monitoring of chemical and biological pollutants (responsible for serious damages toward the Art-Work objects).

Materials and methods: For the nanoparticles synthesis, an Al_2O_3 template nonporous (homemade) membranes have been applied and also specific enzymes provided nanostructured matrix/platform for the nanoparticles/nanotubules growth [3]. Furthermore, the Analyst passive diffusive samplers are assembled with selective impregnated filters, suitable to uptake gaseous pollutants and fine dust (fine Particulate Matter, as: PM_{10} and $PM_{2.5}$).

(A)

(B)

Figura 1. (A) Analyst assembling and (B) typical movable Datalogger for the thermo-hygrometric parameters recording.

Conclusions: In this study, several important results and goals have been reached by applying new green nanotechnology for the restoration, cleaning and conservation of Cultural Heritage. At the same time, important information have been discovered about the surface damages provoked by environmental pollutants, thanks to the application of new portable and smart devices capable of monitoring the concentration levels of the pollutants involved in the photochemical smog processes (present in both, indoor and outdoor environmental areas).

***Acknowledgements**: POR-FESR 2014-2020 Regione Lazio project (Principal Investigator/PI Envint and Tor Vergata University); Brevetti + Invitalia (PI Envint and Tor Vergata University);PoC Proof of Concept Valorizzazione dei Brevetti di Tor Vergata Università (MISE; PI Tor Vergata University).*

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ALTERNATIVES AFFINITY LIGANDS IN BIOSENSING TECHNOLOGY: PROMISES AND CHALLENGES

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Keywords: biosensors, aptamers, molecularly-imprinted polymers.

Antibodies are the most successful affinity tools nowadays used in research area, but also for many analytical applications used in food industry (components, toxins, pollutants, adulterants…) and biomedical fields (diagnostics and therapeutics). However, these remarkable recognition elements do have their limitations, mainly related to high production costs and low stability. In recent years, intensive research has been dedicated to the development of alternative affinity ligands, among which the major candidates are nucleotidic aptamers and molecularly-imprinted polymers. Despite their very different structures, these compounds share the ability to be produced for a wide variety of target compounds, ranging from ions to cells, they are selected using non-invasive in vitro screening procedures and they can be easily reproduced once optimized. Although these synthetic recognition elements are not yet commonly applied in conventional analysis, their applications have steadily increased in recent years. This presentation will thus focus on some applications of aptamers and MIPs in biosensing technology, highlighting the issue of signal transduction and chemical labelling.

ANTI-OBESITY POTENTIAL OF PLANT NATURAL COMPOUNDS

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Obesity has outreached the dimensions of a health problem and has established as a global epidemic (named Globesity) over the past decades [1], [2]. Excessive body weight appears among the top five risk factors in terms of attributable deaths and metabolic complications development [2], [3]. Consequently, management of obesity (*i.e.*, prevention and treatment) is subject of undergoing intense research [4].

In this respect, plant extracts and compounds of natural origin attract profound interest as candidates for obesity management. We have examined the potential of plant extracts and their bioactive principles to affect adipogenic differentiation in human adipocytes.

The potential mechanisms of action were studied by using transcriptional analysis through real-time quantitative PCR and protein abundance evaluation by Western blotting. The key adipogenic transcription factors – peroxisome proliferator-activated receptor gamma (PPARγ) and CCAAT-enhancer-binding protein alpha (C/EBPα) – appeared strongly decreased at a protein level by treatments with plant extracts and pure compounds. Moreover, the phosphoinositide 3-kinase (PI3K)/protein kinase B (AKT) signaling pathway was found to be involved in the anti-adipogenic effect of the plant extracts and pure molecules. Collectively, our findings indicate that selected plant extracts and their active compounds hampered adipocyte differentiation through PI3K/AKT inhibition. Among the selected compounds, betulinic acid and maackiain exhibit the most promising anti-adipogenic activity [5], [6]. Furthermore, the research has been translated from *in vitro* human adipocytes to the *in vivo Caenorhabditis elegans* model [7].

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MICRO AND NANOTECHNOLOGICAL ADVANCES IN DIABETES MANAGEMENT

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Diabetes is defined as a chronic elevation of glycemia. Due to acute and chronic complications, the disease poses a major economic, social, and medical burden on society worldwide. Diabetes is characterized by insufficient insulin plasma level to meet the organism demand. In type 1 diabetes, absolute deficiency of insulin production results from massive auto-immune destruction of pancreatic beta cells. For this reason, the main therapy consists in delivering exogenous insulin. The treatment methods require numerous daily injections of insulin administered by subcutaneous needle injection, insulin pen and catheters connected to insulin pumps. These methods are however both painful and inconvenient as the invasive multiple injections of precisely calculated amounts of insulin present a significant deterioration of the life quality of the diabetic patients. The discomfort associated with this type of administration has led diabetic patients to neglect or even give up the therapy. There is thus an increasing demand for the design of new insulin administration systems and this has led to the investigations of oral, nasal, buccal, pulmonary, rectal, ocular and transdermal routes. Buccal insulin (Oral-lynTM) and pulmonary insulin (ExuberaR) were launched on the market although with small positive feedback by consumers. Oral administration of insulin is encountered with major problems such as hydrolysis in the low pH of gastric medium, splitting by proteinases in the stomach and weak penetration through the membrane of epithelial cells of the intestine.

Transdermal delivery of insulin, a simple and painless method, represents a viable alternative for the controlled release of insulin over time together with high patience compliance. Insulin delivery through the skin has several advantages, including avoidance of the first-pass metabolism, avoidance of gastrointestinal side effects, possibility of extended therapy, therapy at demand, painless and friendly application. However, transdermal delivery is limited by the low permeability of the stratum corneum, the skin outermost layer, allowing only small (<500 Da) hydrophobic molecules to be delivered.

In this presentation, I will discuss our original contribution on insulin transdermal delivery upon photothermal or electrothermal activation.

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ELECTROCHEMICAL (BIO)SENSOR ARRAY COUPLED WITH MULTIVARIATE DATA ANALYSIS FOR THE ASSESSMENT OF VIRGIN OLIVE OIL QUALITY

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Keywords: biosensor; virgin olive oil; voltammetry; biomarker; data analysis.

Introduction: Olive oil is obtained from the fruit of olive tree (*Olea europea* L.), one of the oldest known cultivated tree in history [1]. Olive oil is widely appreciated for the nutritional value, numerous healthy effects and for the sensory properties [2],[3]. Because olive oil is a high value product could be subject of different adulterations. The practices are diluting olive oil with other vegetable oils, e.g.: canola, sunflower, hazelnut, deodorized olive oils, olive oil obtained by extraction with solvents, olive pomace oils etc. [4]. Therefore, the development of rapid, cheap and portable systems for detection of olive oils adulteration is of great interest.

Materials and methods: The sensors and biosensors developed in this study were based on functionalized carbonaceous nanomaterials such as graphene oxide, gold nanoparticles and enzymes (laccase and tyrosinase). The detection method employed for quantification of biomarkers and classification of samples was cyclic voltammetry. For data analysis PCA (principal component analysis), SIMCA (Soft Independent Modelling of Class Analogy), PLS1 regression models were used.

Results: The detection of virgin olive oil adulteration is a complex analysis and it can be mainly achieved by obtaining its chemical fingerprinting or by detecting the biomarkers. The extra virgin oils extracts were analyzed using the biosensors and the biomarkers such as tyrosol, hidroxytyrosol and oleuropein were quantified based on the calibration curves. This method permits the detection of adulteration if the level of adulterant is higher than 10%, when the concentration of biomarkers are significantly different at a 95% confidence level. The input matrix consisting in the cyclic voltammograms of all (bio)sensors immersed in the extracts of all samples under study was used for the development of PCA; SIMCA and PLS 1 models. The results have shown that the method could be able to detect the adulteration of extra virgin olive oils at levels below 2%.

Conclusions: In this study, an accurate method to evaluate the adulteration of extra virgin olive oils has been established. It was demonstrated that voltammetric curves can be used as input variables in multivariate data analysis. It has been shown that is possible to discriminate and classify extra virgin olive oils adulterated with seed oils. Classification models were shown that is possible to classify appropriately the adulterated oils at a concentration level of adulterant oil lower than 2%.

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EMERGING ANTIMICROBIAL NANOTECHNOLOGIES WITH POTENTIAL USE IN THE PRESERVATION OF THE CULTURAL HERITAGE AND PREVENTING MICROBIAL RESISTANCE

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Keywords: surface treatment, antimicrobial nanotechnology, degradation of pollutants

Introduction: The work is presenting three approaches in modifying the (inner or outer) surface of different materials.

Materials and methods: Two approaches are designed to modify the surface of different materials, including stone, marble, glass, concrete, wood etc., these materials being used for civil engineering (buildings, bridges, wastewater plants, etc.) but also for the protection of the national and international cultural heritage. For this purpose, two approaches are considered, a biomimetic one using chemically bonded surfactant-like moieties and a nanotechnologically modified technique based on chemically bounded nanoparticles with antimicrobial activity. Om both cases the chemically attachment is important in long-lasting effect but also in avoiding the release of these agents into the nature and thus to induce pollution. A third approach will be applied to modify some porous materials by developind photocatalysts inside the pores. In this case, the pollutants, especially antibiotics will be absorbed and degraded to eco-friendly substances, which will not enhance the antibiotic resistance. This approach is easy to be implemented in the wastewater treatment (especially municipal, zootehnical but also from hospitals) requiring only an additional treatment tank.

Results: The first two approaches are involving chemical attachment of the antimicrobial agents onto different surfaces and thus will last for a longer period of time and the negative, environmenta impact will be low because these antimicrobial will not be released (leaked) into the nature. The third approach is easy to be implemented in the wastewater treatment (especially municipal, zootehnical but also from hospitals) requiring only an additional treatment tank. Comparing to the classical, pure adsorption route, where the sorption / desorption equilibrium assure a long term release of the antibiotics, at low level and thus induce a long-term contact of these antibiotics with the bacterial strain and generate resistance, the as proposed technology assure the degradation of these pollutants and thus a lower risk of antibiotic resistance.

Conclusions: The proposed nanotechnological solutions can be effective ways to protect surfaces (especially those of cultural heritage (but also suitable for civil applications) and also could be used in reducing the risks associated with the development and dissemination of the antibiotic resistance.

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CARBON MATERIALS FOR CO_2 ABATEMENT AND HYDROGEN FUEL

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Keywords: hydrogen storage; hydrogen production;carbon dioxide.

Introduction: Increase of worldwide CO_2 emissions from transport and industry is among the main contributors for global warming. 90% of total world demanded energy is supplied by thermal power plants working with fossil fuels, including coal, oil and gas - they provide 50% of total CO_2 emissions [1]. Till now various sorbents were applied for CO_2 removal from air: carbon materials, zeolites, ordered mesoporous silicas, metal organic frameworks, etc., whereas low-cost nanoporous carbons demonstrated high adsorption capacity and easy regeneration.Hydrogen is a renewable and clean energy carrier that can store or deliver large amount of energy.“Blue hydrogen” is produced when methane is converted to hydrogen and CO_2 by two main processes: steam methane reforming (SMR) or auto thermal reforming (ATR). Emitted CO_2 is captured and stored by so called carbon capture usage and storage process (CCUS). If CO_2 is not captured, the term “grey hydrogen” is used.The term “green hydrogen” refers to hydrogen produced by electrolysis of water, powered by renewable energy sources, such as wind or solar.“Pink hydrogen” is also made by electrolysis, but when using nuclear energy as a power source. “Yellow hydrogen” is also produced by electrolysis exclusively from solar power. Hydrogen is considered to be the fuel of the future; however there are problems with storage of this explosive and flammable gas. The researchers around the world are trying to find appropriate materials and methods for hydrogen storage. One of the methods of solid-state hydrogen storage is in the form of metal hydrides, which provides safer storage by using smaller volume tanks. Mg based materials are promising for hydrogen storage, despite their slow kinetics and increased enthalpy, resulting in high desorption temperatures. It should be noted that among the materials capable of absorbing hydrogen, reversibly, low-cost Mg has an extremely high hydrogen storage capacity. Many efforts were made to obtain magnesium based materials which have a sufficiently high absorption capacity, and also enhanced kinetics of hydriding/dehydriding, and thus providing milder conditions of the sorption processes as compared to pure magnesium.

In this study nanoporous carbons with different textural and chemical surface characteristics were synthesized from various precursors. The obtained nanoporous carbons and metal-carbon composites were characterized, and their catalytic properties were tested in methanol decomposition to CO and hydrogen. In addition, the absorption-desorption characteristics during prolonged cycling towards hydrogen of Mg-C composite are investigated. CO_2 adsorption experiments were carried out.

Materials and methods: Synthetic carbons was prepared after thermo-oxidation treatment of the precursors. The solid product was subjected to hydro-carbonization at 850^{o}C. The obtained nanoporous carbons and metal loaded samples were characterized by various physicochemical methods.

Results: The catalytic properties of metal-carbon composites are tested in methanol decomposition to hydrogen. The absorption-desorption characteristics during prolonged cycling towards hydrogen of Mg-C composite obtained by ball milling under Ar atmosphere are studied. Adsorption tests have been carried out in lab-scale fixed-bed column, at different temperatures and CO_2 concentrations, in order to investigate both kinetic and thermodynamic aspects. Regeneration studies have been conducted in order to investigate the possibilities for carbon adsorbent reutilization, to determine its CO_2 adsorption capacity within consecutive cycles of adsorption–desorption and to assess the optimal operating conditions for CO_2 recovery by desorption.

Conclusions:

It was established that the synthesized nanoporous carbons have very good CO_2 adsorption capacity. Experimental results confirm that CO_2 adsorption is a reversible process.

The catalytic properties of metal-carbon composites were tested in methanol decomposition to hydrogen. Synthesized carbon materials are appropriate additive to magnesium based materials for hydrogen storage.

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2. *Section 1* - Multifunctional materials, nanocomposites, innovative technologies & cultural heritage preservation

ORAL Communications

CATIONIC DYE REMOVAL USING MATERIALS BASED ON XANTHAN OR ESTERIFIED XANTHAN/COBALT FERRITE-LIGNIN HYBRID

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Keywords: ferrite-lignin hybrids, xanthan, adsorbents, cationic dye removal

Introduction: Water pollution with organic dyes represents one of the most severe environmental problems and can lead to various imbalances for all ecosystems [1],[2]. Cationic dyes have been proven to be dangerous due to nitrogen or a –N=N– group attached to an aromatic ring [3]. This is why, diverse systems able to retain dyes from different types of water have been developed. This study presents the adsorptive properties of xanthan/esterified xanthan and ferrite-lignin hybrid, able to retain Basic Fuchsine dye (BF) from polluted water.
Materials and methods: Ferrite-lignin hybrids (CFLB and CFLO) were obtained by the sol-gel auto-combustion method, by using organosolv lignin (LO) and Lignoboost® (LB) as chelating-fuel agents. Xanthan gum (XG) was esterified with acrylic acid, resulting xanthan acrylate (XGAC). Further, hybrids were embedded in xanthan (XG)/xanthan acrylate (XGAC) matrix, resulting new materials (XG/CFLB, XGAC/CFLB, XG/CFLO and XGAC/CFLO). Density, porosity and swelling ratio of all the materials were determined. The dynamic water vapor sorption capacity of the samples was also measured (DVS analysis). Equilibrium, kinetic and thermodynamic studies have been performed to investigate the adsorption behavior of BF from aqueous media at different dye solution concentration (15, 50 and 70 mg/L). SEM images of adsorbents, before and after dye adsorption experiments were recorded and analyzed.
Results: Density and porosity of the materials was influenced by the nature of the polymeric matrix and also by the structure of embedded hybrid. The swelling ratio in water of the adsorbents was studied at different pH values (5, 7, 8.5, and 10). All of them exhibited rapid swelling behavior (equilibrium was reached in 80 min), the process being pH sensitive. It was proved that the polymeric matrix influences the water sorption capacity. The materials based on esterified xanthan presented lower sorption capacity as compared with those based on unmodified xanthan.

The investigation of adsorption kinetics is helpful in predicting the adsorption rate and its mechanism. The correlation coefficients, R^2, of the pseudo-first-order kinetic model were found to range from 0.931 to 1.000, which demonstrates the chemical nature of the adsorption process. Thus, interactions involving electron exchanges could be formed between the lateral bonds of the dye molecules ($=NH_2^+$) and the adsorptive materials. XG/CFLO, XG/CFLB and XGAC/CFLO materials retained the highest amounts of BF dye (44.73, 37.54 and 24.54 mg/g). The experimental data of the adsorption equilibrium of BF dye onto XG/CFLB, XG/CFLO, XGAC/CFLB and XGAC/CFLO are well fitted by the Dubinin-Raduchkevich model (R^2 presents values between 0.942 and 0.997), while the adsorption equilibrium of BF onto the CFLB and CFLO adsorbents is well described by the Jovanović model. After the dye adsorption experiments, structural modifications could be observed for all the adsorbents (according to SEM images). The unidirectional channels are spaced apart or even destroyed. The effect of temperature on the adsorption capacity of the prepared materials was investigated at 20, 35 and 45ºC, using a dye solution of 15 mg/L concentration. It was evidenced that the BF retention is an endothermic and spontaneous process (except the cases where the adsorbents retained the smallest quantities of dyes).
Conclusions: XG and XGAC were used as polymeric matrices. CFLB and CFLO hybrids were added into the matrix, forming new adsorptive materials. Batch adsorption experiments revealed that XG/CFLO, XG/CFLB and XGAC/CFLO retain the highest amounts of BF dye. The chemical nature of the adsorption process was demonstrated through kinetic studies. Equilibrium experimental data were better fitted to the Dubinin–Raduschkevich and Jovanović isotherm models. The thermodynamic study evidenced the endothermic and spontaneous nature of the adsorption process.

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DETECTION OF LIPOPOLYSACCHARIDES FROM MULTI-DRUG RESISTANT BACTERIA USING MODIFIED PLASTIC SCREEN-PRINTED CARBON ELECTRODES

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Keywords: lipopolysaccharides, molecular imprinting, printable carbon paste

Introduction: Nowadays, the upward rate of severe infections caused by multi-drug resistant Gram-negative bacteria (MDR-GNB) has been in strongly connection with a worldwide increase in morbidity, mortality, high cost per hospitalized person and a very reduced palette of antibiotics usable in infections [1]. In this manner MDR-GNB infections would not only be a triggered alarm to human health but also for the economy, being speculated that in Europe more than €1.5 billion are annually attributed to this cause [2]. Therefore, the development of new, low-cost methods of bacterial detection are more than necessary to extend the life span of the remained antibiotics in use. Regarding this aspect, this work describes the development of modified screen printed carbon electrodes on plastic substrate using a printable paste doped with molecular imprinted polymers (MIPs) particles which will function as the working electrode after the printing process. The main target is represented by the lipopolysaccharides (LPS, the most important component of the of GNB cell-wall consisting in 75% of its surface) from the second most concerned MDR-GNB according to World Health Organization [3] namely *Pseudomonas Aeruginosa.*

Materials and methods: To develop the modified plastic screen-printed carbon electrodes, one of four series of MIP particles with the most adequate characteristics, previously synthesized in laboratory through a sol-gel method, was chosen to be incorporated in a mixture based on nano-ZnO electroactive particles, a compatible solvent, carbon paste and a binder in order to obtain the printable paste. Further on, the screen-printed carbon electrodes were obtained by printing the prepared paste on the plastic support. In this respect, a hybrid method for printing was used, in which case the contacts and the reference electrode were prepared by serigraphic methods while the functionalization of the working electrode and the auxiliary electrode by inkjet technology.

Results: The obtained plastic screen-printed carbon electrodes were characterized using modern techniques, such as structural, morphological and rheological analyses to highlight the successful incorporation of MIP particles and to establish an optimal flow profile for the printable paste. The obtained screen-printed electrodes were subjected to cyclic and differential pulse voltammetry analyses to determine the sensitivity for LPS, followed by selectivity measurements against LPS from other MDR-GBN such as *E.Coli* and *Salmonella Enterica*.

Conclusions: Consequently, the obtained plastic screen-printed carbon electrodes can be a sustainable alternative for LPS detection from *Pseudomonas Aeruginosa* due to the low-cost of manufacture.

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EPHEDRINE HYDROCHLORIDE DETECTION BASED ON MIP PARTICLES/CONDUCTIVE CARBON PASTE MODIFIED ELECTRODE

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Keywords: sensors;MIP; ephedrine; SPCE; detection

Introduction: Ephedrine and pseudoephedrine are illicitly used to improve athletic performance and for this reason, they are included in the list of banned drugs of the International Olympic Committee[1]. They are also among the most used precursors in the illicit production of methamphetamine. Thus, it is necessary to find a fast, cost-effective, reproducible, sensitive, and specific method to detect these drugs in wastewater and biological fluids. Molecularly imprinted polymers (MIPs), synthesized using molecular imprinting technique (MIT) possess a strong binding affinity towards a chosen template molecule, due to the imprinted cavities formed in the polymerization step[2].The electrochemical detection combined with MIPs as receptors is one of the most used methods to quantify the template molecule in the sample[3]. In recent years, screen-printed electrodes (SPE) were employed as miniaturized electrochemical devices which led to multiple advantages such as portability[4].
Materials and methods: The development of the MIP sensors involved two steps, namely (1) the synthesis of the MIP particles; (2) the incorporation of MIP particles in a commercial conductive carbon paste and the deposition of the resulted paste on the surface of the working electrode of SPCE by drop-casting. The preparation of the MIP particles consisted in a sol-gel process using two silanes as functional and structural monomers and pharmaceutical ephedrine hydrochloride as template molecule. The template molecule was removed by several washing steps using water and ethanol. The same procedure was applied in order to obtain the control particles, non-imprinted polymers (NIP), but without the template addition.
Results: The synthesized particles were characterized by various techniques including structural (FT-IR), dimensional (DLS) and morphological (BET, SEM) analyses, while the sensors were electrochemically characterized using cyclic and differential pulse voltammetry (CV and DPV). The sensitivity and selectivity for ephedrine hydrochloride were assessed using the aforementioned electrochemical techniques.
Conclusions: In this work we successfully developed electrochemical sensors based on MIPs particles for ephedrine detection. The removal of the ephedrine hydrochloride from MIP particles was highlighted by BET surface analysis as the washed MIP particles had a larger surface area, pore surface area and pore volume compared to the particles before washing. By SEM, the spherical particles were shown to form aggregates with sizes in the micrometer range revealed by DLS. Through DPV method, the sensitivity of sensors was highlighted; sensors were able to detect ephedrine even at low concentration in aqueous solution. Furthermore, the sensors present a good stability at re-use and reproducibility.

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NUMERICAL MODELING OF INTEGRATED OXIDATION, BIOFILTRATION AND ADSORPTION PROCESSES WITH APPLICATIONS IN THE DESIGN OF DRINKING WATER TREATMENT TECHNOLOGIES

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Keywords: numerical modeling; water treatment; advanced oxidation; biofiltration; adsorption

Introduction: Currently, water intended for human consumption is subject to complex physico-chemical and biological purification processes, from source to consumer, mainly due to the increasing degree of water pollution and higher quality requirements imposed by regulations. The degree of complexity of these processes depends in particular on the quality of the water source, which in most cases could present a combined pollution with pollutants such as inorganic ammonium compounds, organic pollutants and heavy metals. The design of an effective treatment technology requires the synergistic integration of several unit stages, each of which has specific goals. A complex engineering approach is required that includes specialties related to hydraulics, physical engineering, chemical engineering, electrical installations and industrial automation.
Materials and methods: The complexity and the degree of interconnection of the processes involved in a water treatment technology determine the numerical modeling and simulation of the processes as a mandatory step in the design of an integrated technology. The integration of oxidation, biofiltration and adsorption processes as effective pollutant reduction methods requires a holistic approach to exhibit high operational efficiency and low energy consumption. The present paper proposes an approach to the modeling and simulation of specific processes in water treatment plants, involving the development of the numerical model on two levels: the modeling of individual processes and the technological modeling (hydraulic and operational) of the entire process flow. The first level allows the advanced modeling of the selected processes, in order to develop and implement them and the modeling of the active elements of the specific equipment. The second level refers to the integration of individual processes into the global model of the water treatment plant for operational simulation, optimization of energy costs and also for the evaluation of specific scenarios. The methodology used to design specific processes (e.g. oxidation/advanced oxidation, biofiltration, adsorption) is based on a multiphysics modeling concept using the Finite Element Method (FEM) and on the hydraulic modeling of the entire water treatment flow based on a software package (EPANET 2.0) developed by the U.S. Environmental Protection Agency (EPA). A particular application related to an integrated water treatment technology for the reduction of ammonium, Fe Mn and As as target pollutants is presented.
Conclusions: The unit process modeling approach presented in this paper and the results obtained from numerical modeling and functional simulation are used as a basis for the development of technical specifications for the development of new equipment configurations and unit processes that provide a basis for real projects.

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NEW MESOPOROUS SILICA MATERIALS LOADED WITH FERULIC ACID AS FOOD SUPPLEMENTS FOR ORAL ADMINISTRATION

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Keywords: mesoporous silica, trans-ferulic acid, food supplement

Introduction: The work consists in obtaining mesoporous silica, its functionalization and loading with trans-ferulic acid. Ferulic acid is a polyphenol with multiple biological properties that can be used in various biomedical applications, especially as dietary supplements.

Materials and methods: As a carrier, two types of mesoporous silica were proposed and obtained according to the classic templating method with cetyltrimethylammonium bromide - CTAB under alkaline conditions. The surface of the mesoporous silica was modified using 3-aminopropyl triethoxysilane, and loading of the materials with trans-ferulic acid was done under vacuum.

Results: The materials obtained were characterized by Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy, X-Ray Diffraction, Brunauer-Emmett-Teller Method and Complex Thermal Analysis - DTA-TG.

Conclusions: In this study, mesoporous silica systems loaded with trans-ferulic acid were obtained, functionalized and characterized. To study the application of the obtained systems, we performed release studies in two types of biological fluids, simulated gastric fluid and simulated intestinal fluid. Different release profiles were obtained in these release studies, which demonstrates that these systems can be used in different applications such as dietary supplements.

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PROPERTIES OF RECYCLED POLYPROPYLENE COMPOSITES WITH ALUMINO SILICATE INDUSTRIAL WASTE

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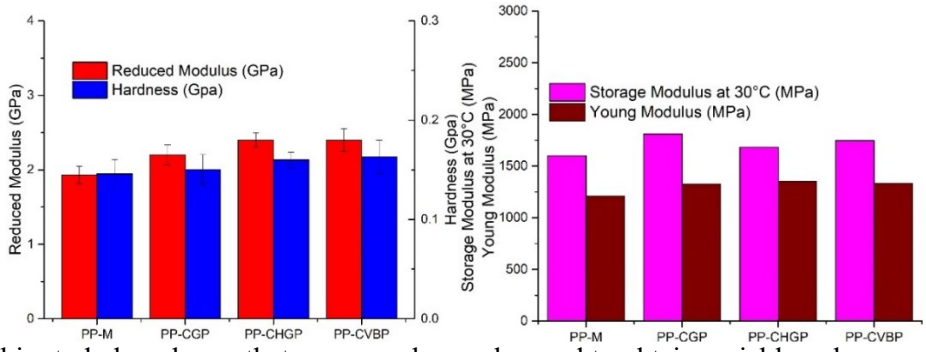
Keywords: polypropylene; aluminosilicate; nanoindentation; mechanical properties; thermal properties

Introduction: In the last decades, world governments have shown more interest in the -capacity of recycling polymeric composite materials due to the dangerous increase of waste and the pollution it causes to both nature and human health [1],[2]. Face masks represent such a waste material, especially in recent years with the onset of the COVID-19 pandemic [3]. Recycled polypropylene from recovered face masks can be easily mixed with different types of natural and synthetic (nano) fillers, resulting in polypropylene-based composites with applications in various industries. For uses in construction or the automotive industry, it is requested to improve the mechanical strength and rigidity of polypropylene. During the last 10 years, a great deal of interest has been paid to the use of fly ash (from thermal power plants), a silico-aluminous recycled material The objective of this work is to study the properties of the composites based on recycled polypropylene recovered from face masks and aluminosilicate industrial waste.

Materials and methods: Recycled polypropylene (PP) recovered from face masks, 3 aluminosilicate ashes in the form of powder with particle sizes <90 microns (2 from the thermal power plant and 1 ash from the electrofilter, resulting from the process of obtaining basalt wool) (CG, CHG, and CVB), and a dispersion agent, poly(propylene glycol adipate) (P) were used. Samples, with 5% treated aluminosilicate ash, were prepared in dynamic conditions through melt processing methods. The mechanical tensile properties of the obtained samples were tested with Instron and Zwick devices, dynamic mechanical and thermal properties were performed with DMAQ800 and TGAQ5000, nanomechanical tests were performed on a TI Premier system and structural tests were performed on X-ray Diffractometer SmartLab.

Results: Nanomechanical analysis showed an increase of reduced modulus ranging from 12 to 14% for composites with ash powder content compared to neat PP. A similar increase is observed from mechanical and dynamic mechanical properties where the young modulus and storage modulus of the composites are higher compared to neat PP. No significant change in the crystal structure of PP was detected after the addition of ash. However, the disappearance of the βcrystalline form was observed in the case of power plant ash composites. This justifies the decrease in impact strength of these composites. TGA analysis showed that the thermal stability of the composites is similar with that of the neat PP.



Conclusions: This study has shown that worn masks can be used to obtain a viable polymer matrix for further use in the industry. The addition of aluminosilicates industrial waste leads to an increase in rigidity when it is mixed through melt processing with PP from used face masks, without significantly reducing other properties. Further investigations are needed to exploit the studied materials and to find applications in an industry.

Acknowledgments: The work on this paper was supported by UEFISCDI Romania through the framework of project POC 2016 SECVENT, P_40_352, MySMIS: 105684 and the Core Program 23N?

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ADDITIVE MANUFACTURING OF BIOMIMETIC SCAFFOLDS WITH POTENTIAL IN BONE TISSUE RECONSTRUCTION

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Keywords: hydroxyapatite, barium titanate, robocasting, scaffold, bone defects, 3D printing parameters

Introduction: Bone is a material that preponderantly consists of an organic phase, an inorganic phase and cells. The organic component of hard tissue is represented by collagenic and non-collagenic proteins, while the mineral component consists mainly of hydroxyapatite. Due to its composition, hard tissue presents unique properties that enable it to self-repair in modeling and remodeling processes. This outstanding characteristic of the bone is based on its piezoelectric properties, which subsequently impact the metabolic activity. However, if the defect present in the bone structure has critical dimensions, the self-regeneration is no longer possible. In this situation, a bone graft is required. Since autografts, allografts and xenografts have their limitations, the need for a synthetic graft with adequate characteristics arises. A synthetic graft that can mimic the composition and properties of the bone could be an interesting approach. A well-known biocompatible material with piezoelectric properties is barium titanate. Therefore, a composite based on the main inorganic component of bone, hydroxyapatite, and barium titanate could lead to a material with outstanding performances [1],[2]. Simultaneously, the use of an additive manufacturing technology to process this material could facilitate the control of scaffold internal architecture. The purpose of this study is to obtain via robocasting a scaffold with potential biomimetic characteristics using a composite made of hydroxyapatite and barium titanate.

Materials and methods: Barium titanate powder was obtained via a conventional method briefly called solid-state route. To obtain the composite material, chemical precipitation was considered. Thus, hydroxyapatite was precipitated in a stable suspension of barium titanate. The obtained powder was further characterized using X-Ray Diffraction, Scanning Electron Microscopy and Brunauer-Emmett-Teller Analysis. Further on, the powder was mixed with various biocompatible additives in order to obtain a paste with rheological behavior adequate for the 3D printing process. Using 3D Bioplotter Starter Series equipment, 3D structures with various printing parameters were obtained by means of robocasting technology. The morphology of the 3D printed scaffolds was analyzed using Scanning Electron Microscopy. Additionally, a simulation of the mechanical resistance of the obtained 3D constructs was performed with the aim of predicting the appropriate relationship between the pore size, inner architecture and mechanical stress resistance.

Results: In this study, barium titanate in the tetragonal phase was obtained by the conventional method. According to the analysis, hydroxyapatite-barium titanate based powder with good characteristics for the printing process was synthesized. The obtained composite material was processed via robocasting technology. The 3D printed constructs present slight deviations from the printing parameters that have been set. Lastly, the prediction of the scaffold's behavior, at a pressure similar to the one that the cancellous bone withstands, was performed using static simulation.

Conclusions: The composite material with good characteristics was successfully obtained. The 3D structures based on hydroxyapatite-barium titanate were processed using the robocasting technology and from morphological point of view it can be said that the printing parameters of these structures were slightly modified. Finally, the prediction of the mechanical behavior indicated that the 3D structures could withstand the pressure that appears at the hard tissue level. Further investigations should be carried out to determine the biological performances of this type of scaffolds.

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PROPERTIES OF COMPOSITES BASED ON RECYCLED POLYPROPYLENE AND LIGNOCELLULOSIC AGRICULTURAL WASTE

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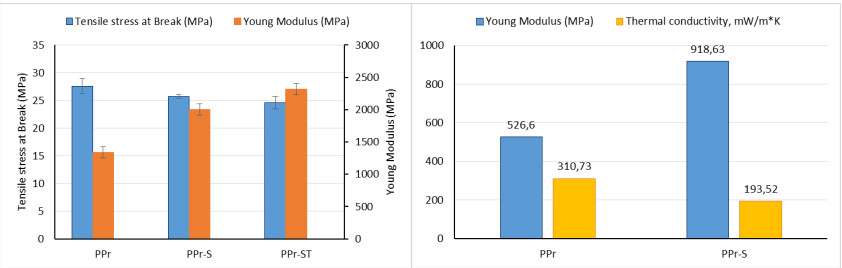
Keywords: face mask, lignocellulosic agricultural waste, PP recycled, thermal insulation properties

Introduction: The beginning of the COVID-19 pandemic has led to increased interest in the possibilities of recycling and reusing disposable face masks in new products or applications. In general, masks are made of plastic material (melt blown polypropylene nonwoven fabric). Although the amount of waste from used masks is increasing, only a small part is recycled [1]. Another large amount of waste, which creates serious management problems, both economically and environmentally, comes from the agro-industrial sector. The use of these wastes is known in the production of bioethanol, as animal feed, as fertilizer in the harvested field, as a substrate for the cultivation of edible mushrooms or as cheap biodegradable fillers to obtain thermoplastic composites with improved properties [2].

This study shows the improvement of the thermal and mechanical properties of bio-composite materials based on recycled polypropylene from used face masks and chitin-enriched sawdust from borhot-treated maize cob pellets from brewing, which can be used as construction materials.

Materials and methods: In this study we used polypropylene recycled from used face masks (PPr), as polymer matrix, polypropylene functionalized with maleic anhydride (PP-MA), as compatibilizing agent, lignocellulosic agricultural waste consisting of depleted granulated lignocellulosic substrate from *Pleurotusosteratus* culture (S) and poly (propylene glycol adipate) (PAPG), used as sawdust surface treatment agent (ST). The composites with 30% S/ST, obtained by extrusion on a double screw extruder, equisens, were processed by injection (into specimens) and by pressing (into plates). Thermal conductivity, thermal stability (TGA) and tensile mechanical and dynamic mechanical (DMA) properties were analyzed.

Results: The composites processed by injection molding are characterized by 50-80% improved stiffness, 20-40% improved thermal insulation properties and thermal stability similar to recycled polypropylene, without the maximum 11% decrease in tensile strength by a compared to recycled polypropylene. The composite material processed by pressing is characterized by 70% improved rigidity and 40% better thermal insulation properties compared to recycled polypropylene.



Conclusions: In conclusion, the obtained materials, with improved properties, easy to process into finished products by injection or pressing, recyclable and easily biointegratable at the end of the life cycle, represent a solution for the recovery of used facial masks and lignocellulosic wastes, with applications in construction.

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OBTAINING POLY(3-HYDROXYBUTYRATE) OLIGOMERS VIA THE CONTROLLED THERMAL DEGRADATION OF POLY(3-HYDROXYBUTYRATE) IN THE PRESENCE OF METAL COMPOUNDS

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Keywords: poly(3-hydroxybutyrate); thermal degradation; molecular weights; metal compounds;

Introduction: Poly(3-hydroxybutyrate) (PHB) is a natural aliphatic polyester that is usually obtained by bacterial fermentation of different carbon sources under controlled nutrition conditions. The most appealing characteristics of PHB reside in its origin from renewable sources, biodegradability, non-toxicity, and biocompatibility [1]. Additionally, its melting temperature, elastic modulus, and tensile strength, similar to those of polypropylene, and the possibility of processing PHB by all the techniques characteristic to conventional petroleum-based plastics make PHB an attractive environmentally friendly substitute for the fossil-based, non-biodegradable plastics. Nevertheless, its low elongation at break which derives from its high crystallinity, and its thermal degradation at temperatures just above its melting temperature limit the production and use of PHB at an industrial scale [1],[2]. Besides plasticization, copolymerization, and blending with a more flexible polymer, a method to improve the properties of PHB consists in the use of various nanofillers, great attention being paid in the last years to nanofillers such as metals and metal oxide nanoparticles, cellulose nanocrystals or nanofibers and montmorillonite. Very important in this case is the existence of a good compatibility between the PHB matrix and the nanofillers so that a homogeneous dispersion of the nanofiller in the polymeric matrix is obtained and an improvement in the properties of PHB is achieved. Since many bio-based nanofillers are hydrophilic, presenting low compatibility with the hydrophobic PHB matrix and the tendency to self-aggregate, the chemical modification of their surface with agents that increase their hydrophobicity or/and possess some structural similarities with the PHB matrix becomes imperative. Since the surface grafting of the nanofillers with the PHB polymer is difficult, leading to very low grafting degrees and yields due to the high molecular weight of PHB, an alternative is the use of PHB oligomers [2]. Therefore, in the present work, a simple method of obtaining PHB oligomers via the thermal degradation of PHB in the presence of different metal compounds is proposed. In addition, the characterization of the obtained oligomers in terms of chemical structure, viscosity, thermal properties, and molecular weight is also presented.

Materials and methods: PHB oligomers were obtained via the thermal degradation of PHB in the presence of various metal compounds. The thermal degradation of PHB took place at constant temperature for 10 min. The chemical structure of the PHB oligomers was examined by Fourier transform spectroscopy (FTIR), while the thermal properties of the products were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The number and weight average molecular weights (M_n and M_w) of the prepared PHB oligomers were determined by gel permeation chromatography.

Results: A decrease in the molecular weight was observed following the thermal treatment of PHB in the presence of metal compounds, proof that the thermal degradation and the cleavage of the macromolecular chains of PHB took place. The modifications in the chemical structure of PHB were highlighted by FTIR while the TGA and DSC analyses indicated changes in the thermal stability and melting behavior of PHB.

Conclusions: The thermal degradation of PHB in the presence of different metal compounds led to the obtaining of PHB oligomers with potential uses as plasticizers or agents for the surface hydrophobization of different hydrophilic fillers.

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ELECTROANALYTICAL METHOD FOR DETERMINATION OF ROSMARINIC ACID BASED ON CHEMICALLY MODIFIED SENSORS

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Keywords: rosmarinic acid; sensor; peptide; graphene oxide; cyclic voltammetry

Introduction: Rosmarinic acid (RA), as a bioactive phytochemical, endows notable pharmacological activities which can combat several diseases like cancer, diabetes, and cardiovascular diseases [1]. It has the capacity to defend the attacks of virus, reactive oxygen species and inflammation, revealing a great potential to be a therapeutic drug [2]. As a natural compound, it is difficult to assess RA in a complex system because of the interferential phenomena [3], which sets a strict requirement for the analytic methods of RA [4] . Therefore, developing rapid strategies for the sensor construction and enhancing the detective ability are of great significance for the analysis of RA.

Materials and methods: The new voltammetric sensor described in the present study was obtained using a zwitterionic peptide attached via a cross-linking agent to the surface of the screen-printed carbon electrode modified with a graphene oxide composite film. Cyclic voltammetry was used to characterize working electrodes as well as the stage of RA detection in the solution prepared with pure substance and in the solutions prepared with the cosmetic samples.

Results: We have demonstrated that the strong interaction between the immobilized peptide on the surface of the sensor and RA favors the addition of RA on the surface of the electrode, leading to an efficient preconcentration that determines a high sensitivity of the sensor for the detection of RA. The experimental conditions were optimized using different pH values and different amounts of peptide to modify the sensor surface, so that its analytical performances were maximal for RA detection. This new sensor allowed low values of the detection and quantification limit, 0.0966 $\mu mol \cdot L^{-1}$ and 0.322 $\mu mol \cdot L^{-1}$, respectively, which shows that the electroanalytical method is feasible for quantifying RA in real samples represented by three cosmetic products. The results obtained were validated by means of the spectrometric method in the infrared range, the differences between the values of the RA concentrations obtained by the two methods being under 5%.

Conclusions: A sensitive, simple, low-cost and rapid label-free peptide-modified sensor was proposed for the electrochemical determination of RA in cosmetic products. The use of cyclic voltammetry as a detection method allowed the study of RA detection, reaching excellent analytical performance applicable in electroanalysis. The approach was based on the interaction between RA from solution and zwitterionic peptide immobilized on the electrode surface. The proposed electrode is capable of distinguishing one oxidation step of RA with an improved sensitivity. The results obtained from the analysis of the three cosmetic products were satisfactory when compared with the spectrometric method indicating that RA was successfully determined. Moreover, the method can be extended to the analysis of RA on other types of samples, such as food samples, nutraceutical formulations or human serum samples, indicating it could be a promising candidate for quality control and investigation of drug metabolism.

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SOLID POLYMER COMPOSITE ELECTROLYTES FOR ALL-SOLID-STATE RECHARGEABLE LITHIUM BATTERIES

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Keywords: solid-state polymer electrolytes; Li-based batteries; ionic conductivity; ionic liquids; rigid-rod polyelectrolyte

Introduction: Polymer electrolytes have received substantial attention in the effort to revive high-energy-density Li-based batteries. In order to increase the capacity of Li-based batteries, researchers have largely focused on new electrode materials: regarding cathodes, Li–air and Li–sulfur batteries represent leading frontier candidates while at anode, Li-metal can replace graphite to increase anode energy density by approximately tenfold. Anyway, electrode advancements require an enabling electrolyte to combat irreversible reactions and dendrite growth during long-term charge/discharge cycling. In order to avoid these issues, solid-state polymer electrolytes should not only provide mechanical stiffness to block dendrites, but also should deliver safer (thermal stability without the leakage, flammability or volatility) operation compared to liquid electrolytes. Ionic liquid gel polymer electrolytes, made by immobilizing Li-salts dissolved in ionic liquids in a polymer matrix or polymerized ionic liquids have received increasing attention due to their potential applications in electrochemical devices. However, because of the trade-off between mechanical properties and ionic conductivity, the preparation of ionic liquid gel polymer electrolytes with both high ionic conductivity and robust mechanical properties remains challenging. In order to achieve high ionic conductivities in these systems, researchers have concentrated in synthesis polymerized ionic liquids with lower glass transition temperatures [1][2][3]; unfortunately, the higher ionic conductivity was achieved in detriment of mechanical properties.

Materials and methods: We have recently developed a class of solid electrolytes[4], termed solid polymer composite electrolytes (SPCE), composed of Li-salt dissolved in ionic liquids (IL) and a rigid-rod polyelectrolyte, poly(2,2′-disulfonyl-4,4′-benzidine terephthalamide) (PBDT). Dielectric measurements of the SPCE film were carried out using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer. The ionic conductivity of the SPCE membrane was measured as a function of temperature and frequency. Temperature-dependent shear storage and loss moduli (G′ and G″) were measured using an Advanced Rheometric Expansion System (ARES)-G2 rheometer from 0 to 200 °C and stress–strain tests were measured on a Inspect Table from Hegewald & Peschke (Nossen, Germany)- 1.5 kN force transducer@ 5 mm/min using DIN 53504 S3A.

Results: SPCE materials, obtained through an ion-exchange process between IL and PBDT aqueous solution, possess an unprecedented combination of high ionic conductivity (>3 S/cm @RT), high thermal stability, low flammability, and widely tunable tensile storage moduli. The SPCE materials shows ductile behavior, with significantly larger elongation at break of up to 17% where rigidity of the samples is retained up to 200^0C, which suggests that the intermolecular interactions responsible for mechanical properties in SPCE are not weakened at high temperature. Electrochemical cycling of Li/SPCE/$LiFePO_4$ shows that the specific capacity recovers almost completely when the charge/ discharge rate is slowed, demonstrating excellent electrochemical stability of the SPCE membranes @25^0C at high C rate.

Conclusions: The SPCE material fabrication platform shows promise for safe and high-energy-density energy storage and conversion applications, incorporating the fast transport of ceramic-like conductors with the superior flexibility of polymer.

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DESIGN, SYNTHESIS, MOLECULAR DOCKING AND ANTIBACTERIAL EVALUATION OF THE QUINOLONES COMPOUNDS

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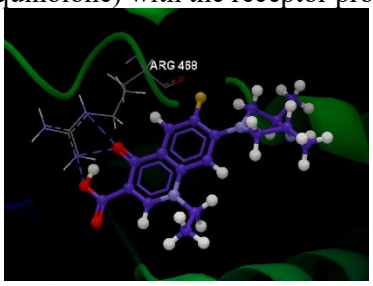
Keywords: quinolones; fluoroquinolones; drug design; molecular docking; antimicrobial activity.

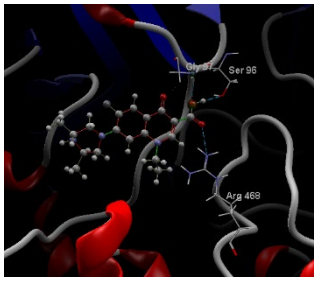
Introduction: Quinolone compounds represent one of the extensively utilized antimicrobials. In the previous decades new quinolones have been developed, such as moxifloxacin, delafloxacin and finafloxacin which possess a broader spectrum of activity and enhanced bioavailability [1]. A series of quinolone compounds have been obtained [2-5] and characterized by physico-chemical methods and antimicrobial activity against *Escherichia Coli* ATCC 8739 and *Staphylococcus aureus* ATCC 6538. Compound FPQ 55 shows a good activity against *Escherichia Coli* ATCC 8739 and *Staphylococcus aureus* ATCC 6538.

Materials and methods: ***Molecular modeling*** Molecular, topological, conformational characteristics on 3D optimized structure have been calculated using Spartan 14 Software. The DFT/B3LYP/6-31G* level of basis set has been used for the computation of molecular structure, vibrational frequencies, and energies of optimized structures. ***Docking studies*** have been conducted in order to achieve accurate predictions on optimized conformation for both, the quinolone derivatives (as ligand) and their target to form a stable complex. The protein-ligand complex has been realized based structure of Ciprofloxacin (CPF) with *Escherichia* coli Topoisomerase IV ParE 24kDa subunit which was available through the Protein Data Bank (PDB:ID 1T9U) (https://www.rcsb.org). The score and hydrogen bonds formed with the amino acids from group interaction atoms are used to predict the binding modes, the binding affinities, and the orientation of the docked ligands derivatives in the active site of the protein-receptor. The docking studies have been carried out using CLC Drug Discovery Workbench Software and Molegro Molecular Docker Software.

Results: A new series of fluoroquinolone compounds have been obtained. The compounds have been characterized by physico-chemical methods and by antimicrobial activity against Gram-positive and Gram-negative microorganisms. For the synthesized compounds have been performed calculations of characteristics and molecular properties, and molecular docking studies to identify and visualize the most likely interaction of the ligand (quinolone) with the receptor protein.



Hydrogen bonds (3) between the residues of the ARG 468 and FPQ 55 ligand (CLC Drug Discovery Workbench Software)



Hydrogen bonds (3) between the residues of the ARG 468, SER 385, and ASN 298 and FPQ55 ligand (Molegro Molecular Docker Software)

Conclusions: Some quinolone compounds were designed, synthesized, and characterized by antimicrobial activity. A correlation of the predicted data with the experimental data were observed.

Acknowledgements: *This paper has been financed through the NUCLEU Program, which is implemented with the support of MCID, project no. PN 19-41 01 02*

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3.*Section 1* - Multifunctional materials, nanocomposites, innovative technologies & cultural heritage preservation

POSTER presentations

CARBON NANOPOWDER BASED STOCHASTIC SENSOR FOR ULTRASENSITIVE ASSAY OF CA 15-3, CEA AND HER2 IN WHOLE BLOOD

Oana-Raluca MUȘAT[1*], Raluca-Ioana STEFAN-VAN STADEN[1,2], Damaris-Cristina GHEORGHE[1, 2], Ruxandra-Maria ILIE-MIHAI[2], Jacobus (Koos) Frederick VAN STADEN[2]

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Keywords: CA15-3; CEA; HER2; nanocarbon; stochastic microsensor

Introduction: CA 15-3, CEA and HER2 have a role of prognostic biomarkers and can facilitate personalized treatment for breast cancer. Early diagnosed breast cancer as well as prescribing a personalized treatment for the confirmed breast cancer patient have a major impact on the patient's health as well as closely related to test results, rapid, reliable and accurate screening [1],[2]. This paper proposed two new stochastic microsensors based on carbon nanopowder modified with gold nanoparticles and two porphyrins for the simultaneous assay of CEA, CA15-3, and HER2.

Materials and methods: Two microsensors obtained by physical immobilization of 5,10,15,20-tetraphenyl-21H,23H-porphine (TPP) and 5,10,15,20-tetrakis (pentafluorophenyl chloride)-21H,23H-iron (III) porphyrin (Fe(TPFPP)Cl) in carbon nanopowder decorated with gold nanoparticles (AuNPs) were designed, characterized, validated, and used for the molecular recognition and simultaneous ultrasensitive determination of CEA, CA15-3 and HER2 in whole blood.

Results: High sensitivities were recorded for both microsensors. Low limits of quantification were recorded for all biomarkers CEA (12.8 pg mL^{-1} by using Fe(TPFPP)Cl/AuNp, and 190 fg mL^{-1} by using TPP/AuNp), CA 15-3 (100 fU mL^{-1} for both microsensors), and HER2 (3.9 fg mL^{-1} by using Fe(TPFPP)Cl/AuNp, and 35fg mL^{-1} by using TPP/AuNp). A very good correlation between the results obtained using the proposed microsensors and ELISA certified by the Student t-test proved that the screening test can be used for ultrasensitive assay of the three biomarkers in whole blood.

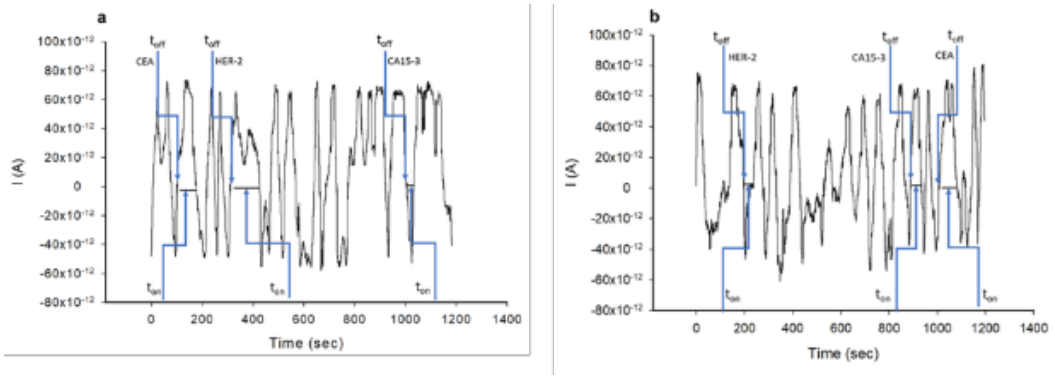

Figure 1. Pattern recognition of CA15-3, CEA and HER2 in whole blood samples, using stochastic microsensors based on: a) Fe(TPFPP)Cl/AuNp, and (b) TPP/AuNp.

Conclusions: The proposed stochastic microsensors were used for the simultaneous assay of CA15-3, CEA, and HER2 in whole blood samples. The screening test based on utilization of the two microsensors as screening tools may be used for early detection of breast cancer, for determining the need of a personalized treatment, as well as for the determination of the efficiency of the breast cancer treatment.

***Acknowledgements**: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, projects numbers PN-III-P4-ID-PCE-2020-0059, within PNCDI III and PN-III-P2-2.1-PED-2021-0390.*

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RELEASE KINETICS OF CURCUMIN FROM PULLULAN-BASED NANOPARTICLES

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Keywords: nanoparticles, pullulan, curcumin, cancer therapy

Introduction: The purpose of this study was to evaluate the release behaviour of curcumin from pullulan-based nanoparticles. Curcumin is a polyphenol derived from the rhizome of *Curcuma longa* with promising results in chemoprevention of various types of cancer such as: colon, oral, and hepatic carcinoma. However, curcumin has drawbacks like low water solubility, poor absorption, rapid metabolism, and quick systemic elimination which limit its therapeutic applicability. A solution to overcome these drawbacks is the encapsulation of curcumin in nanoparticles [1-3].

Materials and methods: Curcumin-loaded pullulan nanoparticles with high entrapment efficiency (> 85%), nanometric size (< 260 nm) and narrow polydispersity index were obtained by nanoprecipitation method. The drugs release from pullulan-based nanoparticles was determined by a dialysis membrane method under sink conditions. The whole system was kept under stirring at 100 rpm, using phosphate buffer (PBS), pH 7.4 and pH 5 as release media. The released drug in each time point was determined by spectrophotometry using a UV-VIS spectrophotometer.

Results: *In vitro* release data showed a biphasic profile characterized by an initial "burst effect" followed by a slower release reaching a maximum after 72 h (88.02 % for PBS 0.1 M pH 7.4 and 83.09 % for PBS 0.1 M pH 5), respectively. In order to evaluate the *in vitro* drug release data, various kinetics models (Zero-order, First-order, Korsmeyer-Peppas, Higuchi and Hixson-Crowell) were applied. The release was best described by the Korsmeyer-Peppas model indicating a Fickian diffusion mechanism.

Conclusions: These data shows that curcumin encapsulated in pullulan nanoparticles could represent a feasible strategy for cancer treatment. However, further *in vitro* studies on various cell lines are needed to demonstrate the therapeutic effect.

Acknowledgements: *This work was supported by Ministry of Research, Innovation and Digitalization program NUCLEU PN 1941-04 01.*

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HYDROGEL COATINGS FOR CBRN APPLICATIONS

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Keywords: peelable hydrogels, nanocomposites, CBRN, decontamination, photopolymerization

Introduction: The present study aims the synthesis and the characterization of nanocomposite hydrogel peelable films. Products referred to as "hydrogels" are a class of polymeric materials that can retain a significant amount of water in their three-dimensional networks due to their hydrophilic nature [1]. Hydrogels posses a variety of unique characteristics: tunable porosity, high swelling/deswelling abilities, biocompatibility, thus being relevant for a wide range of possible purposes, including CBRN applications [2]. The goal of this study was to obtain peelable hydrogel coatings that are able to absorb, entrap and neutralize/inactivate chemical and/or biological agents (BCA) from a targeted contaminanted surface. For this purpose, various hydrogel-generating formulations were synthesized and characterized. Two types of active nanoparticles, TiO_2 and ZnO, were incorporated in the hydrogels, in order to investigate their influence on themechanical properties, adsorptive performances and decontamination efficacy.

Materials and methods: The following materials were employed: N, N′-methylenebis(acrylamide), 2-hydroxy-4'-(2-hydroxyetoxy)-2-methylpropiphenone, N-vinyl pyrrolidone, acrylic acid, hydroxypropyl methacrylate, acrylamide, titanium dioxide, zinc oxide. The nanocomposite hydrogel films resulted via photopolymerization, and were characterized through: FT-IR, SEM, micro-CT, TEM, TGA, DMA, tensile tests, compression tests, equilibrium swelling estimations, microbiological investigations, and specific decontamination tests.

Results: The neat hydrogel films and their analogous nanocomposite hydrogel coatings, developed in this study, acquired a remarkable mechanical strength and a homogeneous distribution of the nanofillers inside the polymeric structure. Additionally, they demonstrated great adherence, nevertheless they are also easy to remove by simply peeling the coating. They exhibited quick swelling/deswelling abilities, which are crucial in decontamination procedures, for an effective entrapment of the contaminants inside their polymeric matrix. The synthesized materials managed to efficiently decontaminate the tested surfaces.

Conclusions: The unique properties of these novel photocrosslinkable nanocomposite hydrogel coatings demonstrate their potential for CBRN decontamination applications.

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HYDROGELS FOR WOUNDS CAUSED BY BLISTER AGENTS

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Keywords:blister agents, sulfur mustard, biomaterials, gelatin,hydrogels, wound management;

Introduction: Blister agents (BA) cause severe skin burns and blisters. In addition to these, respiratory and ophthalmological complications may occur. Limited studies have been done on the physiotherapy of blister-induced dermatological lesions. In the early stage, erythema and blisters are determined by the separation of epithelial cells [1]. Given the way wounds manifest, wound management (WM) represents one of the most important healthcare and financial burdens. Researchers focus their studies on the development of products able to stimulate tissue regeneration, allow for a controlled release of drugs, and emphasize the state of healing. Currently, WM products are limited to covering the wound bed. Frequently used as wound management products are hydrogels, not only for their mechanical and structural similarities with the dermal tissue but also for their ability to stimulates kin regeneration and act as drug delivery systems. Modern biomaterials used in wound allografts comprise natural origin (collagen, gelatin) or synthetic polymers (polyurethane, polyethylene glycol). Despite improved healing response and modern fabrication, natural polymers typically dissolve or present insufficient mechanical/thermal robustness under physiological conditions. To address this limitation, the biomimetic cell-adhesive and polymerizable gelatin methacrylamide (GelMA) was chemically combined with synthetic polymers to improve the hybrid properties with respect to individual components [2].

Materials and methods: In order to develop new modern biomaterials, to create and improve scaffolds for tissue restoration that can efficiently promote cell regeneration, a series of gelatin hydrogels were developed as freeze-dried porous membranes and as electrospun microfibrous scaffolds. Crosslinking was performed using glutaraldehyde.

Results: The most appealing biomaterials used in wound management are hydrogels because they can develop into 3D tissue scaffolds and promote cell regeneration. The significant potential of these materials in military applications has not yet been demonstrated, thus the aim of this study was to perform some preliminary investigations for identifying several hydrogels formulations suitable for the treatment of injuries caused by chemical weapons. Gelatin-based scaffolds with various morphology ranging from porous scaffolds obtained by freeze drying to electrospun thin meshes, as such or combined to generate layered structures with different porosity were obtained. The morpho- structural characterization was performed by scanning electron microscopy.

Conclusions: Due to their promising behavior, similar to the natural biological tissue of humans, biomaterials such as functionalized gelatin-based hydrogels, present a high potential for treating casualties related to military operations.

Acknowledgements: *This work was financially granted by the Ministry of Research, Innovation and Digitalization (UEFISCDI) through PN-III-P2-2.1-PTE-2021-0357, ctr.105PTE / 2022 and PN-III-P1-1.1-PD-2021, ctr.PD69/2022.*

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SYNTHESIS OF GOLD NANOPARTICLES USING WATERCRESS SEEDS

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Keywords: gold nanoparticles, watercress seeds, green chemistry

Introduction: The goal of this paper is based on a modern and "green" method of synthesizing gold nanoparticles with the help of natural extracts from watercress seeds, for obtaining sensing platforms with high selectivity and specificity able to detect microbial pathogens from food matrixes. Cruciferous vegetables, including watercress seeds, turnip, radish, etc. are among the agricultural crops produced in the largest quantities and their residues (seeds, leaves) have become a burgeoning environmental problem [1],[2].

Materials and methods: Hydroalcoholic extracts were obtained from watercress certified seeds through two extraction methods (temperature and microwave. Applying a method that involves the obtaining of nanostructures from plant waste highlights the importance of minimizing and reutilizing residues from primary and secondary processing via chemical and social intervention thus contributing to the sustainability needs of the planet and its inhabitants. Also, the agro-food quality will be enhanced through performant and eco-friendly detecting systems for different pathogens which alter food matrixes and transform them more rapidly into food wastes [3]. For the phytosynthesis of the gold nanoparticles (AuNPs), each extract was mixed with 1 mM aqueous solutions of chloroauric acid ($HAuCl_4$), in an Erlenmeyer flask and incubated at room temperature for 30 min.

Results:

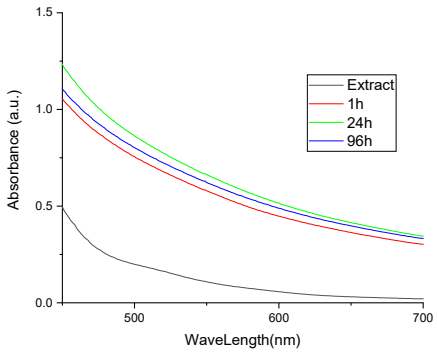

Figure 1. UV-Vis spectra of the classic extract and the corresponding NPs

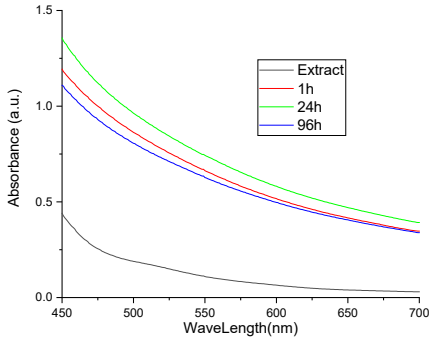

Figure 2. UV-Vis spectra of the microwave extract and the corresponding NPs

Conclusions: A horticultural circle was created to save other horticultural crops with the help of residues from horticulture. Hydroalcoholic extracts were obtained from watercress seeds through two previously established methods. These methods were successfully used for the phytosynthesis of gold nanoparticles. The obtained nanoarchitectures were investigated from the antioxidant point of view.

***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-2021-0042, within PNCDI III.*

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METHACRYLATE MODIFIED HALLOYSITE AS 5-AMINOSALICILYC ACID TRANSPORTER USED IN INFLAMMATORY BOWEL DISEASES TREATMENT

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Keywords: halloysite, 5-aminosalicilyc acid, pH sensible, inflammatory bowel disease

Introduction: There are two types of diseases that are classified as inflammatory bowel diseases (IBD), Ulcerative colitis (UC) and Crohn's disease (CD), and autoimmune pathologies that produce chronic inflammation at gastrointestinal tract level [1]. One of the oldest and most efficient types of drugs used in the treatment of IBD are aminosalicylates, especially 5-aminosalicilyc acid (5-ASA) [2]. But 5-ASA presents several disadvantages concerning its medical utilization such as low solubility in water, poor stability in solution influenced by temperature, light exposure, and pH and it's easily oxidized [3] and is rapidly and extensively absorbed from the proximal part of the gastrointestinal tract before reaching the ileum and colon causing low drug bioavailability and low efficiency for IBD being also a less efficient inhibitor of cyclooxygenase (COX) enzymes. In this regard the first solution is to create a pH sensitive 5-ASA carrier by encapsulating mesalazine within a natural clay like halloysite and then dispers it within an alginate matrix in order to obtain beads like materials. The disadvantage of this materials if that still a part of the encapsulated active ingredient is release, up to 6%, at gastric level reducing it's therapeutic effect at intestine/colon level. The aim of this study is to modify halloysite with different types of coupling agents that contain one or two methacrylate functional groups in order to obtain a drug delivery system that releases the active substance straight to intestine. This beads are characterized through modern techniques like FTIR, XPS, TGA and the release profile will be determined using UV-VIS spectrophotometry.

Materials and methods: 5-ASA was used as an active substance. Polietilen glicol metacrilate (PEGm) and polietilen glicol dimetacrilate (PEGdm) the coupling agents were used to modify the clay. Halloysite (HNT) was used as a drug carrier. The modification of halloysite with PEGm or PEGdm was realized in nitrogen. The encapsulation of 5ASA within the modified HNT was realized under vacuum.

Results: Using TGA analysis the modification of HNT with the coupling agents was demonstrated by the increase of the weight loss from 17% HNT to 21% modified HNT. The release of 5ASA was monitored in simulated gastric fluid and in simulated intestinal fluid to monitor the influence of methacrylate functional groups.

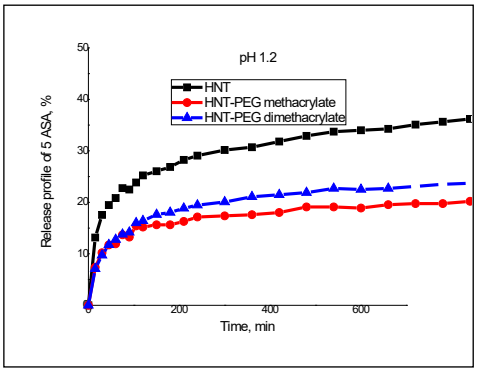

Figure 1. 5-ASA release profile in simulated gastric fluid

Conclusions: The modification of HNT with PEG-methacrylate and PEG dimethacrylate was demonstrated by different spectral (FTIR, XPS) and thermal (TGA, DSC) techniques. The EE % is not strongly influenced by the type of clay (21-28%), but if a higher amount of clay is added EE % increases at 43% in the case of Hd5. The presence of methacrylate groups of HNT surface reduces the drug release amount in SGF with 60 %.

Acknowledgements: *Executive Agency for Higher Education and Research Funding (UEFISCDI) and National Research Council (CNCS) are gratefully acknowledged for the financial support through the PN III research project 'New technology for pH sensitive hybrid materials based on halloysite and cyclodextrin for Inflammatory Bowel Diseases treatment' no. 604PED/2022.*

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INNOVATIVE CARBON MATERIALS WITH ELECTRIC AND MAGNETIC PROPERTIES

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Keywords: carbon, sensors, water purification, magnetic properties

Introduction: Magnetism in carbon structures is sometimes related to the role of metallic impurities. The iron content of the earth's crust is around 5%, whereas the carbon content is less than 0.01%. When iron impurity atoms (20–100 ppm) are uniformly distributed in the material, they cannot contribute to magnetization, due to the large interatomic distances. The magnetic effect due to the presence of iron appears when the iron content is> 68%.

Studies on carbon ferromagnetic materials obtained from various nitrogen-containing substances show that the structure of these materials is often amorphous and disordered. The magnetic properties are most likely related to the presence of various radicals, which are mainly nitroxides that exist at the edges of graphite-like structures [1]. A ferromagnetic carbon substance has never been separated, but a ferromagnetic phase typically occurs in the form of inclusions in the non-magnetic matrix.

The synthesis of organic magnetic materials involves complex chemical processes and multiple reactions, and sometimes the results are difficult to reproduce. The origin mechanism of ferromagnetism in carbon structures that do not contain metal atoms remains unclear, therefore more studies are required in this field. Organic substances are subjected to multiple pyrolysis stages, sometimes in the presence of a magnetic field, and the synthesis process is stopped halfway to graphitization. Carbon structures that contain nitrogen, boron, or phosphorus show different degrees of magnetization. Magnetic carbon structures usually contain ferromagnetic phases, due to the presence of π-delocalized spins caused by a trivalent element in the carbon skeleton.

The objective of this work is the synthesis of new carbon materials with magnetic properties. Different synthesis methods were used for carbon synthesis. The obtained carbon materials have possible applications as sensors for adsorption and medical application.

Materials and methods: Carbon powders are produced from polymer waste by thermo-chemical oxidation with mineral acids at 200ºC, carbonization at 600ºC under argon atmosphere and subsequent hydro-pyrolysis at 800ºC. Afterwards, the obtained samples are characterized by BET, XRD, SEM, and elemental analysis.

Results: The obtained carbon materials are distinguished by high surface area, proven by BET, and a high degree of graphitization, detected by XRD. Moreover, the samples also show magnetic properties.

Conclusions: The synthesized materials have as potential fields of application the efficient water purification, in medicine, and electronics.

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NOVEL PYRAZOLO-BENZIMIDAZOLE HYBRID MANNICH BASES WITH ANTIMICROBIAL AND ANTIBIOFILM ACTIVITIES

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Keywords: pyrazoles; benzimidazoles; hybrid heterocyclic molecules; cytotoxicity; antimicrobial; biofilm formation

Introduction: Both pyrazole and benzimidazole rings constitute an important class of heterocyclic compounds, which have attracted attention due to their diverse pharmacological effects, anti-inflammatory, antimicrobial, antioxidant, antidepressant, anti-influenza and anti-cancer [1–7]. The benzimidazole core attached to other heterocyclic moieties have resulted in hybrid molecules with improved anti-cancer [1] or antimicrobial action [5]. So far, the literature has not presented many hybrid type pyrazolo-benzimidazoles [1], [8]. Thus, a new series of pyrazolo-benzimidazole-type Mannich hybrid bases was synthesized, which was characterized from a physico-chemical point of view (^{1}H-NMR, ^{13}C-NMR, IR, UV-Vis, MS and elemental analysis) [10].

Materials and methods Commercial reagents were used in the synthesis of intermediate pyrazole and benzimidazole compounds. All synthesized pyrazolo-benzimidazole compounds were characterized by physico-chemical methods. The MTT method was used to determine cytotoxicity.

Results The results obtained by the antimicrobial testing of the newly synthesized hybrids showed that these compounds have superior antimicrobial activity to the mononuclear heterocycles from which they originate.

Conclusions: It can be concluded that generally synthesized Mannich bases have good antimicrobial activity and inhibit biofilm, therefore they are good candidates for therapeutic purposes.

***Acknowledgements**: Thanks for the assistance provided by Marilena Ferbinteanu from the University of Bucharest.*

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DEVELOPMENT OF PHYTOSYNTHESIZED NANOPARTICLES WITH ENHANCED BIOLOGICAL PROPERTIES

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Keywords: phytosynthesis; medicinal plants; silver nanoparticles; biological active materials.

Introduction Alongside other day-by-day uses, nanomaterials find several applications in the medical area. Among the materials of real interest in the biomedical field, silver nanoparticles managed to become one of the most promising materials, due to their structural properties and potential antifungal, antioxidant, and antibacterial effects [1]. From the synthesis methods associated with "green chemistry", phytosynthesis represents one of the most promising alternatives [2].

Materials and methods: Different parameters of the phytosynthesis protocol were investigated in order to evaluate their influence on the nanoparticles' final properties. Thus, using medicinal plants, the influence of the extraction procedure (classical temperature extraction and microwave-assisted extraction) as well as that of the concentration of the extract used in phytosynthesis on the final properties of the silver nanoparticles were studied. The extracts were characterized using phytochemical assays (total phenolics content, total flavonoid contents) and chromatographic methods (HPLC), while the resulting nanoparticles were characterized from a structural and morphological point of view (using X-ray diffraction and transmission electron microscopy), as well as for potential biomedical applications (by assessing their antioxidant and antimicrobial properties).

Results: The results revealed an increase in both the antioxidant and antimicrobial properties of the silver nanoparticles upon phytosynthesis, as well as an important effect of the extracts' concentration on the physical properties of the nanoparticles [3].

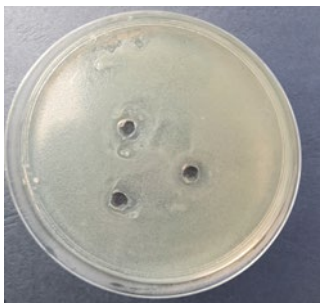

Figure 1. Antimicrobialeffect of one of the phytosynthesized nanoparticlesagainst*Escherichia coli* ATCC 8738

Conclusions: The results obtained suggest the potential of the obtained nanoparticles for biomedical applications, topical dermal applications being envisaged.

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HYBRID COATINGS FOR PROTECTING METALLIC OBJECTS WITH CULTURAL VALUE

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Keywords: hybrid materials; coatings; metallic objects; natural products; cultural heritage

Introduction:
Since ancient times, there has been an interest in protecting personal objects (such as the tools for preparing or storing the food, for hunting, etc.) against corrosion and degradation processes using natural products such as waxes, gelatins, or oils [1]. Nowadays, the interest of the researchers is directed to finding efficient solutions, based on ecological materials (cheap and "*eco-friendly*") to protect these objects from deterioration factors, objects which are now artifacts and offer us a link between past and future.
Coatings based on chemically synthesized compounds such as triazole, silanes, and fluoropolymers are replaced with a new generation of materials (nanocomposites) to act as a hydrophobic barrier [2].

Materials and methods:
The present paper is a critical discussion regarding hybrid coatings for the protection of ancient metallic objects, with emphasis on coatings obtained with the aid of natural products, especially phytoconstituents from plants.
The present paper is based on published articles (from the ScienceDirect data base) from the last ten years and presents some theoretical aspects regarding methods of extraction of natural compounds, specific compounds with anticorrosive and protective effects, and some examples regarding the application of these compounds on ancient objects with different degrees of degradation.

Conclusions:
The development of new materials with anticorrosive and protection effects must be affordable from an economic and environmental point of view, but must preserve the value of the protected object, presenting both durability and removability (reversibility).

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DEVELOPMENT OF ADSORBENT NANOMATERIALS – FROM LABORATORY TECHNOLOGY TO INDUSTRIAL SCALE DEMONSTRATOR – OXYADS PROJECT

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Keywords: adsorbent apatitic materials; water depollution; heavy metals; organic pollutants.

Introduction: Ever since ancient times, the need for potable water sources has represented an important requirement of everyday life. Particularly in the present times, when the general drought phenomenon greatly affects the available potable water sources, the need for efficient water treatment technologies becomes stringent.

Materials and methods: The pollution of the drinking water sources (surface and especially underground), with heavy metals together with the presence of arsenic (As) at concentrations above the maximum allowed limit make water sources' treatment a challenging task. Several laboratory technologies focused on the potabilization of water sources containing different pollutants were developed in the INCDCP-ICECHIM's core project [1], [2]. These technologies, alongside the published results on this topic [3],[4] , constitute the basis of the technology transfer project "Integrated technology for advanced removal of heavy metals and arsenic from complex matrices using adsorbent nanomaterials" (OxyAds), project implemented in the period 2022-2024.
The OxyAds project aims to:

- Document the industrial scale transfer of validated laboratory technology and identify the possibilities for its optimization;
- Transfer and optimize the proposed technology in the industrial environment;
- Validate the efficiency of the proposed technology;
- Demonstrate the efficiency of the technology implemented in the industrial environment.

Conclusions: The main goal of the project is represented by the transfer and the development of a technology for the depollution of water containing heavy metal and arsenic, found in a complex polluting matrix. Preliminary studies performed on water samples suggested a very good ability of the developed materials to perform as efficient adsorbents in the targeted matrix.

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TAILORING PROTECTIVE COATINGS FOR THE PROTECTION OF CULTURAL HERITAGE INORGANIC OBJECTS – InHeritage PROJECT

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Keywords: cultural heritage; inorganic materials; consolidation; self-cleaning; anti-microbial effect.

Introduction: The field of cultural heritage represents not only an important socio-economic resource [1], but its current state of preservation also represents an indicator of the civilization and awareness of a particular nation [2]. Thus, the need to develop tailored formulations, validated thorough scientific studies, for the protection, preservation, and restoration of cultural heritage objects becomes of particular importance.

Materials and methods: Given the background of the consortium [3-5], the project "Innovative multifunctional composites for the protection of cultural heritage objects" (InHeritage), implemented in the period 2022-2024, aims to develop multi-component materials having several functions (consolidation, self-cleaning and anti-microbial) for the protection of inorganic substrates.
The particular consolidants, tailored for each type of substrate, will ensure the best compatibility with the treated artifacts. The final composites will also encompass an antimicrobial phase (to provide a prolonged protection against biodeterioration), while the self-cleaning and photocatalytic coatings will also contribute to the final protection of the treated objects.
Collaboration agreements were already signed with several Romanian museums, in order to access different types of cultural heritage objects of inorganic nature, which will be subjected to preliminary evaluation and further employed as supports for the application of the developed treatments.
After the evaluation of the targeted materials collected from the museums, model artifacts were obtained, in order to preliminary asses the solutions developed in the project.

Conclusions: Multipurpose composites will be developed by the consortium in the timeframe of the project and their efficiency will be demonstrated by their application on both simulated and real artifacts.

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A NEW COMPOSITE BASED ON PYRENE THIAZOLE AND GRAPHENE OXIDE-SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL EVALUATION

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Keywords: pyrene thiazole; graphene oxide; carbon screen printed electrodes, electrochemical evaluation

We describe the obtaining of a new and innovative material starting from pyrene thiazole and graphene oxide for physicochemical characterization and electrochemical evaluation. The synthesis protocol *was achieved by activating the carboxylic groups on the surface of graphene oxide using the reaction with thionyl chloride followed by the coupling with the amino group of pyrene thiazole to obtain the new material named GO-PTC.*

Numerous characterization methods have been used to certify this material, such as IR, Raman spectroscopy, fluorescence, X-ray photoelectron spectroscopy, scanning electron microscopy, and *transmission electron microscopy.* The electrochemical investigation consisted of evaluating the redox behavior of the carbon-screened electrodes modified with GO-PTC, using the caffeic acid as an analyte (linear working range: 0.005 - 0.1 mM).

Also, investigations revealed that modifying the screen-printed electrodes with the GO-PTC showed a quasi-reversible redox the peak separation of (ΔEp) is being 90 mV. The redox couple is pH dependent and the electron transfer is coupled with the transfer of one proton.

From the analytical point of view, it is important to be able to quantify the presence of the analyte, and for this reason, we can consider that GO-PTC modified carbon screen printed electrodes could be considered promising for other electrochemical investigations.

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NEW COSMETIC FORMULATIONS OBTAINED BY APPLYING INTEGRATED AND SUSTAINABLE BIOECONOMY APPROACHES – BioProtect PROJECT

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Keywords: cosmetic formulation; grape waste; bioeconomy; natural compounds, UV blocker.

Introduction: Chronic exposure of human skin to solar UV radiation is widely recognized as the key factor responsible for photo-ageing. For this reason, photoprotection plays a crucial role in avoiding skin cancer and other undesired effects. Many phenolic compounds have been identified in grape pomace, where the most abundant are anthocyanins, hydroxybenzoic and hydroxycinnamic acids, flavan-3-ols, flavonols and stilbenes, which can possess therapeutic properties such as anti-ageing, antioxidant, UV filter activity etc.

Materials and methods: Based on the experience of the consortium [1-4], the project "Formulations of protective cosmetic products obtained by applying integrated and sustainable bioeconomy approaches - BioProtect" will be implemented in the period 2022-2024, and proposes the use of nanomaterials both as active ingredients and as delivery systems for bioactive compounds (mixtures of phenolic compounds-rutin and quercetin) recovered from grape industry by-products, for the 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 substituted hydroxyapatite (with Fe - FeHAP). The use of FeHAP has a double role: active ingredient with UV protection properties and delivery system for the bioactive molecules.

Results: The experiments carried out regarding the extraction and separation of bioactive compounds from grape marc showed that the type and amount of compounds obtained are strictly dependent on the type of solvent used and on the variety of grapes. Extracts rich in flavonoids are obtained when organic solvents (ethanol, acetone) or their aqueous solutions, but with a high organic solvent content (70-90%), are used as solvents for extraction.. Preliminary studies carried out by incorporating 5-15wt% extracts into a natural cream base (ELEMENTAL) and analyzing the UVA sun protection factor of the resulting products via the COLIPA method [5], showed $SPF_{in\ vitro}$ values between 5 and 20, depending on the amount of extract added.

Conclusions: Therefore, this combination will be also able to enhance the sunscreen efficacy by protecting against photo-degradation and by boosting the target tissue endogenous defense from UV-driven inflammation.

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DIRECT SYNTHESIS OF BIMETALLIC SYSTEM USING NANOSILICA AS SUPPORT

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Keywords: bimetallic system; catalyst; nanosilica

Introduction: Nanosilica-type MCM-41 represents a versatile material applied in various domains, such as catalysis (as support), pharmacy (drug delivery) or gases separation and wastewater treatment (as membranes or adsorbents) [1]. Nowadays, the use of heterogeneous catalysis instead of liquid acid catalysts has become a useful tool in the development of more environmental-friendly reactions [2]. One of the most used methods to use MCM-41 as support for catalysts obtaining is the replacement of some Si atoms with transition metals, such as Cu. Promoters such as Zn have been successfully applied in order to increase the stability of Cu-based catalysts, the metals interaction conducting to the decrease of reaction temperature. In this study, one direct synthesis method starting from an organic silicate is presented.

Materials and methods: Tetraethylorthosilicate (TEOS) and hexadecyltrimethylammonium bromide was dispersed in ultrapure H_2O, the mixture being stirred for 1 hour at ambient temperature, after which it was heated up to 70 °C. When this temperature was reached, 2M NaOH was added and stirring was continued at 70 °C for one hour. Then $Cu(NO_3)_2$.2.5 H_2O and 0.364 g $Zn(NO_3)_2$.6 H2O (dissolved in a minimal amount of ultrapure water) were added. After approximately one hour, the mixture was filtered, washed with ultrapure water, methanol and acetone, dried under vacuum and at a temperature of 80 °C, resulting in a blue precipitate. After calcination at 550 °C for 6 hours, a sandy gray precipitate resulted. The material was characterized by SEM-EDS, FTIR, specific surface and pore-size distribution, as well as elemental and AAS analysis.

Results: The content of Cu and Zn was determined by atomic absorption spectrometry (AAS), resulting 4.06 wt.% Cu and 0.89 wt.% Zn. Once the metals were introduced, the specific surface area of the support decreased, to 798 m^2/g, and the average pore diameter was 2.97 nm. The bimetallic system presented morphology with spherical and partially elongated particles, with the maintenance of the ordered morphology typical of MCM-41. Metals interactions increased the distortions of the silicon-oxygen tetrahedron, conducting to a pronounced asymmetry. After metals introduction, the typical FTIR spectrum of the MCM-41 suffered some changes: a shoulder appeared at 577 cm^{-1}, assigned to Si-O-metal vibrations, which indicated that Cu species were successfully impregnated on MCM-41. The introduction of metals was also confirmed by the disappearance of the peak at 615 cm^{-1}, confirming the positioning of the metal on the silica surface.

Conclusions: The introduction of Cu species positively affects the physicochemical properties of MCM-41 mesoporous silica, increasing its efficiency as catalysts. Furthermore, the addition of Zn increased the acidity of the system by providing active sites and improving the bond breaking capacity and deoxidation performance. The new obtained bimetallic system can be applied in various reactions, such as: aromatization, decarboxylation, decarbonylation, dehydration, or Diels – Alder reactions.

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POLY (UREA-URETHANE) / MULTIWALL CARBON NANOTUBES NANOCOMPOSITES FOR DEFENCE APPLICATIONS

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Keywords: polyurethane, polyurea, MWCNT, nanocomposites

Introduction: This study describes an efficient method for obtaining various types of polyurea-polyurethane matrices and analogous polyurea–polyurethane-multiwall carbon nanotubes (PU-PUR-MWCNTs) nanocomposites, generally suitable for defence industry products, but also for other fields. New applications are being discovered for both the thermoplastic elastomer polyurethane and the elastomeric thermoset polyurea [1]. Polyurethane-polyurea based formulation can be used to develop coatings with excellent protection against moisture, abrasion, corrosion, or chemical attack [2] and as binders in various formulations (e.g. solid rocket propellants [3], or other energetic materials). Additionally, PU-PUR-MWCNTs nanocomposites attracted interest due to their exceptional qualities, which are important in the development of novel materials for applications requiring superior mechanical resistance (e.g. ballistic protection coatings). To find the appropriate formulation of specific polyurea–polyurethane based products, designed for defence industry, our work was focused on the variation of the chemical composition of the polymeric matrix and the type of functionalization chosen for MWCNT. The innovative materials developed in this study mainly targeted two research directions: coatings for ballistic protection and binders for solid energetic formulations.

Materials and methods: Commercial polyol Setathane®D1160 or polyester-polyol blends (resulted from post-consumer PET bottles degradation) and a commercial polyisocyanate (Desmodur® 44V20L) were employed for obtaining several binder formulations, which were subsequently examined through specific thermal (DTA and TGA) and mechanical investigations (DMA, tensile test, etc.). Two types of Poly (propylene glycol) bis(2-aminopropyl ether), Mn 2000 Da and 4000 Da, were combined with various chain extenders and polyisocyanate to obtain polyurea and hybrid poly(urea-urethane) coatings for ballistic protection purposes. MWCNT with distinct types of functionalization were utilized for obtaining the PU-PUR-MWCNTs nanocomposites.

Results: The synthesized polyurea-polyurethane-based binders demonstrated that they can enhance the thermal performances of the energetic formulations, while their high flexibility ensures resilience and superior mechanical resistance. Polyurea-based nanocomposite coatings demonstrated their suitability for ballistic applications, owing to their high capacity of absorbing energy, hence protecting the structure on which they are applied. Dynamic regime tests confirmed that the nanocomposite allowed the coated metal sheets to preserve their integrity.

Conclusions: Novel poly(urea-urethane)-based binders and coatings were successfully synthesized and characterized through numerous analytical techniques. The unique set of properties of polyurea-polyurethane matrices and the multiple advantages of using MWCNTs demonstrated the suitability of these innovative materials not only for military industry, but also for other civilian applications.

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POLYVINYL ALCOHOL/SODIUM ALGINATE/NICKEL (II) PHTHALOCYANINE ACTIVE PEELABLE HYDROGELS FOR DECONTAMINATION

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Keywords: polyvinyl alcohol, sodium alginate, nickel phthalocyanine, decontamination, chemical and biological agents

Introduction: This paper proposes a new approach for obtaining active peelable hydrogels for the fast and efficient removal of biological and chemical agents from contaminated areas. The necessity to developing a new technique for the neutralization and elimination of biological and chemical agents (BCA) has gained special attention due to the extremely important issues related to the terrorist interests / threats regarding the utilization of chemical, biological, radiological, and nuclear (CBRN) agents. This can also be extended to environmental protection, because it is preferable to use non-toxic materials that do not affect the environment in the decontamination process and do not damage the surface on which they are applied [1], [2]. The novelty of this study resides in the novel method proposed for BCA active decontamination, using non-toxic water-based polyvinyl alcohol/sodium alginate/nickel phthalocyanine peelable hydrogels which have the ability to inactivate/neutralize and entrap the contaminants (and/or their degradation products).
Materials and methods: The following materials were employed: polyvinyl alcohol, sodium alginate, nickel (II) phthalocyanine-tetrasulfonic acid tetrasodium salt, titanium dioxide, deionized water, and zinc acetate. The peelable hydrogels resulted through the generation of new bonds between alginate chains, via ionic crosslinking method. The decontaminating solutions were subjected to viscosity measurements and the properties of the resulting peelable hydrogels (obtained via multivalent cation crosslinking) were investigated by FT-IR, thermal analysis, and mechanical analyses (shear, compressive and tensile tests). Their performances in decontaminating metallic and glass surfaces were evaluated through specific chemical and biological decontamination tests.
Results: Three types of new decontaminating aqueous solutions containing hydrophilic polymers (polyvinyl alcohol and sodium alginate), a reactive-oxygen-species generator (hydrosoluble nickel phthalocyanine derivate), active nanoparticles (titanium dioxide) and a reinforcing agent (bentonite nanoclay) were applied on the contaminated surfaces. An UV-lamp was employed to facilitate the generation of reactive oxygen species and the neutralization of the contaminants. For the entrapment of the degradation products in the polymer-clay system, a zinc acetate aqueous solution was sprayed over. After curing, these formulations turned into strippable gels that could be easily removed from the decontaminated surface.

Conclusions: Decontamination tests revealed that herein reported formulations exhibited a high efficiency in entrapping and neutralizing the BCA contaminants.

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'ECO-FRIENDLY' FORMULATIONS FOR CBRN DECONTAMINATION

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Keywords: nanocomposite films, decontamination, chemical and biological agents

Introduction: Decontamination plays a vital role in biological, chemical, radiological and nuclear (CBRN) defence. The present work comprises a series of 'eco-friendly' formulations designed for the decontamination of CBRN agents. These decontamination solutions possess the ability to entrap contaminants (or their degradation products) and generate strippable films [1], [2] which can be easily compacted andremoved. Depending on the target contaminant, decontamination formulations contain various types of active nanoparticles/active ingredients that provide significant improvements on their efficiency in contaminant removal.

Materials and methods: The decontamination formulations were obtained by employing the following materials: hydrophilic polymeric matrices (polyvinyl alcohol, sodium alginate, gelatin), various types of nanofillers (Ag, Cu, ZnO, TiO_2, bentonite), 'green' chelating agents (2-phosphonobutane-1,2,4-tricarboxylicacid, iminodisuccinic acid), plasticizer (glycerol) and distilled water as solvent. Depending on the type of CBRN agent expected to require decontamination, the composition of the solution employed may vary. The solutions designed for decontamination were subjected to rheological measurements, evaporation rate tests and the resulting nanocomposite films were analyzed via FT-IR, SEM-EDX, TEM, thermal analyses (DTA, TGA), mechanical analyses (single cantilever DMA, tensile tests). Decontamination efficiency was calculated, according to the type of contaminant: AAS (for heavy metals), radiometric measurements (for radionuclides), GC-MS (for chemical agents) or microbiological investigations (for biological contaminants).

Results: Novel environmentally friendly decontamination solutions were successfully prepared. These formulations were able to entrap heavy metals and radionuclide contaminants and neutralize/inactivate and entrap chemical and biological agents. For the tested micro-organisms, the decontamination efficiency varied between 93% and 97%, while for the chemical agent sulfur mustard the maximum decontamination factor obtained was 90.89%. Nerve agent simulant (Dimethyl methylphosphonate, DMMP) was almost completely removed from the contaminated surfaces (99.97%). The nanocomposite films revealed high decontamination efficiency for heavy metals (approx. 95–98%) and for radionuclides ^{241}Am, ^{90}Sr-Y and ^{137}Cs (approx. 91–97%).

Conclusions: The particularity of these decontamination solutions consists of their environmentally responsible formulations, their ability to form highly resistant and elastic strippable nanocomposite films, and their high potential to entrap and neutralize CBRN contaminants.

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THE INFLUENCE OF CETRIMONIUM BROMIDE SURFACTANT ON THE PHOTOCHEMICAL DEGRADATION OF $PbCrO_4$

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Keywords: lead chromate, precipitation, colorimetry, photodegradation

Introduction: Crystallized lead chromate is an inorganic compound well known as "chrome yellow" and which was widely used as a yellow compound in paints or in decorative systems [1].The photodegradation has a significant influence on the preservation of old paintings. The aim of this work is to emphasize the influence of the addition of different amounts of cetrimonium bromide (CTAB) surfactant on the photochemical degradation of lead chromate ($PbCrO_4$).

Materials and methods: Lead chromate nanorods were prepared via precipitation technique, based on the reaction between Na_2CrO_4 and $Pb(CH_3COO)_2$ using different amounts of surfactant [2],[3]. After applying the samples on canvas and exposing them to natural sunlight (100 nm < λ <400 nm), the colorimetric parameters, L, a, b were measured using a Konica Minolta colorimeter, and the FTIR spectra have been obtained with a FTIR spectrometer GX (PerkinElmer, Waltham, SUA).

Results:
The FTIR spectra reflect specific bands (847-885 cm^{-1}) assigned to CrO_4 groups from the chemical structure of these pigments [4]. The broadening of the carbonyl group with the characteristic peak at 1738 cm^{-1} shows the initiation of the photodegradation process, in good agreement with the literature [5].
It was observed that after exposing the sample for 50 hours to the sun, the "L" value for the sample with the maximum amount of CTAB decreases by 2.96%. By comparison, the sample with the minimum amount of CTAB has the "L" value 3.39% lower. The "b" parameter for this sample showed a smaller decrease after 50 hours of exposure, with only 12.81%.

Conclusions:
Based on FTIR and colorimetric measurements, it could be concluded that the sample with the highest amount of surfactant presents better stability at photodegradation.

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PET VALORIZATION BY ENZYMATIC DERIVATIZATION OF PET SURFACE: POTENTIAL FOR BIOSENSORS?

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Keywords: ***PET valorization, Enzimatic derivatization, Biosensors***

Introduction: Plastic waste accumulation has been growing in recent years and it became one of the most severe environmental and social issues. The research community has already started to search for new alternatives to plastic valorization. The general strategy of this issue is actually chemical/biochemical transformation [1].
We proposed a different strategy for biocatalytic modification of PET in order to offer new value-added perspective of plastic materials in the context of a cyclic economy. In this context, different methods of PET pretreatment coupled with biochemical modification of PET surface were tested evaluating as valuable strategies. The BHET model was used to set up the optimum experimental conditions of the developed system. Application of derivatized PET for designing immobilized enzymes will be presented [2].

Materials and methods: Three different methods were used for the derivatization:
1) Reaction of PET with DMC (0.01 g PET, 500 µL DMC, 500 µL Tris hydrochloride, and 1 mg of enzyme Novozyme 425).
2) Reaction of PET/BHET with thiols (0.001 g of BHET reacted with 25 mM of each thiol, 1000 µL Tris hydrochloride, and 1 mg of enzyme Novozyme 425-for BHET reaction- and 0.01 g of PET with 90 mM of thiols, 1000 µL Tris hydrochloride and 1 mg of Novozyme 425-for PET reaction).
3) Reaction of PET/BHET with aniline (100 µL peroxidases (1mg/mL) were put in reaction with 894 µL Tris hydrochloride, 5 µL H_2O_2, 1 µL aniline and 0.001 g BHET-for BHET reaction- and 0.01 g PET, 5 µL H_2O_2, 9 µL aniline and 886 µL Tris hydrochloride-for PET reaction).
Analysis of the liquid phase after PET derivatization was performed using the HPLC-DAD method. In this way, the process efficiency was evaluated monitoring the reaction products. Additionally, the characterization of the PET surface after derivatization has been done using the FTIR technique. Identification of a new band in the PET spectrum after derivation was clear evidence of the success of the derivation approach. Based on the experimental data, optimum experimental conditions were set up for developing new materials such as derivatized PET useful for the preparation of a stable entrapped cavity of immobilized enzyme.

Results: PET powder/film treated with 5 pre-treatment methods were tested for derivatization with DMC. The best results were obtained for the PET powder exposed to a UV lamp for several days in the dark and under H_2O_2 action and set up as optimum experimental conditions.
Derivatized PET surfaces were characterized using FTIR analysis. Excepting the reaction with aniline when no new bands were observed, for the thiol and DMC methods, new bands were seen noticed for N-H, S-C, and C=O bonds for the thiol reaction and carbonyl/carboxyl bands for the DMC reaction. In this way, the success of the derivatization methods was demonstrated. Derivatized PET was used to prepare immobilized lipase based on the entrapment strategy using sodium alginate and k-carrageenan.
Seeing the good results that were obtained for the derivatization of PET with thiols, another application for this type of reaction can be improving the electrochemical biosensors with thiols for raising their stability [3].

Conclusions: New derivatization methods based on biocatalysis have been developed for PET leading to the insertion of -NH_2, -SH, or -CO groups into the PET surface. In this way, modified PET will be a good candidate for stabilizing the polysaccharide (alginate/carrageenan) cavity prepared for enzyme immobilization. Enzyme stabilization would be a good asset for developing high-performance biosensors.

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SELECTIVITY IMPROVEMENT OF THE INHIBITION-BASED BIOSENSORS. APPLICATION TO ALDEHYDE DEHYDROGENASE-BASED DETECTION OF THIRAM

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Keywords: selectivity; enzyme; electrochemical biosensors; inhibition; pesticides

Introduction: Selectivity is a major issue for biosensors, in particular for the enzymatic ones due to the large spectrum of recognized substances by the biocomponent. There are various strategies to improve or circumvent the selectivity issue, ranging from the simple repurposing of the biosensors to detect an entire class of compounds instead of a single analyte or limited usage into samples with known simpler matrix to the complex combination of data obtained from different enzymes/biosensors/kinetic mechanisms for a better characterization of the sample. From the later cases, we discuss the determination of L-cysteine using tyrosinase (Tyr) biosensor [1] and the detection of β-Carbolines [2]. Preliminary results for the detection of thiram on vegetables' surface are also included.

Materials and methods: The inhibition by thiram of a novel aldehyde dehydrogenase from the Antarctic bacterium Flavobacterium PL002 was studied by spectrophotometry. The enzyme was immobilised on carbon nanofiber-modified electrodes by cross-linking with glutaraldehyde. In a second approach, a carbon nanotube electrode was modified with magnetic particles coated with Ni-nitrilotriacetic acid complex and the histidine (His)-tagged enzyme was immobilized by Ni-His affinity. A tomato was spiked with thiram solution and after drying, the thiram was recovered and tested with aldehyde dehydrogenase.

Results: L-cysteine was determined using a tyrosinase (Tyr) biosensor without interferences from thiolic compounds based on a combination of two mechanisms all thiols including the analyte react with the enzymatically produced quinones while Tyr is inhibited only by the xenogeneic thiols. Another example is the detection of β-Carbolines, which are inhibitors of two type of monoamine-oxidases (MAO-A and MAO-B) with different specificities: all β-carbolines inhibit MAO-A, while only norharmane MAO-B. Thus, two biosensors were able to evaluate both the total content of β-Carbolines and the concentration of norharmanein presence of other β-carbolines. The determination of thiram based on the inhibition of aldehyde dehydrogenase was confirmed by spectrometry. Thiram recovered from the surface of a spiked tomato was succesfully determined. F-ALDH biosensors were obtained by immobilizing the enzyme on the surface of a CNF or CNT electrodes by cross-linking with glutaraldehyde [3] or by Ni-His affinity. The selectivity towards thiram will be explored by coupling the test with Raman spectroscopy detection [4].

Conclusions: Inhibition-based enzymatic biosensors are valuable analytical tools for determining pesticides. Selectivity is a critical issue to advance from lab concepts to real world applications.

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FILM-FORMING PROPERTIES OF ENZIMATICALLY HYDROLYSED CORN STARCH

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Keywords: enzymatic hydrolysis; corn starch; films; packaging

Introduction: Currently there is an increased demand for environmentally friendly materials for the food packaging industry, with the aim of reducing the use of synthetic films. Biopolymers films based on native starches have received considerable attention in the last years because they are known as renewable resources, are highly available at a low price. Native starches can be physically and/or chemically modified by different methods, thus being able to improve their film-forming properties. The main advantage of this type of biopolymer films is the ability to be totally biodegradable in a short time. Native corn starch can be enzymatically hydrolysed in order to improve its functionality [1],[2]. The aim of this study was to evaluate the film forming properties of enzymatically hydrolysed corn starch using glycerol as plasticizer.

Materials and methods: Corn starch (SCM Colin Daily, Romania) was enzymatically hydrolysed with α-amylase, from *Bacillus amyloliquefaciens* (A7595, Sigma-Aldrich) based on the method described by Kong H et al. (2018) with minor modifications [3]. Hydrolysed corn starch films were developed by solvent casting technique. The effect of glycerol content ratio (1:1, 1:2 and 1:3 based on the dry basis of hydrolysed corn starch) on the film-forming properties was also investigated. The surface morphology, barrier, hygroscopic and optical properties were investigated. The hygroscopic properties such as: moisture content, moisture adsorption, swelling index and solubility were determined according to the methods described by Kumar R et al. (2020) [4]. Water vapor permeability (WVP) was measured by a gravimetric method according with the protocol described in ASTM E96 [5]. The optical properties, opacity and light transmittance were evaluated using a spectrophotometric method according with Lopez OP et al. (2007) [6]. The surface and cross sections of the obtained films were observed with a scanning electron microscope (SEM) according to Caba et al. method [7]. FTIR analysis was carried out according with Liu F et al. (2020) protocol [**Error! Bookmark not defined.**].

Results: The results obtained for the hydroscopic properties increased with the content of glycerol. The hydrolysed corn starch films enriched with a ratio of 1:2 glycerol (content based on the dry basis of hydrolysed corn starch) presented enhanced film properties like moisture content (25 %), moisture adsorption (0.0028 %), solubility (45 %), swelling index (38%), WVP (0.445 g.mm/ m^2.h. kPa) compared to the other obtained films. The determined values for the optical properties were in accordance with those obtained in Miao Z et al. study (2021) [8]. SEM images confirmed that the obtained films were smooth and shiny.

Conclusions: The hydrolysed corn starch films obtained with a glycerol content ratio of 1:2, presented good film properties especially the hygroscopic and barrier properties, compared to other corn starch films.

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BIOMATERIAL COMPOSITE WITH THERAPEUTIC ACTION

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Keywords: gelatin; vegetal extract; hydrogel; cytotoxicity

Introduction: This paper presents a method for elaboration and characterization of gelatine hydrogels coupled with vegetal extracts. Cucurbita pepo are frequently used in therapeutics for their anti-inflammatory, antioxidant, vitamin (A , B9), enzymes and mineral contents. In this sense, hydroalcoholic vegetal extracts at concentrations of 20% and 50%, were prepared and included in gelatine gels 1.5%

Materials and methods: The biocompatibility was evaluated by MTT assay with mouse fibroblast cell culture type NCTC (L 929), spectrophotometric method for determination of cytotoxicity.

Results: *In vitro* biocompatibility test: Biological test for evaluating material cytotoxicity indicated that samples ware non-toxic to testing cells. All biomaterials are a good biocompatibility.

Morphology observations: The morphological testing of the samples from this experiment shows that, at the concentration of 50, 100 and 250 µg/ml, they are not cytotoxic, no changes are observed in the morphology and cell density, the samples being similar to the control culture (MC), specific to the NCTC cell line.

The results obtained from the application of the MTT test demonstrate that the hydrogels do not release cytotoxic compounds, and therefore the hydrogels could be examined in the future for a number of additional biomedical applications.

Conclusions: The obtained results showed that the biomaterials can be considered promising candidates for biomedical applications.

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NITRITE DETERMINATION IN SOIL USING A MINIATURIZED FLEXIBLE NANOMATERIAL-BASED SENSOR

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Keywords: nitrite; nanocomposite; soil solution; lysimeter

Introduction: Nitrite represents an essential plant nutrient and an important part of the plant nitrogen cycle. Its accumulation in soils can lead to eutrophication bodies of water and growth of toxic algae and nitrite is also harmful to animals and humans in large concentrations [1],[2]. Miniaturized electrochemical sensors modified with nanocomposite materials are promising tools for fast and sensitive detection of nitrite levels in the environment.

Materials and methods: Screen-printed flexible carbon electrodes (SPEs) were modified with nanomaterials based on carbon nanotubes. Several matrices of incorporation were studied, in order to ensure a high stability of the functional material at the sensors surface. Thus, sol-gel, Nafion or polymeric film were used to enhance the stability of the immobilized material. Cyclic voltammetry (CV), amperometry and electrochemical impedance spectroscopy (EIS) were used to characterize and to optimize the developed sensors, and the surface morphology of the active surfaces was investigated using SEM and FTIR techniques.

Results: CV measurements in acetate 0.1 M and PBS 0.1 M, pH ranging from 4 to 8 showed a decrease of the oxidation potential of nitrite on the nanomaterial-modified sensors compared to the bare ones. Amperometric measurements revealed a high sensitivity for nitrite oxidation at the developed nanomaterial-based sensors, at an acceptable working potential. The linear range extends up to 2 mM, and the detection limit drops below 10 μM. SEM studies showed a uniform distribution of the nanomaterials which confirm the formation of the stable active layer at the surface of the sensors. Nitrite levels were electrochemically detected using the soil solution extracted with a suction lysimeter.

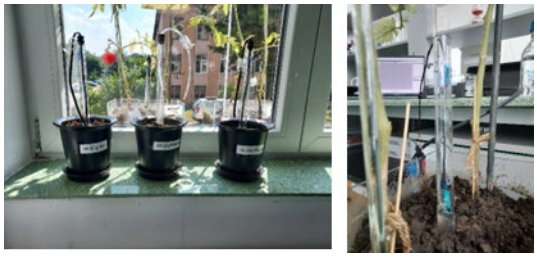

Figure 1. Direct detection of nitrite in soil solution.

Conclusions: The developed flexible miniaturized sensors showed good performances in detection of nitrite in soil solution samples. A decrease of working potential has been achieved by functionalization of the working surfaces with nanomaterials based on carbon nanotubes, which significantly improves the analytical performances of flexible developed sensor for nitrite detection.

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BIOGENIC AMINES - FROM IDENTIFICATION AND ISOLATION OF THEIR PRODUCING MICROORGANISMS IN FOOD SAMPLES TO DIFFERENT DETECTION APPROACHES

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Keywords: biogenic amines; bacterial strains; food; nanocomposites

Introduction: Biogenic amines (BAs) are compounds generated from the biochemical or microbial degradation of amino acids, with harmful effects for humans [1]. The accumulation of BAs in food occurs due to microorganisms that possess amino acid decarboxylase activity, such as *Escherichia, Enterobacter, Pseudomonas, Salmonella*, *Shigella, Clostridium perfringens, Streptococcus, Lactobacillus* and *Leuconostoc* [2]. BAs such as histamine, putrescine and cadaverine are important chemical indicators of bacterial spoilage in food- products, namely meat, fish and cheese products.

Materials and methods: For microbiological assays, the food samples, such as cheese, meat (chicken) and fish (trout) were crushed and homogenized with buffered peptone water. The mixtures were incubated in a rotatory shaker, followed by inoculation on specific media, in order to isolate aerobic mesophilic bacteria, lactic acid bacteria (LAB), enterococci, yeasts and molds, enterobacteria. For putrescine, cadaverine and histamine determination different approaches were studied using electrochemical sensors modified with nanocomposites materials. Thus, different electrode supports were used to characterize and optimize the amperometric detection. Cyclic voltammetry (CV), amperometry and electrochemical impedance spectroscopy (EIS) were used to characterize the electrochemical properties of the modified sensors. The surface morphology of the functionalized active surfaces was studied using SEM and FTIR spectroscopy. Mono- and bi-enzymatic systems were approached in the development of biogenic amines-based biosensors, using Diamine oxidase (DOA) and horseradish peroxidase (HRP).

Results: Microbial colonies were purified by subsequent subcultures and colonies with different shapes and colors were selected for further analysis, in order to identify the microbial strains. Identification of bacteria strains was done using specific microbiology tests including Gram-staining for detecting morphology and biochemical tests. The development of biosensors for biogenic amines detection was achieved using different strategies for enzymes immobilization. The entrapment of enzymes in the sol-gel matrix demonstrated to be the most appropriate method for ensuring a stable and sensitive determination of putrescine, cadaverine and histamine. EIS measurements on modified and unmodified SPEs showed that metallic nanoparticles used in preparation of nanocomposite material improved the electron transfer to the sensors surface. Thus, the nanomaterial enhances the electrocatalytic properties of the sensor. The detection of putrescine, cadaverine and histamine was achieved in less than 15 seconds using biosensors based on carbon nanotubes and Pt nanoparticles, at an applied potential of -0.2 V vs Ag/AgCl.

Conclusions: Gram-negative bacterial strains (*Escherichia coli, Enterobacter sp., Klebsiella sp*., etc.). were isolated from meat and fish samples, using MacConkey selective medium, while cheese samples developed yeasts and lactic acid bacteria (LAB on the SDA medium with antibiotic, respectively MRSA medium. The ability of strains isolated from food samples to produce BAs will be evaluated electrochemically.

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ECO-FRIENDLY METHOD FOR MESOPOROUS SILICA SYNTHESIS

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Keywords: environment, mesoporous silica, microstructural characterization, microwave synthesis

Introduction: Mesoporous silica was promoted since 1970 thanks to its very useful properties like high surface area, large pore volume, homogeneous pore size and distribution and uniform particle size distribution. Some varieties of mesoporous silica are notorious for their well-ordered pore structure, so MCM-41 and SBA-5 exhibit hexagonally ordered mesopores, while MCM-48, SBA-16 or KIT-5 have cubic pore symmetry [1]. These engineered materials have found applications as catalyst support, as adsorbent of the environment pollutants, for energy and for controlled drug delivery. In order to synthesize mesoporous silica an environmental friendly method based on microwave power was used.

Materials and methods: Mesoporous silica was synthesized starting from tetraethylortosilicate precursor using a surfactant cetyl trimethylammonium bromide (CTAB) with the role of pore forming template [2]. After the synthesis of silica networks around the CTAB micelles, the template must be removed from the silica, in order to empty the pores. To this effect, the silica particles were treated in the microwave, in acidic solution of dioxane or ethyl alcohol, at 110 °C for 2 hours.

Results: The effect of solvent on CTAB removal and particles or pore dimension was followed through elemental analysis, electron microscopy and Energy Dispersive X-Ray Spectroscopy (SEM-EDX). Structural characterization of the mesoporous silica nanoparticles was performed by Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD). Analytical results, such as the decrease of carbon percentage in elemental analysis or in EDX scans and the disappearance of specific peaks from 2900-2800 cm^{-1} in the FTIR spectra of the silica, after microwave treatment confirm the elimination of surfactant. The small angle XRD spectra show an ordered structure with a pattern suggesting some similarities with 2D hexagonal structure of mesoporous silica MCM-41. The particle size distribution, determined through Dynamic Light Scattering method, shows that the mean diameter of the particles range between 180-220 nm.

Conclusions: The results obtained from the analysis of the silica samples support the possibility to obtain the mesoporous silica particles by green synthesis using a microwave assisted method and ethanol as eco-friendly solvent.

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Also acknowledge the Romanian Ministry of Research, Innovation and Digitalization, for founding by NUCLEU Program, under Project PN 19 11 03 01 "Studies on the obtaining and improvement of the acido-basic properties of the nanoporous catalytic materials for application in wastes valorisation".

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DESIGN OF INNOVATIVE HYDROGEL-FULLERENOL BASED NANOCOMPOSITES FOR SENSING APPLICATIONS

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Keywords: hydrogels, fullerenol, nanocomposites, sensing

Introduction: The application of nanotechnology and nanomaterials for (bio)electronics and biosensing tools production led to an wide range of applications, allowing miniaturization and enabling their integration in many other devices. The design and development of miniaturized (bio)analytical tools is based on the use of nanomaterials, either directly as sensing elements or as associated materials, to detect specific molecular interactions occurring at nanoscale [1]. Fulleronols have attracted great interest due to its high solubility in water (and polar solvents) and stability, possessing significant photo and electron acceptor features, being important for organic electronic applications, for instance in solar cells [2]. Several studies have been carried out on the formation of composite hydrogels based on biopolymers and electroconductive polyaniline, where the advantages of the interaction between components, have been extensively explored. The use of hydrogels as support materials for nanocomposites design and bioreceptors immobilization is justified by a higher water content that provides biocatalysis conditions close to homogenous catalysis, but also close to the selective permeability of hydrogels.

Materials and methods: The biopolymer-polyaniline composite films were prepared by *in-situ* polymerization of aniline in the microporous biopolymer support. In order to confirm the development of the interpenetrated polyssacharide-polyaniline network, the obtained films were characterized by FTIR spectroscopy, SEM and TGA analyses. Fullerenol and activated fullerenol were synthesized through hydroxylation of fullerenes in a mixture of NaOH, H_2O_2 and tetrabutyl ammonium hydroxide in toluene, to obtain a dark brown precipitate. The characterization of fullerenol was performed by TGA and FTIR analysis. Fullerenol derivatives were synthesized by activation of hydroxy groups and characterized by ^{1}H, ^{13}C NMR and FTIR spectroscopy methods. Screen-printed carbon paste electrodes (SPE) were modified with crosslinked biopolymer with and without polyaniline. The electro polymerization of aniline was performed directly on the surface of the working electrode through cyclic voltammetry method. Characterization of the functionalized sensors was carried out using cyclic voltammetry (CVs) and electrochemical impedance spectroscopy (EIS) using $Fe^{3+/4+}$ redox couple solution.

Results: Biopolymer films present unique properties, such as increased adhesion, permeability to water, biocompatibility and high mechanical resistance. Moreover, these biopolymeric films, being porous by nature, may function as a template for the stabilization of polyaniline in film form. Fullerenol derivatives show good water solubility, stability for bio-applications and good versatility, being easily functionalized. CV and EIS measurements carried out on bare and modified SPEs showed that the biopolymer-polyaniline composite film facilitates the electron transfer between the redox probe in solution and the sensor surface, demonstrating good electrocatalytic activity.

Conclusions: The obtained results demonstrated the processability of polysaccharide-polyaniline biopolymeric composites as a stable electrode film-forming material, in order to allow further development of nanocomposite based biopolymeric films for (bio)sensing applications.

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THE INFLUENCE OF DIFFERENT METAL PHTHALOCYANINES ON THE ELECTRO-REDUCTION OF PEROXYNITRITE FOR BIOSENSING

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Keywords: peroxynitrite, biostimulant, metal-phthalocyanine, biosensors, plants.

Introduction: The role of short-living peroxynitrite (the structural isomer of nitrate, that acts as a powerful oxidant, similar to free radicals) in plants in response to stress and its role in signaling is not studied enough, although it is thought to play a very important role [1],[2]. The lack of knowledge is also determined by the lack of rapid, accurate and sensitive methods for the detection of peroxynitrite (PON) in plants. In this work we propose the study of different metal-phthalocyanines as potential catalysts for the electro-reduction of PON, to develop a reliable biosensor.
Materials and methods: Different metal phthalocyanines (MPcs) or metal free phthalocyanine (H_2PC) were used to modify screen-printed carbon electrodes (SPCEs), using different deposition methods. The electrochemical parameters of these modified SPCE were studied by Cyclic Voltammetry (CV). PON was also detected with MPcs/SPCE using both CV and/or Chronoamperometry (CA). SEM was used to study the morphology of the modified SPCEs. FTIR was used to assess the presence of appropriate functional groups.
Results: Cobalt phthalocyanine catalyzes the reduction of PON thorough a two-electron mechanism (Fig. 1), according toCV. Similarity of other phthalocyanines to scavenging proteins (hemin and myoglobin) hasalso been proven to promote the reduction of PON. CA was performed at the corresponding anodic current peak for the different MPcs modified electrodes, resulting in PON detection.
Future perspective: The calibration of the electrodes for the detection of PON will be further performed. The potential of MPcs as PON catalysts can be further investigated using Density-Functional Theory calculations.

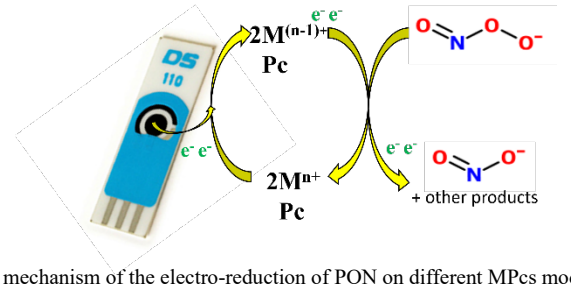

Figure 1. Proposed mechanism of the electro-reduction of PON on different MPcs modified SPCEs (adapted from [3])

Conclusions: Studying different MPcs for electro-reduction of PON is of great interest to both biosensor community and the biostimulant industry, as using MPcs sensors for fast and precise screening of biostimulants is desirable.

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WASTE POLYMER DERIVED CARBON

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Keywords: waste polymer; carbon; porosity.

Introduction: Many materials in everyday life are produced from plastics and other petroleum derivatives. Plastics have unique properties and strong chemical bonds, which are not biodegradable, thus contributing to environmental pollution after use. Utilization of plastic waste can be performed by using various methods of thermal destruction: pyrolysis, catalytic cracking, gasification, hydrocracking.

One of the appropriate methods of utilization of polymer waste is conversion by pyrolysis into carbon materials. Carbon can be produced from different polymers, polymer resins and polymer waste. Thermoplastic polymers, such as polyethylene, polypropylene, polyvinyl chloride, polyamide, polystyrene, polyacrylic, etc. are aminly used; thermo-setting resins, such as epoxy resins, formaldehyde resins, melamine resin, etc./ also are suitable precursors.

The aim of the study was to develop a new method for conversion of polymer waste into liquid, gas, and solid nanoporous carbon product.

Materials and methods: Different polymer wastes were used as a precursors.After thermo-oxidation treatment and hydropyrolysis, nanoporous carbons with a high surface area of 800-100 m^2/g were synthesized.

Results: The initial material was examined by TG and DSC analysis. The resulting carbon adsorbent was characterized by BET, Elemental Analysis, DTG, XRD, etc.

Conclusions: The obtained results show that the obtained carbon material has suitable properties which implies that it could be used for water and air purification.

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POROUS TEXTURE STUDY OF NEW CARBON MATERIALS BY LOW-TEMPERATURE NITROGEN SORPTION

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Keywords: carbon, nitrogen sorption, porous texture

Introduction:
The pore texture and pore classification are essential to carbon materials. The properties and performance of different porous carbon materials strongly depend on the internal carbon pore structure.

To elucidate the processes, taking place in a porous material, a complete characterization of the porous texture is required: this includes the determination and analysis of the pore volume, pore size distribution, the magnitude of the specific surface area, etc.

Materials and methods:
To evaluate the porous texture of the obtained porous carbon materials, low-temperature nitrogen sorption was performed using modern AutosorbiQ-MP Quantachrome instrument (2019).

Results:
The results obtained for pore volume, pore size distribution, and the size of the specific surface area of nanoporous carbons and carbon foam samples, obtained from different raw materials and using various treatment conditions are presented.

Conclusions:
Based on the obtained results, a preliminary assessment of the possibilities of their application was established.

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CARBON NANOTUBES-POLYANILINE (CNT-PANI) COMPOSITES. HYDROTHERMAL SYNTHESIS AND PRELIMINARY ELECTROCHEMICAL CHARACTERIZATION

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Keywords: carbon nanotubes; polyaniline; hydrothermal synthesis; modified glassy carbon electrodes.

Introduction: Heavy metals have a major contribution to biosphere pollution due to toxicity. The detection and monitoring of the environmental agents in soil, water and air is very important for the general health of humans and animals. It has been recently shown that electrochemical techniques such as differential pulse voltammetry (DPV) and square wave anodic stripping voltammetry (SWASV) using modified electrodes are very attractive methods for detecting heavy metals [1-3]. The aim of this paper is to demonstrate the potential of hydrothermal process combined with electrochemical techniques to obtain modified electrodes based on functionalized carbon nanotubes (CNTs) and polyaniline (PANI) for metals detection.

Materials and methods: Commercial multi-walled carbon nanotubes (MWCNT) were functionalized by a mixture of HNO_3/H_2SO_4 and further used for hydrothermal synthesis of CNT-PANI composites with different mass ratios. The resulted powders were analyzed by spectral (Fourier-Transform Infrared Spectroscopy) and thermal (Differential Scanning Calorimetry) methods, and then dispersed in a surfactant/electrolyte solution for preliminary electrochemical experiments (cyclic voltammetry, CV and DPV) to obtain modified electrodes.

Results: The influence of the CNT: PANI mass ratio and the synthesis time on the formation of composites with the desired structural and electrochemical properties were studied.
It was found that CNT-PANI composite powder having mass ratio 1:4 and synthesis time 3h has the best structural and thermal characteristics and formed a weakly conductive film on the surface of the glassy carbon electrode. Preliminary electrochemical tests revealed the electroactive forms of polyaniline, through the presence of characteristic oxidation peaks but also reduction peaks, corresponding to reversible redox reactions, demonstrating that glassy carbon electrode has been electrochemically modified with CNT-PANI coatings [4].

Conclusions: The results obtained by CV for GCE modified with coating deposited from CNT-PANI composite powder having mass ratio 1:4 correlates well with the conclusions drawn from synthesis and characterization of this composite powder, confirming the presence of the organic phase on GC modified electrode. Further studies will be conducted to test the potential application of glassy carbon electrode modified with CNT-PANI coatings as electrochemical sensor for heavy metals detection.

***Acknowledgements**: This work was performed through the Core Program, carried out with the support of MCI, project no. PN19190501/2019-2022, "Innovative electrochemical processes with applications in surface engineering and non-ferrous metal recovery" and INOVADIT project of the Ministry of Research, Innovation and Digitization through Program 1 - Development of the national research-development system, Subprogram 1.2-Institutional performance-Projects for financing excellence in RDI, Contract no. 9PFE/2021.*

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ONE POT SYNTHESIS OF Ag-MODIFIED LAYERED DOUBLE HYDROXIDES WITH POTENTIAL ANTIMICROBIAL PROPERTIES

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Keywords: LDH, antimicrobial,Cultural heritage

Introduction: Silver is a well-known antimicrobial agent extensively used in many applications such as biomedicine or conservation of cultural heritage elements prone to biodeterioration [1]. A crucial phase in their antimicrobial activity is the silver ions (Ag^+) leakage from the material to the microorganisms. In the recent years, a lot of focus has been placed on the silver (nano)particles incorporated or supported on 1D, 2D, and 3D inorganic materials[2]. Among 2D compounds layered double hydroxides (LDHs) are interesting materials for developing 0D/2D nanostructured architecture. The use of LDH surface as a substrate or support for the antimicrobial component allow combination of the LDH biocompatibility and ion exchange properties with the bacteriostatic properties of silver[3].

Materials and methods: The Ag-LDH materials were prepared by the coprecipitation of the corresponding metallic nitrate salts with sodium hydroxide followed by the ageing and washing of the precipitate. The materials were characterized by X-ray diffraction, FTIR and XRF in order to understand the phase, crystallinity and composition of the materials. The antimicrobial properties of the materials were investigated on the following microbial strains: Gram-positive bacteria Staphylococcus aureus ATCC 25923, and the fungal strains Candida albicans ATCC 10231, Asperillus niger, Penicillium chrysogenum.

Results: The X-ray diffractograms of Ag-LDH exhibit the diffraction lines characteristic to poorly crystallized LDH phase with broad lines, characteristic to multi-cationic LDH and additional lines at 2 theta, 29.4°, 32.9°, 38.3°, 55.2° and 66° that belong to a Ag_2O phase. XRF results showed that the silver content and the ratio between M2/M3 in the materials is close to the intended values and that no amount of Ag was lost during washing.The FTIR spectra of the materials also shows the bands at 3300-3700 cm^{-1} -associated with OH stretching vibration of hydrogen-bonded metal hydroxide layer and interlayer water molecules, 1639 cm^{-1} - suggests the bond between carbon and oxygen present at carbonate anion structure, while the band at 1380 cm^{-1} is due to the nitrate ion. Finally the region between 1200 and 400 cm^{-1} is probably relative to M-O stretching on the structure layer[4]**.** The antimicrobial activity was evaluated by measuring the diameter of the inhibition area, the clear area (halo) that appears around the sample's inoculation.

Conclusions: MgAl(Ag)-LDH were prepared via a coprecipitation method. The broad diffraction lines present in the X-ray diffractogram, suggest that some amount of Ag cations entered the brucite layers where the rest of the silver is present as silver oxide.The antimicrobial activity of the sample increased in the following order: *C. albicans* (17.0 mm) >*S. aureus* (16.0 mm) >*P. chrysogenum* (12.0 mm) >*A.niger* (10.0 mm). In general, *C. albicans* was the most sensitive to the inhibitory action of clay samples, followed by *S. aureus*, the most resistant being *Aspergillus niger* for which the lowest values of diameters of the inhibition areas were recorded. .This study will be continued by studying the effect of different Ag loading and different types of Ag-modified LDH.

***Acknowledgements**: **Acknowledgements**: This work was supported through Program-Nucleu, with the support of MCID, project no.23N/2019*

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4. *Section 2* - Bioresources, biotechnologies and biorefining

ORAL Communications

ADDRESSING NON-SPECIFIC ADSORPTION IN PROTEIN BIOSENSING

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Keywords: biosensor; lysozyme; non-specific adsorption; self-assembled monolayer.

Introduction: Lysozyme is an antibacterial protein present in body fluids and tissues. Increased levels of lysozyme represent a non-specific biomarker for several inflammatory diseases [1]. Protein determination with biosensors confronts with major non-specific adsorption (NSA) leading to reduced sensitivity [2]. For efficient electrochemical aptasensors, one strategy to minimize NSA is to immobilize the aptamer using self-assembled monolayer (SAM) and backfilling with chemisorbed thiolated molecules such as mercaptohexanol (MCH) or polyethylene glycol (PEG) derived compounds. We aim to test several compounds to address the NSA in developing an aptasensor for the detection of lysozyme in both monomer and aggregate form.

Materials and methods: Aptamer modified and control, thiol blocked gold screen printed electrodes (Au SPE) were used to measure different concentrations of lysozyme. Preventing NSA was addressed using thiols, PEG derivates and bovine serum albumin (BSA). Each blocking thiol was 1 mM concentration in PBS buffer with 7.4 pH and was incubated for 1 h on Au SPE. A 1 mg/mL solution of BSA in buffer was deposited by pulsed amperometry (PDA) on Au SPE, by switching between -0.2 V and 0.5 V for 10 ms each with total time of 180 s [3]. Measurements were conducted by cyclic voltammetry (CV) at a 100 mV/s scan rate. The analytical signal coresponds to the variation in anodic peaks' intensites of the ferrocyanide/ferricyanide (HEX II/ III) couple before and after incubation with the sample. Samples consisted in 1 µg/mL lysozyme solutions-fresh, monomer or aggregated fibrils. The fibrils were obtained by heating solutions of 10 mg/mL lysozyme pH 2, at 60° C and were characterised by atomic force microscopy (AFM), spectrophotometry using Congo Red amyloid marker and fluorimetry with Thioflavin T dye.

Results: Characterization of amyloid fibrils showed the correlation between time and amyloid fibril formation. Moreover, it provided the fibril state of lysozyme sample for the electrochemical detection. The sensitivity of aptamer and control Au SPEs was very similar (Fig. 1A), indicating significant NSA. NSA was studied on thiol-coated Au SPEs by CV, observing that mercaptoundecanol (MCU), PEG4-SH and BSA were the most effective in reducing NSA for both monomeric and fibrils form (Fig. 1B).

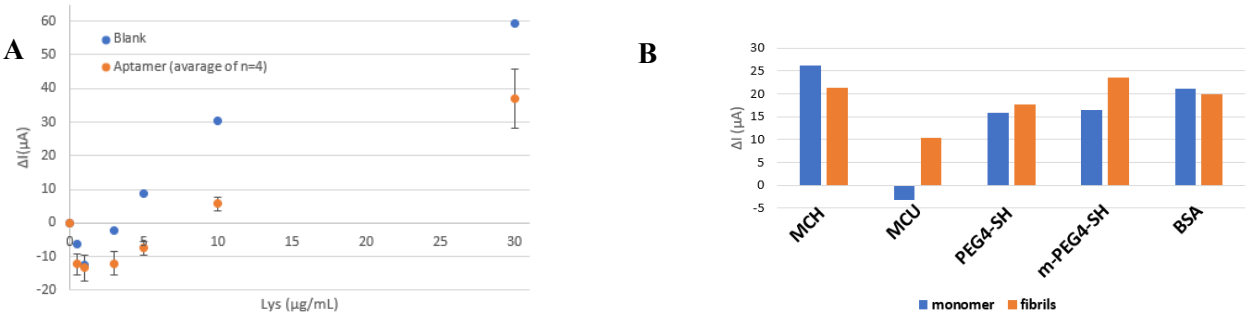

Figure 1. (A) Analytical response for increasing concentration of lysozyme monomer obtained with aptamer modified and control electrodes, respectively. (B) Intensity difference of anodic currents after 30 minutes incubation with 1 µg/mL monomer lysozyme (blue), fibrils lysozyme respectively (orange).

Conclusions: Employing thiols or PEG derivates can be a good solution to reduce NSA in electrochemical biosensors. For high sensitivity electrochemical detection of lysozyme in monomer and fibril state, mixed coatings of MCU, PEG4SH and BSA will be further investigated.

Acknowledgements: *Financial support by the Romanian Executive Agency for Higher Education, Research, Development and Innovation (UEFISCDI), PN-III-P4-ID-PCE-2020-2297 E-MAP project, contract 84/0.9.02.2021 (for A.V and RMB) is gratefully acknowledged.*

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METHODS FOR EVALUATING THE EFFICIENCY OF SOME SELECTED MICROBIAL CULTURES ABLE TO BE USED FOR INDUSTRIAL WASTEWATER REMEDIATION

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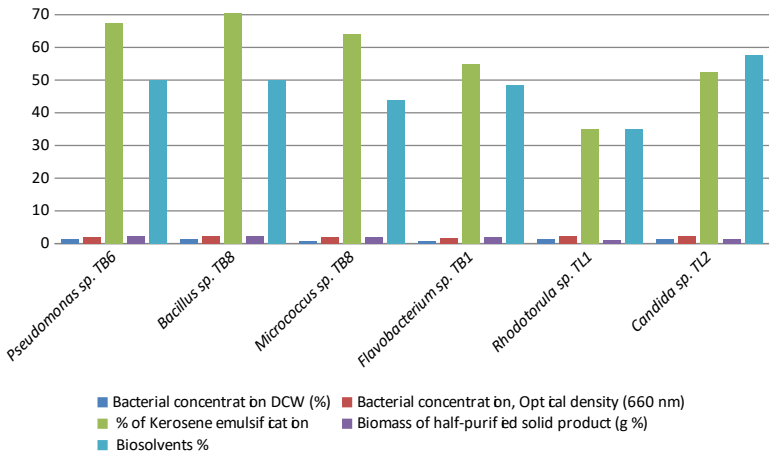
Keywords: wastewater, bacterial remediation

Introduction:

Related with the wastewater recovery, even if some old methods were represented by the physicochemical processes, recent researches have the issue to apply modern biotechnological ways, by using bacteria selected strains or some fungal strains, different species of algae and other aquatic plants [1], [2].

Materials and methods: The wastewater samples were taken from some water pools wich are present inside a pharmaceutical plant. Our studies were realized by using the bacteria strains *Pseudomonas sp*., *Bacillus sp., Micrococcus sp., Flavobacterium sp.* and 2 yeast strains*: Rhodotorula sp,* and *Candida sp.*

Results:



Conclusions: Our selected microbial strains presented good properties concerning the wastewaters remediation, but the results obtained by using bacterial strains were better.

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AUTHENTICATION AND DETECTION OF ADULTERATION OF EXTRA VIRGIN OLIVE OIL BASED ON THE COMPOSITION OF PHENOLIC COMPOUNDS

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Keywords: vegetable oils; biophenols, HPLC-MS/MS, statistical analysis

Introduction: Compared to other edible oils, extra virgin olive oil (EVOO) is unique due to the presence in its composition of phenolic compounds, including phenolic acids and alcohols, secoiridoids, flavonoids and lignans which contribute to his sensory qualities and nutritional value [1],[2]. Due to its relatively low production and higher prices compared to vegetable oils obtained from seeds, olive oil and especially EVOO is one of the most adulterated food products in the world. In this regard, mislabelling, false declaration of geographical origin and substitution with other types of oil are the main types of adulteration of olive oil.

Materials and methods: In this study, phenolic composition of different type of pure vegetable oils (extra virgin olive oil (EVOO), walnut oil (N), grape seed oil (STR), pumpkin oil (D), linseed oil (I), soybean oil (SO), sesame oil (SU), hemp oil (C), poppy seed oil (M), sunflower oil (FL), corn oil (P)) and controlled adulterated extra virgin olive oil with different percentages (0.5-50%) of corn oil was investigated by liquid chromatography coupled with high resolution mass spectrometry (UHPLC-MS/MS). Principal component analysis (PCA) was used to discriminate between different oil type and for identification of specific markers.

Results: EVOO has a special composition of phenolic compounds, being similar to that of walnut oils, but also to sunflower and corn oils. Specific phenolic markers of extra virgin olive oil are coumaric and cinnamic acids, apigenin, quercetin, isorhamnetin, pinocembrin and (+)-catechin, while the specific phenolic markers of walnut oil are p-hydroxybenzoic, chlorogenic and abscisic acids, but also flavonoids such as galangin, rutin, kaempferil, hesperidin. As can be seen, based on the minority phenolic compounds, there is a very clear differentiation of EVOO compared to other vegetable oils, being grouped in a well-defined group (Figure 1a). Adulterated EVOO oils with lower percentages of corn oil (0.5%, 1% and 2.5% - A2, A3 and A4) are grouped alongside pure EVOO (Figure 1b).

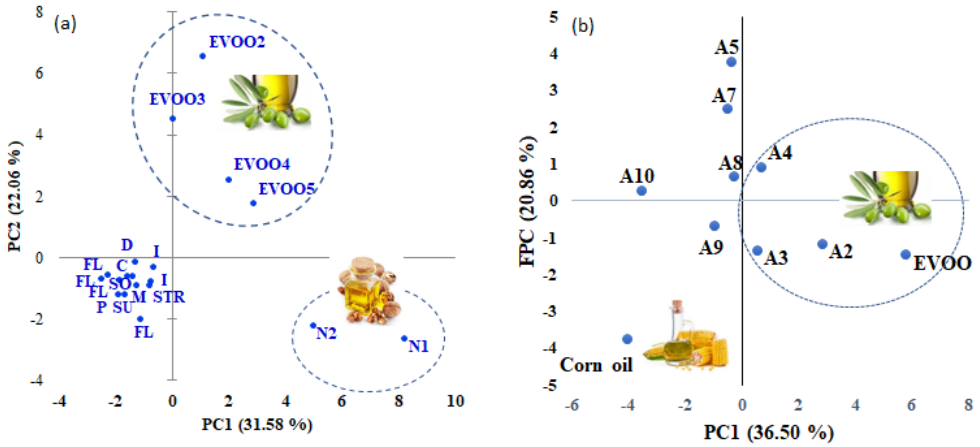

Figure 1. Principal component analysis: (a) discrimination of different vegetable oils and (b) discrimination of adulterated EVOO

Conclusions: Sunflower and corn oils can be potential adulterants of EVOO by adding them, in different percentages to EVOO. PCA analysis of the quantitative data related to phenolic compounds allowed the discrimination of different types of vegetable oils and the identification of specific polyphenolic markers for extra virgin olive oil, but also the discrimination of adulterated EVOO oils with more than 3% corn oil.

***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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CHARACTERIZATION OF 3D PRINTED LAPONITE/DIATOMITE/HYDROXYAPATITE/SODIUM ALGINATE SCAFFOLDS WITH POTENTIAL USE AS BONE IMPLANTS

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Keywords: 3d printing; thixotropic; sodium alginate; diatomite

Introduction: One of the most promising direct use of 3D printing in tissue engineering is the creation of artificial bone implants of custom dimensions and shapes. In this study, a versatile material based on ingredients used before for paste 3D printing for bone scaffolds such as laponite, sodium alginate and hydroxyapatite and together with diatomite used for the first time as a filler in hydrogel 3D inks is shown to lead to porous scaffolds mimicking a 3D model either by direct 3D printing or by freeze-casting.

Materials and methods: Laponite (RD), hydroxyapatite from animal sources, diatomite from a Romanian source and sodium alginate were used to obtain a material with thixotropic properties following a screening by a partial factorial model with 18 runs which was used to assess qualitatively the apparent properties of the materials. This partial model used the content in laponite, hydroxyapatite, diatomite, sodium alginate and sodium chloride as mixing factors and one process factor which was the ratio between the water and the solid content. After this set of trials, a simplex centroid design which varied only laponite, diatomite and hydroxyapatite percentages was used to investigate the effect on XRD, FT-IR and BET porosimeter results. All runs up to this point (screening and full factorial designs) were obtained by mixing the powder content first for each run and adding it to the required amount of water under high shear conditions using a vortex device which ensured a maximum dispersion of ingredients. The obtained mixtures were left over night to ensure a passive homogenization and then were pressed into 3D printed PLA molds. The best material was used to 3D print a basic construct which was then frozen either in a freezer, liquid nitrogen or liquid ethane. The materials were compared by SEM and TEM.

Results: The approach to initially assess the qualitative aspects of the material was useful to reduce the number of factors in a very short time. The second design showed how the material varies with respect to XRD, FT-IR, BET porosimetry and SEM and allowed to take the decision for the optimal material. Finally the SEM and TEM done on materials freeze-casted in different liquids at different temperatures showed how this step could affect visual porosity of the materials.

Conclusions: This study described a possible combination of materials which could act as a 3D printing ink for bone implants and the various processing steps to achieve this.

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NEW ENGINEERING ASPECTS OF HYDROLYSIS-FERMENTATION AND PYROLYSIS OF BIOMASS RESIDUES

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Keywords: *Biomass, hydrolysis, pyrolysis, biochar,mathematical modelling*

Introduction: Biomass residues are abundant, inexpensive, renewable, and carbon neutral resources, which are increasingly used to produce biofuels and specific materials [1]. These residues can be valorised using different biochemical and thermo-chemical routes.

Materials and Methods: For cellulose hydrolysis we use stochastic mathematical modelling coupled with literature data. For biochar obtaining and for biochar application it is used experimental investigation and statistical modelling.

Results: Regarding biochemical routes, aspects related to the hydrolysis of cellulosic materials [2] and to the importance of coupled processes in fermentation to biofuels [3] will be detailed. Among thermo-chemical routes, pyrolysis is a very promising technology, which involves high added-value products as well as lower energy consumption and costs than other conversion routes [4]. Pyrolysis consists in thermal decomposition of an organic matrix in a non-oxygen limited atmosphere yielding biochar (BC), bio-oil, and pyrolytic gases. Distribution, composition, properties, and applications of the pyrolysis products mainly depend on reaction conditions (*e.g.*, heating rate, temperature, type and flow rate of carrier gas), biomass type, size, and pretreatment. Biomass residues are often burnt, leading to air pollution and significant loss of potential soil nutrients. In order to mitigate these drawbacks, the residues can remain or be added to the soil, but this may increase crop diseases and also greenhouse gas (GHG) emissions. In terms of waste management, climate change abatement strategies, agronomic benefits, environmental degradation, and fossil fuel depletion, the pyrolysis of biomass residues is a promising and relevant conversion technique. The use of BC as a soil amendment can contribute to enhanced soil C sequestration, reduced GHG emissions and nutrient leaching, improved soil fertility and health [5,6]. Moreover, an increase in soil fertility determines a diminished fertilizer input as well as enhanced crop productivity and thus supplementary CO_2 consumption, resulting in agronomic, environmental, and economic benefits [5],[6]. Activated BC can be employed for remediation of soil, water, and air pollution by sorption of different contaminants, *e.g.*, heavy metals, pesticides, GHGs, persistent organic pollutants (POPs), and volatile organic compounds (VOCs) [5,6]. Bio-oil and pyrolytic gases can be directly used for heat and electricity generation and are also valuable source for various chemicals. The efficiency of soil amendment and pollution remediation can be improved by activation/modification (*e.g.*, physical activation with CO_2 or steam, chemical modification with acids, bases, metal salts or oxides) of BC resulting in so called engineered BC [5,6].

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CARBON-CALCIUM BASED BIONANOCATALYST FOR ADSORPTION AND DECOMPOSITION OF ORGANIC POLLUTANTS

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Keywords: bionanocatalyst; adsorbent; nanocarbon; egg shells; hydrothermal carbonization.

Introduction: Hydrothermal carbonization is an ecological method of destructuring the ligno-cellulosic biomass into platform molecules and hydrochar using only water under self-generated pressure in an hermetic reactor [1]. Besides nanocarbon with adsorbent and catalytic properties, eggshells were used as calcium catalysts [2], aiming to obtain a bionanocatalyst with adsorption and catalytic properties for organic pollutants. Cooking oil is an usual organic pollutant and its catalytic conversion into biodiesel is of high interest [3].

Materials and methods: Biomass wastes like corn stalks and chicken eggshells were hydrothermally treated in order to obtain a bionanocatalyst with adsorbent and catalytic properties for organic pollutants as cooking oil. X-ray diffraction (XRD) and infrared spectroscopy (FTIR) were used to evaluate the carbon-$CaCO_3$ nanomaterials at different synthesis steps and after the adsorption and degradation of cooking oil.

Results: Hydrothermal carbon-calcium materials (CCaH) present the characteristic diffraction peaks of calcite ($CaCO_3$) in eggshells and two small amorphous peaks at 2θ around 15º and 21º, respectively a crystallinity of 89% (Fig.1a). After contacting with cooking oil and further hydrothermal treatment at 140ºC for 4h, the solid named CCaF presents only one, more intense, amorphous peak at around 20º, respectively a lower crystallinity of 66%. The FTIR spectra presented in Fig.1b) evidenced characteristic absorption bands for the raw materials cooking oil (Oil), eggshells (Egg), respectively for the newly obtained bionanocatalyst (CCaH) after oil adsorption (CCaHO) and hydrothermal conversion (CCaF). The bionanocatalyst has an adsorption capacity of 2mL/g oil/cat and it drastically influences the absorption band of $CaCO_3$ at 1400 cm^{-1}. After the final hydrothermal step, the C=O band at 1744 cm^{-1} characteristic for oil decreases in intensity, while the C-O-C band receives more absorption bands, suggesting a partial degradation of the adsorbed oil. The liquid phase has a yellowish color and contains water soluble degradation products that will further be studied.

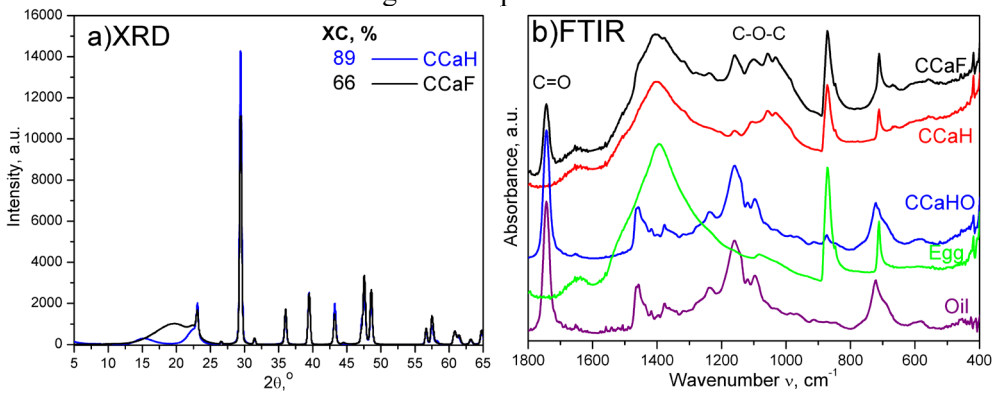

Figure 1. a) XRD analyses and b) FTIR analyses of CCaH and CCaF.

Conclusions: Corn stalks and eggshells were converted by hydrothermal treatment al low temperature into a carbon-calcium bionanocatalyst with adsorption and catalytic properties for cooking oil. Both liquid and solid phases have potential applications in biodiesel additives and fuels.

***Acknowledgements**: This work was supported by the Government of Romania, Ministry of Research, Innovation and DigitalizationNucleu Programme in the frame of the Chem-Ergent project PN19.23.03.01 Contract no. 23N/2019 and Agri-Flux project SMIS 48695 / CF nr. 645/18.03.2014.*

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5. *Section 2* - Bioresources, biotechnologies and biorefining

POSTER Presentations

COMPARATIVE ANALYSIS OF MINERALS AND VITAMINS FROM RED CLOVER AND AMARANTH EXTRACTS

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Keywords: red clover, amaranth, vitamins, minerals

Introduction: Red clover (*Trifolium pratense* L.) seeds extract is used as functional ingredient in food products and dietary supplements for its medicinal properties and also as source of minerals and vitamins [1]. Amaranth (*Amaranthus caudatus* L.) seeds extract has been widely used in food products for people with celiac disease as a replacement for gluten and for its functional properties and high nutritive values [2].
The aim of this paper was to compare the content of minerals and vitamins from red clover and amaranth extracts obtained from germinated seeds. The comparative analysis was carried out in order to select the extract with the highest content in minerals and vitamins for encapsulation and uses as functional ingredient in food industry.

Materials and methods: The red clover and amaranth seeds extracts obtained by autoclave extraction method were chemical characterized by optical emission spectrometry with inductively coupled plasma (ICP-OES), SR EN ISO 11885:2009. The mineralization of the ash obtained at 550ºC was carried out in the digester with HNO_3 65%: HCl 37%. Vitamin C determination was performed according to the method described by Devolli A. et al. (2021) and vitamin A was determined according with Rutkowski M. (2007) protocol with minor modifications, using the spectrophotometric methods [3],[4]. Vitamins B6 and B3 were quantified using potassium iodide and potassium iodate method described by Khateeb M. et al. (2015) [5].

Results: The chemical composition analysis for red clover and amaranth seeds extracts were determined, which refers to phosphorus, potassium, calcium, magnesium, sodium, iron, manganese, zinc, copper and vitamins A, B3, B6, C.
The comparative analysis of the minerals and vitamins composition for both extracts revealed that the red clover seed extract has higher content of phosphorus 1.31 % (w/w), potassium 2,93 % (w/w), magnesium 0.634 % (w/w), sodium 0.067 % (w/w), zinc 26 (mg/kg), copper 13.7 (mg/kg), vitamin C 204 (mg/100g), similar content of calcium 0.114 % (w/w) and vitamin A 53 IU, vitamin B3 1.10 (mg/100g), vitamin B6 1.13 (mg/100g). The content of iron 46.50 mg/kg and manganese 14.70 mg/kg is double for amaranth extract compared with red clover.

Conclusions: Red clover seed extract was selected based on chemical composition as functional ingredient for encapsulation.

***Acknowledgements**:* This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P3-3.5-EUK-2019-0169, within PNCDI III.

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EFFECT OF INCORPORATING AN UREOLYTIC BACTERIUM ON THE PROPERTIES OF MORTARS

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Keywords: Bacillus subtilis, biocement, mortars

Introduction: Concrete, a mixture of cement, coarse and fine aggregate, and water in a certain ratio, is a porous material sensitive to various assaults such as chloride, CO_2, freeze thaw, and others due to the presence of pores. Its degradation and deterioration affect the stability of a wide variety of important structures, including bridges, large buildings, off-shore constructions, airports, and deep foundations. Over the last several years, research into microbial precipitation of calcium carbonate reveals its potential for extending the useful life of cement-based buildings [1-4]. The incorporation of microbial species into mortar has increased its strength and endurance, providing additional benefits as an environmentally friendly and cost-effective alternative. The objective of the research was to study the effect of microbial induced calcite precipitation for improving the physical-mechanical properties of cement mortar. The bacteria induced calcium carbonate precipitation on the surface or inside the pores of mortars, reducing the porosity and blocking the capillary pores.
Materials and methods: The mortar samples were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (DTA/TGA). Also, microscopic observations (optical and scanning electron microscopy - SEM) were performed.
Results: The mortars embedded with bacterial cells presented a certain improvement of their mechanical properties, namely compressive strength, and water absorption, that, through dedicated studies, can be improved to reach values comparable to those in the literature.
Conclusions: The findings in this study demonstrated that *Bacillus subtilis* could be a promising bio-calcifying agent. Therefore, further research should be carried out to find the optimum dosage of bacterial cells to be added in mortar mixture, since there is a significant effect of cell concentration on compressive strength and water absorption. Also, the longevity and durability of bacterium in mortar will be evaluated. We consider that the results can be used to develop an experimental protocol for improving the properties of mortars using biogenic bacteria.

Acknowledgments*: This work was supported by a national grant of UEFISCDI, through project number PN-III-P2-2.1-PED-2019-0991, within PNCDI III. The authors thank to Ministry of Research, Innovation and Digitization of Romania through Program 1 - Development of the national research and development system, Subprogram 1.2 -Institutional performance- Projects to finance excellence in RDI, Contract no. 15PFE / 2021.*

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FUNGAL-MEDIATED BIOSYNTHESIS OF SILVER NANOPARTICLES

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Keywords: silver nanoparticles (AgNPs), basidiomycetes, antimicrobial activity

Introduction Biological organisms such as bacteria, fungi, plants, and algae are able for the synthesis of nanoparticles, microorganisms being the most preferable organisms. The biosynthesis of nanoparticles occurred when the microorganisms take the metal ions from the environment, and, transform into metal element through intracellular or extracellular routes of cell activities. Fungi are preferred since they secrete plenty of enzymes, and are easy to handle. It is considered that in a certain extent, the biogenic process is superior to chemical one, being free from toxic and harmful chemicals. Currently, silver nanoparticles (AgNPs) are of great interest as antimicrobial activities, biocompatibility, high photo-electrochemical activity, chemical inertness, and simple synthesis [1-4]. The antibacterial activity of AgNPs is different according to bacteria type, as gram positive or gram negative, exhibiting *multiple and simultaneous mechanisms of action* [5]. The present study aims to highlight the ability of an edible basidiomycetes fungus, to fabricate silver nanoparticles (AgNPs) with antimicrobial activity.

Materials and Methods. The UV-VIS and FTIR analysis were carried out. Also, microscopical investigations were performed. Antimicrobial activity of AgNPs against several microbial strains was tested in agar disc diffusion method.

Results. The UV-Vis spectra of the bio-synthesized AgNPs scanned at different time intervals showed a characteristic peak at 430 nm, indicating the synthesis of silver nanoparticles from $AgNO_3$ by basidiomycetes. The morphology of AgNPs was confirmed by SEM observations. FTIR provided important information about the chemical bonds and molecular structures involved in the bio-reduction of silver ions and stabilization of the AgNPs. AgNPs presented a good antimicrobial activity against microbial strains with medical importance.

Conclusions. It can be concluded that the green synthesis of AgNPs using edible basidiomycete is an environmentally acceptable method that allowed the production of silver nanoparticles for biomedical applications.

Acknowledgments*: 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-2021-1942, contract no 662/2022– AMI-FOOD. The authors thank to Ministry of Research, Innovation and Digitization of Romania through Program 1 - Development of the national research and development system, Subprogram 1.2 -Institutional performance- Projects to finance excellence in RDI, Contract no. 15PFE / 2021.*

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GRAPE POMACE AS POTENTIAL SOURCE OF BIOACTIVE PHYTOCHEMICALS

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Keywords: grape pomace; polyphenols, UHPLC-MS/MS, statistical analysis

Introduction: The promotion of renewable natural resources, such as grape pomace as biomass for the extraction of valuable bioactive compounds such as polyphenols as potential ingredients for foods, nutraceuticals or cosmetics is of increasing interest [1]. This direction has become more and more applicable thanks to the eco-friendly extraction's methods and the progress for the development of different supports designed to reduce the extract sensitivity and enhance its stability.

Materials and methods:

Grape pomace resulted from white (Tamaioasa Romaneasca - TR, Muscat Ottonel - MO)) and red grape (Cabernet Sauvignon - CS, Feteasca Neagra - FN, Burgund Mare - BM, Merlot -M and Pinot Noire - PN) cultivars obtained at Ștefănești wine center were investigated. Hydroethanolic extracts obtained by microwave-assisted extraction (MAE) were characterized in terms of general phenolic bioactive potential by UV-Vis spectrophotometric methods and individual phenolic composition (flavonoids and phenolic acids) by UHPLC-MS/MS analysis. Multivariate statistical analysis based on heat maps and principal component analysis (PCA) were used to discriminate between different grape pomace types and for identification of specific markers.

Results: Higher bioactive potential were observed for grape pomaces resulted from red grape cultivars BM, FN, M and CS. Heat map profiles of the main bioactive phytochemicals of the investigated grape pomaces indicate a clear differentiation of red grape pomace extracts from the white grape pomace extracts, but also from PN grape pomace (Figure 1A). Principal phytochemical bioactive polyphenols quantified in grape pomace extracts were quercetin, (+)-catechin, (-)-epicatechin, gallic and syringic acids. (+)-Catechin, (-)-epicatechin and rutin are specific phenolic markers of white grape pomace, while, quercetin, syringic acid, t-resveratrol, isorhamnetin and pinostrobin are specific phenolic markers of red grape pomace (Figure 1B).

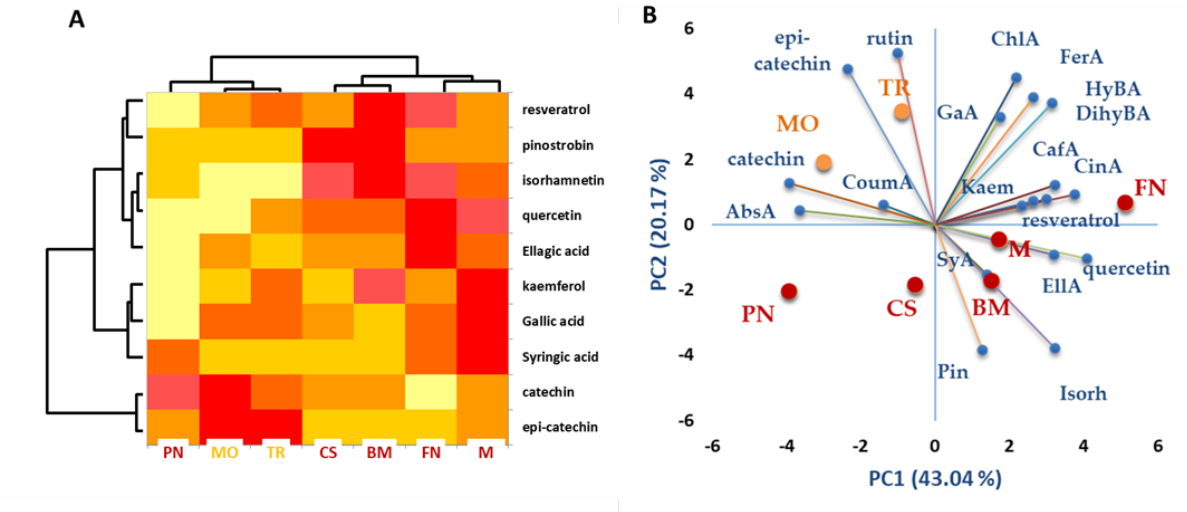

Figure 1. Differentiation of grape pomace based on phytochemical composition: Heat map (A) and PCA (B)

Conclusions: HRMS analysis allows the quantification of phenolic acids and flavonoids and the identification of other bioactive compounds, such as anthocyanins, procyanidins, flavonoids derivatives and amino acids in grape pomace.

***Acknowledgements**: This work was supported by NUCLEU Programe under 9N/2019, project PN 19 11 03 01 and 42N/2019, project PN 19300104*

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HIGHER VALORISATION OF SILYMARIN BY-PRODUCTS VIA PRODUCING NEW FORMULAS WITH ENHANCED BIOAVAILABILITY

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Keywords: silymarin; by-products; phosphatidylcholine; phytozomes; assisted solvent extraction

Introduction: During the processing of fruits and vegetables large amounts of by-products are generated, representing a major disposal problem for the industry in terms of costs and potential negative impact on the environment. However, in some cases, these by-products represent a source of valuable compounds because of their technological and nutritional properties. The aim of current work was to design new extraction processes to improve the safeness and the extraction yield of bio-active compounds, to ensure a better valorization of silymarin by-products.

Materials and methods: Assisted Solvent Extraction method was developed, validated and applied to silymarin complex extraction from by-products. Phytozomes preparation was performed, using contra-solvent method, phosphatidylcholine from egg yolk as phospholipid and silybin standard compound were used. The HPLC - DAD for silymarin complex analysis was employed

Results: The best active compound entrapment was obtained at 1:2 ratio phospholipid:active compound (w : w). The developed preparation protocol was further applied using as active principle silymarin complex recovered from by-products; An entrapment efficiency of 74.10% was reached. Obtained phyto-phospholipids were structurally and morphologically characterized, FTIR data proving the efficient entrapment of active compounds, both when standard compound was used and for recovered silymarin complex. Release profile was drawn for prepared phyto-formulas using two release media, mimicking the gastro-intestinal conditions (Figure 1). According to the HPLC -DAD data, it is found that taxifolin is the compound with maximum release after 8 h, with an almost double content in the medium that simulates the intestinal tract (1937.9 µg/mL versus 1005.5 µg/mL).

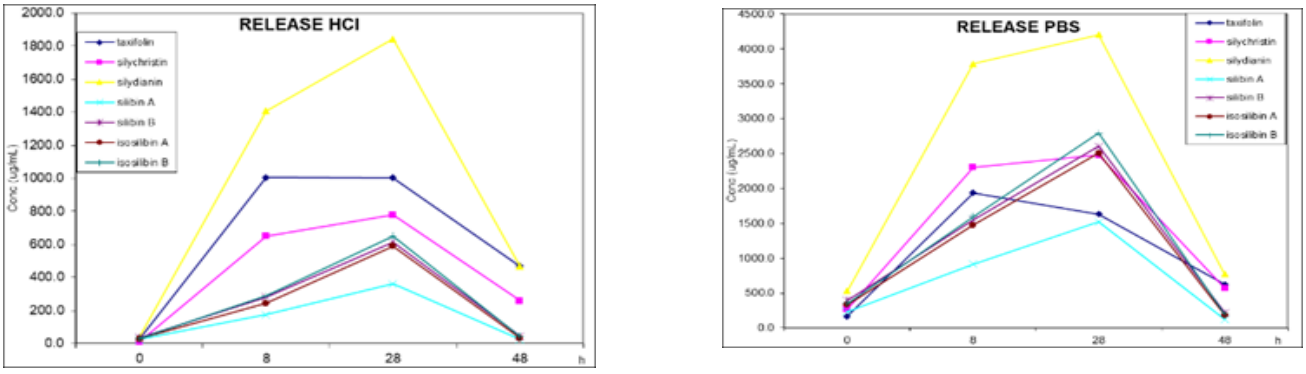

Figure 1. Release profile for prepared phyto-formulas using two release media, mimicking the gastro-intestinal conditions.

Conclusions: Silymarin forms with phosphatidylcholine phytozomes with a ratio 1:2 phospholipid:active compound (w:w). The obtained phytozomes were structurally and morphologically characterized. Release profile was drawn for prepared phyto-formulas using two release media.

***Acknowledgements**: This work was supported by a grant of the Romanian Ministry of Education, CCCDI-UEFISCDI, project number PNIII-P2-2.1-PED-2019-3945, contract no 362PED/2020, within PNCDI III*

FABRICATION OF ENZYME MICROPUMPS BY A SIMPLE CONTACT PRINTING METHOD

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Keywords: enzyme micromotors, contact printing, solutal buoyancy flows, osmotic flows

Introduction: Stirring very small volumes of liquid (*e.g.*, stirring a 20 µL droplet placed onto a glass surface, stirring within a microfluidic channel, *etc.*) is a difficult task as there are hardly any tools facilitating it. Autonomous enzyme micropumps were recently proposed for this task [1]. Such micropumps are small patches of surface immobilized enzyme which, in the presence of the enzyme substrates, generate both solutal buoyancy flows (*i.e.*, bulk flows) and osmotic flows (*i.e.*, surface flows) and, thus, stir the solution bathing them without any external power supply [2],[3]. In the present work we perfect a simple method for building enzyme micropumps with diameters advantageously smaller than the diameters of previously reported enzyme micropumps.

Materials and methods: A simple contact printing procedure was developed in order to build glucose oxidase (GOX)-based micropumps onto glass microscope slides. The procedure involved *i.)* the fabrication of differently sized printing pins out of borosilicate capillaries, *ii.)* the modification of the surface of glass microscope slides by silanization, *iii.)* the preparation of GOX-based printing inks, *iv.)* the actual contact printing of the micropumps onto the silanized glass microscope slides, *v.)* the stabilization of the micropumps by cross-linking with glutaraldehyde (GA), and *vi.)* the "passivation" of the glass carrying the micropumps by incubation with bovine serum albumin. The osmotic flows generated by the obtained micropumps were studied (with an inverted microscope) through the motion of tracer particles let to sediment around the micropumps.

Results: Figure 1 shows images of our largest printing pin (OD = 215 µm) and of the silanized glass surface during the process of printing a micropump. Important to note, each contact in between the printing pin and the silanized glass surface leaves a tiny spot of enzyme on the silanized glass surface. Figure 1 also shows the depletion zone produced by a 200 µm diameter GOX micropump in the presence of 0.2 mM glucose. The depletion zone is due to the tracer particles being subjected to osmotic flows generated by the micropump and to diffusiophoresis. The dimension of the depletion zone is dependent on the amount of enzyme within the micropump and the available concentration of glucose. When investigating the impact of the diameter of the micropump on the dimensions of the depletion zone, we have observed that pumps with average diameter of 249 ± 14.6 µm produce depletion zones which are very similar with those produced by pumps with average diameter of 194 ± 4.4 µm. Materials, methods and results will be presented into details.

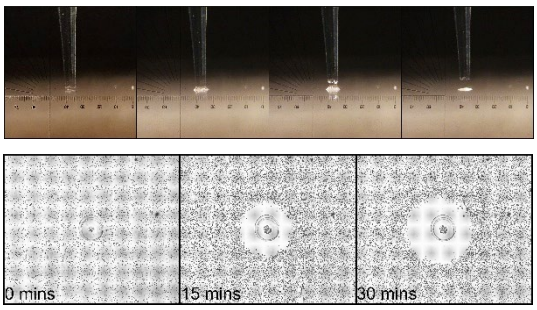

Figure 1. Images of the printing pin (OD = 215 µm) during the process of printing a micropump (upper row) and the depletion zone that develops in time around a 200 µm diameter GOX micropump in the presence of 0.2 mM glucose (lower row). The printing pin is filled with enzyme-based ink before being brought into contact with the silanized glass surface. The depletion zone increases in time in an enzyme concentration and substrate concentration dependent manner.

Conclusions: Our simple and versatile contact printing procedure allowed fabricating some of the smallest enzyme micropumps reported in the literature. The fabricated micropumps generated reproducible osmotic flows in the presence of glucose. The magnitude of these flows did not strongly depend on the diameter of the micropumps (in the investigated range of diameters). Current research is focused on using such micropumps in biosensing.

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EFFECTS OF USING WHEY MODIFIED GROWTH MEDIUM ON MICROALGAL BIOMASS GROWTH AND NUTRIENT METABOLISM

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Keywords: microalgae; whey; water reclamation; waste valorization

Introduction: Embracing the concept of circular bioeconomy in the context of increased social interest for improved environmental protection, requires industries to recalibrate their focus towards reducing or valorizing waste flows. This requirement is also true for the dairy industry, which produces annually large volumes of nutrient rich wastewaters, containing organic and inorganic components suitable for microalgae growth [1],[2].

Materials and methods: The microalgae strain chosen for this study was *Porphyridium purpureum*, which was cultivated in specific growth medium, modified with different ratios of added deproteinized cheese whey, under two types of illumination cycles, continuous and day-night. The metabolism of nutrients present in the modified growth medium by the microalgae were analyzed after a period of one week, through spectrophometric methods. Specifically, the lactose, total nitrogen and phosphorus, and chemical oxygen demand were monitored for each sample in both illumination systems. The effects of the stress factor present in the medium on this microalgae strain was also monitored through determining biomass and biocompounds productivity.

Results: In both types of illumination cycles, the addition of whey to the growth medium led to an increase in biomass production, which in turn also allowed for higher reduction rates to be achieved for all nutrients present. The increase in exopolysaccharide production, proportional with the increase in lactose availability, suggests the presence of a coping mechanism for dealing with the stress of a carbon source excess, which manifests through the consumption of lactose for both cell growth and polysaccharides excretion. In the case of pigments, concentrations were higher for the day-night cycle, as the stress caused by continuous illumination proved to be too disruptive for pigment accumulation. The added stress with the increasing lactose concentration led to a decrease in pigment concentration for both illumination systems.

Conclusions: The obtained results suggest that cheese industry derived wastewaters, rich in organic nutrients can function as a carbon source without having a negative effect on the growth of *Porphyridium purpureum*. The use of microalgae for water reclamation from these types of waste flows, not only helped reduce contaminants below the limitations imposed by existing regulations, which exist in the form of nitrogen, phosphorus and organic compounds, but also allowed for higher biomass productivities to be achieved.

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PLANTS WASTE - RICH SOURCE OF BIOACTIVE COMPOUNDS WITH THERAPEUTIC POTENTIAL

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Keywords: plants waste, bioactive compounds, therapeutic potential

Introduction: In the present eco and bio rush, materials such as essential oils, pharmaceuticals, colorants, dyes, cosmetics and biocides are obtained from plants. Production of bio-products based on natural compounds leads to the transformation of plants in large quantities of waste, such as waste resulting from the processing of the plant material, but also aerial parts of plants, shrubs or trees, etc., which are not used for consumption or obtaining consumer products. Thus, valorization and reuse of plant, fruit and vegetable waste through innovative strategies allow access to different raw materials without increasing the demand for biomass production.
The innovative strategies include extraction and purification of target compounds through modern techniques, such as microwave-assisted extraction, microwave hydro-diffusion extraction in gravitational field, accelerated solvent extraction, centrifugal partition chromatography, etc [1].

Many researchers are operating for the identification, isolation and testing of the bioactive substances in order to gain new effective natural medicines in various diseases. In recent years, numerous bioactive compounds have been isolated from fruit, vegetable and plant wastes [2-4] and the molecular regulatory mechanisms associated with different actions were identified, thus highlighting the therapeutic potential. There is a long history of using plant materials to treat human medical conditions. Although organic compounds from natural plant sources have been used in the past, they are still used today to treat various medical conditions, both in their natural form, as a phytoproduct, and as a ligand molecule for the development of synthetic or semi-synthetic analogs for the development of new, more effective drugs through structural modification.

Materials and methods: This paper represents a critical review on valorization of plants wastes through innovative methods in bioactive compounds with therapeutic potential. The review is based on articles from ScienceDirect database, published in the last 10 years. The electronic search was performed using specific keywords; title and abstracts retrieved by these searches were screened for relevance and deduplication. The selected articles were classified by article type (original research or review) and the validation was performed manually (by reading the entire article).

Conclusions: The valorization of plants waste into valuable bioactive compounds is important not only for a sustainable economic growth, but also for improving the therapeutic solutions by developing new combinations of preventive and curative methods, necessary in modern-day therapeutics.

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METROLOGICAL METHODS DEVELOPMENT FOR THE DETERMINATION OF INORGANIC IMPURITIES FROM SOLID BIOFUELS

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Keywords: wood pellets, wood chips, ICP-MS, method validation

Introduction: The present study aims the developing and validating methods for the identification by ICP-MS and quantification of the inorganic impurities from solid biomass. The development of the new methods, technology and knowledge will have impact on climate and environmental protection. Biomass is renewable organic material that comes from plants and animals. In 2021, biomass provided about 4,8 quadrillion British thermal units (Btu) and of that amount, 2 quadrillion Btu were from wood and wood-derived biomass.Wood chips and wood pellets are the most common type of biomass used as solid raw fuels. The aim of providing such studies is to improve the repeatability and reproducibility of the measurements. Repeatability is commonly used to describe the deviation between successive measurements of the same sample under the same conditions. Reproducibility is another component of the precision of the measurements. It refers to the ability to obtain the same results but performed under completely different conditions including the location and the operator [1], [2].

Materials and methods: The following materials were employed for the digestion process of wood chips and pellets: hydrogen peroxide, nitric acid, hydrofluoric acid, boric acid and ultrapure water. The inorganic impurities were qualitatively and quantitatively analyzed by ICP-MS.

Results: A method for the identification of inorganic impurities from solid biomass was developed. The method was validated by evaluating parameters as detection limit, precision, accuracy, uncertainty, robustness. Qualitative investigation involved the identification of 17 elements as wood chips and pellets impurities: Na, Cr, Ni, Cu, Cd, Pb, Ca, Mg, Al, K, Mn, Fe, Zn, S, Si, Ti, P. All the impurities were quantitatively evaluated. After validating the ICP-MS method, several real high quality wood pellets were prepared by microwave digestion and analysed by ICP-MS. Validated method is planned to be used for the certification (including homogeneity, stability and characterization tests [3]) of candidate wood pellet powder reference material.

Conclusions: This study has a high impact on both producers of solid biofuels and users of these products. Developing ICP-MS validated methods to determine the amount and nature of inorganic impurities in solid biofuels, brings us with one step closer to achieving a cut in greenhouse gas emissions.

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CYTOTOXIC POTENTIAL OF *EPILOBIUM HIRSUTUM*

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Keywords: Epilobium hirsutum, cancer, polyphenols

Introduction: Hairy wilowherb (*Epilobium hirsutum*) it was widely used all over the world as a medicinal plant and as food. The Egyptians, and then the folk medicine in Europe, used the herb to treat inflammations, adenomas and prostate tumors. Native Americans used it for burns when urinating, urinary problems in men, coughs and throat irritations, stomach and intestinal. Regarding phenolic compounds, it has to be noted that the plant biosynthesizes molecules with various pharmacological benefits [1]. The aim of this study was to prove the cytotoxic potential of hairy wilowherb polar and non-polar fractions against three cancer cell lines (Caco2, U87 and B16). The study revealed the potential antitumor activity of *Epilobium hirsutum* (Onagraceae family) selective fractions,the polar fractions having the most significat cytotoxic effect.

Materials and methods: The vegetable material was extracted with ethanol 70% (v/v), a solvent considered optimal for the extraction of a wide range of compounds of interest, respectively vegetable polyphenols, heterosides and aglycones. Next, the filtered crude alcoholic extract was analyzed with regard to the quantitative chemical composition in total polyphenols. Based on the results obtained, the crude hydroalcoholic extract was concentrated and resuspended in a quantity of ethyl alcohol 40% (v/v) so as to finally obtain a standardized extract in alcohol with an identical content in total polyphenols of 5mg total polyphenols expressed in gallic acid (GAE) / 1mL extract. Representative polyphenols were quantified by HPLC. Cell line and viability assay: Caco2 (human colorectal adenocarcinoma), U87 (human glioma) and B16 (murine subcutaneous melanoma) were cultured acording to manufactures instructions (ATCC, USA). Cell viability was evaluated using the MTS assay.

Results: We conducted a screening of cytotoxic potential of selective fractions (1-100µg/ml) isolated from hairy willowherb flowers against three cancer lines after exposure for 48 hours. All selective extracts were more active on B16- cell line, mainly aqueous and acetone solutions, at all concentrations tested.

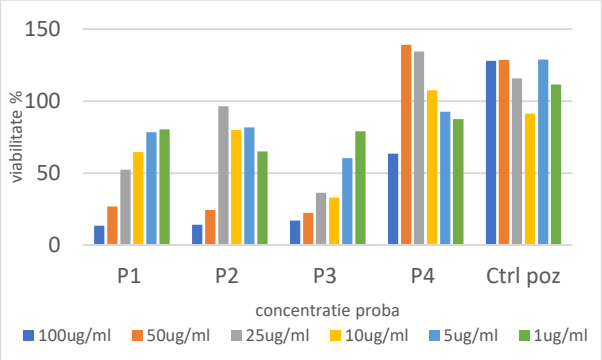

Figure 1. Viability of B16 tumor cells after exposure to plant extracts

Conclusions: The selective extracts in polar solvent proved to be the most effective, with a reduction in cell viability of 3.60-96.93% in the case of the aqueous fraction and of 20.95-92.96% in the case of the acetone fraction.

Acknowledgements: *This work was supported by Ministry of Research, Innovation and Digitalization program NUCLEU PN 1941-01 01.*

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PRODUCTION AND POTENTIAL APPLICATIONS OF BIOSURFACTANTS

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Keywords: biosurfactants, Pseudomonas sp., Bacillus sp., bioemulsifiers, applications

Introduction: Biosurfactants are surface-active biomolecules produced by various microorganisms, with a wide-range of applications. Considering the importance of microbial surfactants, this review paper presents the production of biosurfactants and their potential applications in various industrial fields.

Materials and methods: This paper involved an up-to-date review of literature using different open-access scientific databases, following keywords such as biosurfactants, waste substrates, bioremediation, applications, bioemulsifiers, microorganisms, production, surface tension.

Results: According to the literature, different microorganisms belonging to the genera *Pseudomonas, Bacillus, Candida, Rhodococcus* and *Corynebacterium* are predominantly used for the production of various biosurfactants, *Pseudomonas sp.* being mainly used to produce these important group of bioactive compounds [1]. Biosurfactants are classified in glycolipids (rhamnolipids, trehalolipids, sophorolipids), lipopeptides and lipoproteins, fatty acids, phospholipids, and neutral lipids [2],[3]. The most common carbon source used for production of biosurfactants is glucose. Because it is widely used as an industrial feedstock, it presents the disadvantage of increasing the production costs of microbial surfactants [4]. As an alternative, the development of obtaining processes based on cheap substrates, glycerol as a by-product of biodiesel production or waste oils, would contribute to reducing the gap between these costs and an increased market share of these products, which are superior to the synthetic ones in terms of implications on environment conservation [5]. The distinctive characteristics of biosurfactants are related to their surface activity, tolerance to pH, temperature and ionic strength, biodegradability, low toxicity, emulsifying and demulsifying ability, and antimicrobial activity, making them suitable for application in different areas, including pharmaceutical, cosmetic, food, and petroleum industries, medicine, agriculture and environment (bioremediation) [6].

Conclusions: Due to their unique properties, biosurfactants have potential applications in various industries. The use of waste products as substrates to produce more environment-friendly biosurfactants represent an area of interest for researchers in recent years.

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CHARACTERIZATION OF POROUS BIOMATERIALS BASED ON FISH COLLAGEN AND PECTIN FROM CARROT PULP AND APPLE PEEL FOR TISSUE ENGINEERING

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Keywords: collagen, pectin, sponge, properties, biomaterial

Introduction: Collagen is a polymer available for extraction from a multitude of animal sources, including aquatic ones. Collagen-based biomaterials are widely used for several applications of tissue engineering. It was demonstrated that the biomaterials prepared from mixtures of collagen and polysaccharides showed improved physico-chemical properties, compared to those of collagen biomaterial [1]. This study investigated the physico-chemical, biochemical and biological properties of porous biomaterials based on mixtures of fish collagen and pectin from carrot pulp and apple peel for tissue engineering applications.

Material and methods: The biomaterials were prepared by mixing a solution of collagen enzymatically extracted from fish waste [2] with pectin extracted from carrot pulp and apple peel [3], respectively, in weight ratios of 10:1 and 20:1. These mixtures were finally freeze-dried, to obtain porous 3D matrices. The biodegradability of the prepared matrices was determined by incubation in the presence of collagenase and protein quantification with ninhydrin, at predetermined periods of time. Their porosity and swelling degree were evaluated by gravimetric assays after incubation in TES buffer. Structural observations of porous biomaterials were performed at a scanning electron microscope. The cytocompatibility of prepared biomaterials was assessed in L929 fibroblast culture, by direct contact assay and cell viability evaluation by MTT test, after 48 h of cultivation.

Results: The results showed that porous 3D biomaterials based on fish collagen and pectin from both sources had lower degradation degree, compared to collagen biomaterial. Thus, the biomaterial variants of collagen-carrot pectin and collagen-apple pectin, in a ratio of 10:1, had lower degree of biodegradation than the collagen matrix, with 11.8% and 10.46%, respectively, indicating better stability. The addition of pectin to collagen biomaterial led to porosity decrease. This tendency was also observed for the pores sizes measured by scanning electron microscopy. The swelling degree of porous pectin-containing matrices was higher than that of collagen matrix, due to the water absorption capacity of polysaccharides. All matrix variants showed good cytocompatibility in L929 cell culture and values of cell viability higher than 80%. In addition, stimulation of cell metabolism and proliferation was observed in the case of fish collagen-apple peel pectin variant with 10:1 ratio between components.

Conclusions: All these results demonstrated good physico-chemical and biochemical properties of the porous 3D matrices prepared from mixtures of fish collagen and carrot pulp or apple peel pectin. They presented lower biodegradability and porosity degree, and higher swelling degree than those of fish collagen matrix. All these properties and the high degree of cytocompatibility recommend these biomaterials for tissue engineering applications.

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CYTOTOXICITY AND INFLAMMATORY EFFECT OF AN ALLERGENIC PROTEIN EXTRACT OF ROASTED PEANUTS

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Keywords: peanuts extract, cytotoxic effect, inflammatory effect, allergen

Introduction: The protein content of peanuts is around 25%. Many individuals from North America and Northern Europe developed an allergic reaction to the main peanut proteins, which are Ara h1, Ara h2 and Ara h3, while in Southern Europe the reaction was higher to Ara h8 and Ara h9 [1],[2]. Studies have shown that Ara h1 and Ara h3 were the peanut allergenic proteins that exhibited pronounced stimulatory effects on IL-8 secretion in Caco-2 cell culture [3]. The aim of this study was to investigate the *in vitro* cytotoxicity and inflammatory effect of an allergenic protein extract of roasted peanuts.

Materials and methods: A protein extract was obtained by incubation of defatted flour of roasted peanut in 0.05 M carbonate buffer, pH 9.6, in a ratio of 1:10 (w/v), at 25 °C for 4 h. The extract was then subjected to centrifugation at 10000 rpm, for 30 min, at 4 °C, and the supernatant was collected. The protein content was determined by the Biuret method using a standard curve of bovine albumin. *In vitro* cytotoxicity testing of different concentrations of peanut extract was conducted in an experimental model of direct contact, in a culture of human Caco-2 intestinal cells, according to the international standard ISO 10993-5. The cell viability was evaluated by Neutral Red assay, after 24 and 48 h of cultivation. The inflammatory effect was investigated in Caco-2 intestinal cells treated with a non-cytotoxic concentration of peanut extract for 24 h. The level of IL-8 pro-inflammatory cytokine secretion was analyzed by ELISA assay, at 24 h of cultivation.

Results: The results of protein quantification by Biuret method showed a protein content of 37.8 mg/mL for the peanut extract. Cell viability data indicated that the peanut extract was biocompatible between 0.1-5 mg/mL after 24 h and between 0.1-1 mg/mL after 48 h of cultivation (>80% cell viability) (Figure 1). At higher concentrations, the peanut extract had a mild cytotoxic effect. ELISA assay results revealed that the non-cytotoxic concentration of peanut extract favored an increase of IL-8 cytokine level by 2.2 fold, compared to the untreated cells (control).

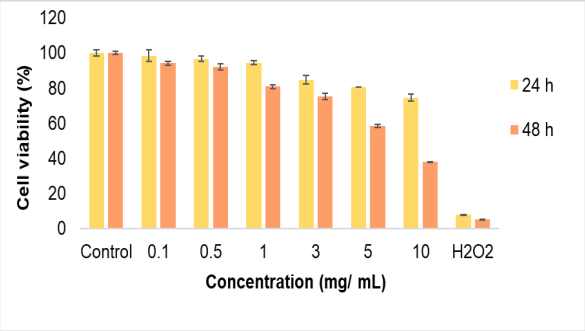

Figure 1. Viability of Caco-2 cells treated with peanut extract for 24 and 48 h, as evaluated by Neutral Red assay.

Conclusions: All these results have demonstrated the ability of the roasted peanut protein extract to induce a local inflammatory response at the level of intestinal mucosa, which might explain its high allergenic potential. Future studies could identify and compare the activity of individual proteins from the roasted peanuts, in order to propose strategies for reducing their allergenic potential.

***Acknowledgement**: This work was supported by the Ministry of Research, Innovation and Digitization within National Programme Nucleu, Project No. 25N/2019-19270102.*

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SYNTHESIS OF GOLD NANOPARTICLES FROM LAVENDER BIOMASS AS A SUSTAINABLE RESOURCE

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Keywords: gold nanoparticles, green synthesis, phenolic compounds, plant biomass wastes.

Introduction: In the near future, aromatic plants biomass waste will become a significant issue unless additional processing is implemented to recover therapeutic chemicals [1], and by adopting the resource efficiency and waste-to-energy transformation (WTE) trends in energy consumption that are prevalent globally [2]. Our aim was to obtain and analyze ecologically synthesized of gold nanoparticles (AuNPs) from lavender biomass waste extracts containing high amounts of bioactive compounds.

The chemical composition of *Lavandula angustifolia* extracts was determined by chromatographic and spectroscopic methods. AuNPs were characterized by UV-VIS, FT-IR spectroscopy, and SEM-EDX. The antioxidant and the antibacterial activity were evaluated.

Materials and methods: For the green AuNPs synthesis, the plant extracts were freshly prepared by a 30 min infusion, followed by a 0.45 mm filtration step. The AuNPs synthesis used the procedure described by Chiravoot et al. [3] with some modifications: 27 mL of 1mM $HAuCl_4 \bullet 3H_2O$ solution were added to 4 mL lavender biomass extract and ultra-sounded for 1h at 35kHz, 100% power. After synthesis, the AuNPs were washed and centrifuged 3 times with deionized water and freeze-dried for storage and analysis.

Results: The phenolic components present in the aqueous extracts acted as mediators for the bio-reduction of gold ions. This reaction was easily visible as a change in color from pale yellow to pink and was afterwards confirmed by UV-VIS analysis with a maximum intensity observed at 535-550 nm.

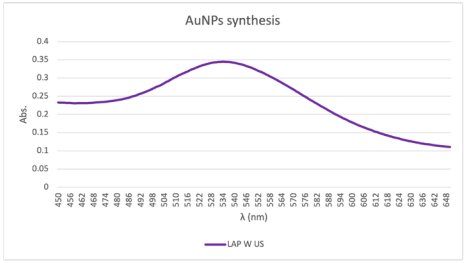

Figure 1. UV-VIS spectra AuNPs

Conclusions: Gold nanoparticles were successfully obtained from phenolic compounds present in the aqueous extracts recovered from aromatic plants biomass wastes. Utilizing plant extracts has several advantages, such as simple accessibility and safety, a wide variety of metabolites, and a rapid synthesis that results in stable, benign, and side effect-free metal NPs.

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RECOVERY OF NATURAL PIGMENTS WITH POTENTIAL APPLICATIONS IN COSMETICS AND FOOD THROUGH CONVENTIONAL AND UNCONVENTIONAL METHODS

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Keywords: phycocyanin, microwave-assisted extraction, ultrasound-assisted extraction

Introduction: *Spirulina plantesis* is a cyanobacterium with valuable nutritious compounds (55-70% proteins, 15-20% carbohydrates, and 7% lipids) and pigments, such as phycocyanin [1]. Besides its use as natural colorant in various foods and cosmetic formulations, the phycobiliprotein also has potential in the treatment of oxidative diseases and as fluorescent marker in biomedical research [1], [2]. Furthermore, spirulina blue can be an environmentally friendly coloring solution which can successfully substitute Brilliant Blue FCF [3]. The aim of the study was to determine the best extraction conditions of phycocyanin from powdered spirulina, in order to utilize it as a natural blue pigment.

Materials and methods: Spirulina, in the form of powder, was subjected to conventional and unconventional extraction methods – ultrasound-assisted (UAE) and microwave-assisted (MAE) extractions. They were carried out using a 0.1M sodium phosphate buffer solution (pH = 7.4), a 1/15.6 (w/V) ratio of vegetal material to solvent, and magnetic stirring. The conventional extractions (CE) were performed at different temperatures (room temperature, 30, and 40 °C) and at different extraction times (up until 330 min, using 30 min increments). The UAE were executed in a controlled-temperature jacketed reactor, using the UP200H Ultrasonic Processor at a 30% amplitude and different cycles (0.5 and 1), for several extraction times (5, 10, 15, 20, 25, and 30 min). MAE was carried out using the Biotage®Initiator at 40 and 50°C and a similar processing time as for UAE. After the extractions, the mixture was centrifuged at 4000 rpm for 15 min at room temperature and the supernatant was further examined. The extracts were analyzed to determine the phycocyanin concentration using a spectrophotometric method developed by Munawaroh et al. [4].

Results: The influence of temperature and time on the extraction efficiency was studied. Good results were obtained for all extraction methods. The CE provided a high phycocyanin content at long extraction times, obtained more rapidly at higher temperatures (comparative results were obtained at RT for 270 min and 40 °C for 120 min). Compared with CE, a higher extraction yield in a shorter time resulted for both UAE and MAE. The best results were achieved for UAE, where the highest phycocyanin content was obtained using a cycle of 0.5 for 15 min. A similar value resulted for MAE, at 40 °C, but a longer time period was necessary.

Conclusions: Spirulina is an important functional food with a probable future in dyeing industry. The aim of this study was to establish the best extraction conditions for phycocyanin – natural blue pigment – from powdered spirulina. The best extraction conditions, considering both time and energy consumption, were using UAE: 15 min, and a duty cycle of 1 s ON and 1 s OFF.

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THE VALIDATION OF A SNACK PRODUCT WITH ADDED FUNCTIONAL INGREDIENTS USING DESCRIPTIVE SENSORY ANALYSIS

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Keywords: optimal profile, descriptive sensory analysis, functional snack bar

Introduction: The association between diet and health leads to the expansion of consumers' horizons regarding food products such as snacks with the addition of functional ingredients that provide benefits for improving health [1],[2]. The purpose of the research was to validate the formula of a snack product with added functional ingredients according to the optimal sensory profile for snack type cereal bars selected based in the benchmarking study.

Materials and methods: The optimal sensory profile according to the preferences and consumption needs of the target consumers was realized by projection the optimal sensory descriptors on a Spider diagram using the descriptive sensory analysis method, with 6 expert evaluators panel, according to SR ISO 6564:2007 standard [3]. The quantification of each descriptor was based on 7-point monopolar scale: from 1 (zero intensity, cannot be perceived) to 7(extremely high intensity). The obtained average values from the individual evaluations of each descriptor were represented on the Spider diagram. Based on this diagram the optimal sensory profile of snack type cereal bars was generated. Using the optimal sensory descriptors, two snack products with added functional ingredients were developed. The experimental sensory profile was created based on the previously mentioned method. To validate the formulation of the experimentally obtained products, both profiles were compared: the optimal sensory profile and the experimental sensory profile.

Results: The comparison of sensory profiles showed a high correlation. The values of the differences between the two overlayed profiles for sensory descriptors were as follows: 0.09 surface texture; 0.91 flavour; 0.18 sweet taste; 0.13 sour taste; 0.21 bitter taste; 0.55 firmness of mastication; 0.13 crumbliness; 0.03 stickiness; 0.42 oily; 0.27 granularity; 0.25 aftertaste duration; 0.25 aftertaste intensity. Taking into account that all the differences were lower than 1 we can mention that there are no significant differences between the two compared profiles.

Conclusion: The formula of the snack product with added functional ingredients presented the following sensory descriptors: compact and semi-glossy outer texture, fruit flavour with slightly above average intensity, moderate sweet taste, semi-hard firmness and crispy parts, compact non-homogenous inner texture, medium crumbliness and pleasant aftertaste medium as intensity and duration. All these descriptors had similar intensities to the descriptors of the optimal sensory profile, resulting experimentally products according to the development hypothesis. Considering the results obtained, the selected descriptive sensory analysis method was an efficient approach to validate the formula of a snack type product with added functional ingredients.

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IMPROVED POROUS 3D BIOMATERIALS BASED ON NATURAL AND SYNTHETIC POLYMERS FOR SKIN REGENERATION

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Keywords: please provide up to five keywords separated by semicolon

Introduction: Although skin has higher self-regeneration capacity than most tissues after being injured, the healing of large-scale or deep wounds is usually limited, suffering from scar formation [1].
The aim of this study was to design and characterize porous 3D biomaterials based on natural and synthetic polymers enriched with biomolecules like fibronectin and heparin in order to improve their surface cell adhesion properties and facilitate the regeneration of injured skin tissue.
Materials and methods: The proposed experimental variants are based on natural components, gelatin (Gel) and sodium alginate (Alg), and synthetic components, polyvinyl alcohol (PVA) and methyl cellulose (MC1500), in different combination ratios: Gel-Alg (1:0,75 g/g), Gel-Alg-PVA (1:0,41:1,66 g:g:g), Gel-Alg-MC1500 (1:0,41:0,55 g:g:g). The porous 3D biomaterials were obtained by freeze drying after ionic cross-linking with 2% $CaCl_2$. Physicochemical characterization was performed in terms of density and porosity determination, swelling degree and biodegradation. In order to improve cell adhesion capacity of these biomaterials, heparin and fibronectin were added in the proportion of 0.1% and 0.01%, respectively. *In vitro* biological evaluation was carried out on two cell lines, L929 murine fibroblasts and human HaCaT keratinocytes, by measuring cytotoxicity [2] and cell adhesion capacity using the quantitative MTT assay and qualitative fluorescent Live/Dead test.

Results: The addition of synthetic compounds to the 3D biomaterials has resulted in a decrease in density and an increase in porosity. A lower density and a higher porosity and degree of swelling was observed for the Gel:Alg:APV variant (0,076 g/cm^3, 62.50% and 727.68%, respectively). The biodegradation results indicated that the porous 3D biomaterials did not cause the blocking of the collagenase action site, thus, a time-controlled biodegradation was observed. The results of the MTT test showed a high degree of cytocompatibility of the porous biomaterial variants tested on both cell lines. Thus, cell viability values remained above 80% (non-cytotoxic effect) for all tested samples after both 24 and 48 hours of treatment. The Live/Dead test showed that after 48 hours, the cells adhered to the surface of the biomaterials and remained viable, the proportion of dead cells being insignificant. Also, no important changes in cell morphology and density were observed, both cell types maintaining their normal morphological appearance. Furthermore, the enrichment of the biomaterials with heparin and fibronectin have led to an increase in cytocompatibility and cell adhesion.

Conclusions: The tested biomaterials presented suitable properties, such as porosity, biodegradability, swelling degree, cytocompatibility and cell adhesion capacity that could recommend them as temporary dressings for wound healing.

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