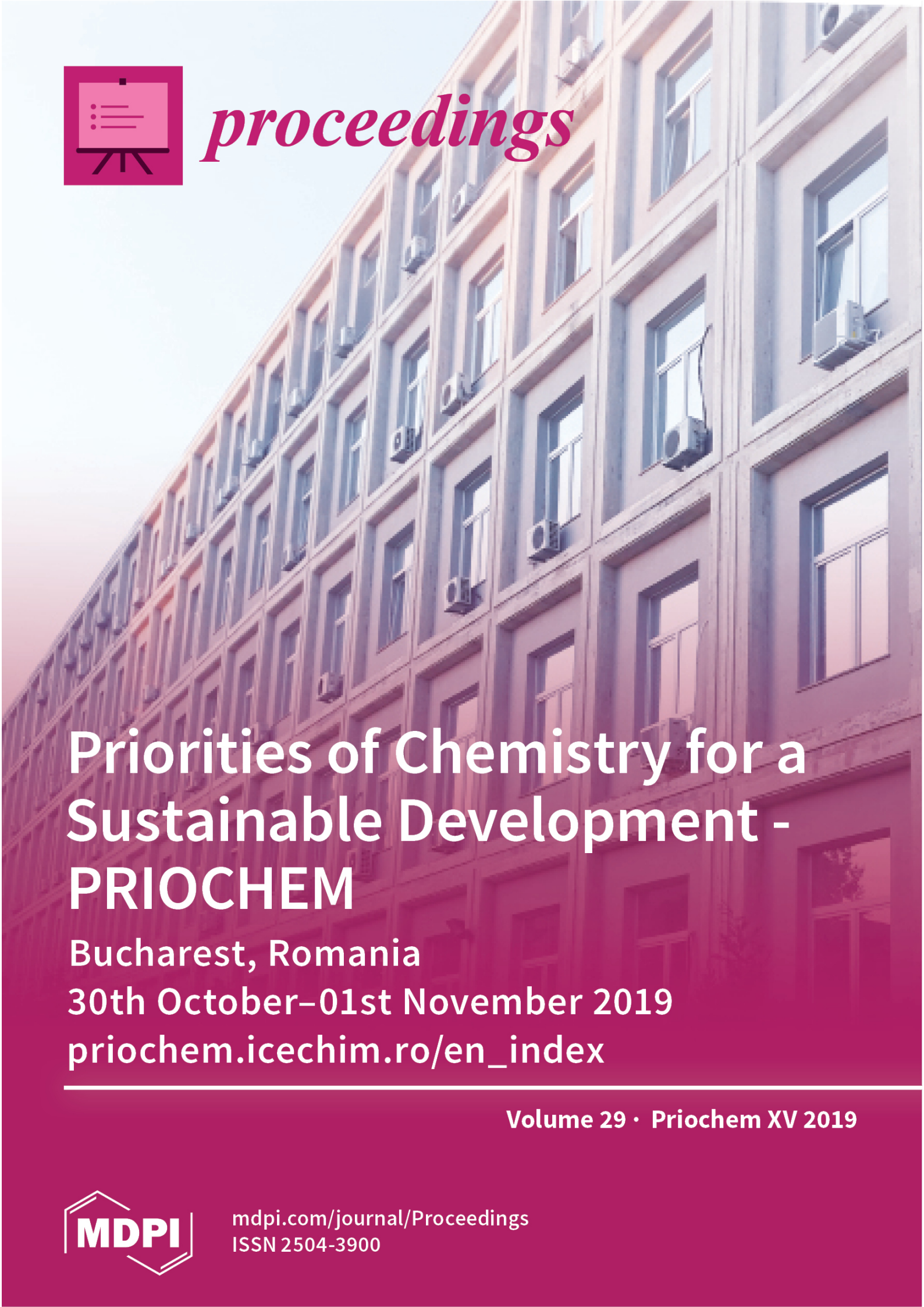

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Abstract Book of Priochem XV 2019

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Abstract

Metal Specific Functionalized Nanofibers †

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Keywords: nanofiber; chelating ligand; polyacrylonitrile; polystyrene; polyethylene terephthalate; 2-(2′-pyridyl)imidazole; 2-pyridine amidoxime; diglycolic anhydride ligand; nickel; lead

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Functionalized nanofibers made by electrospinning technique are one respectable option for metal removal and purification from aqueous solutions. Due to the simple and versatile process resulting in high porosity and high specific surface area structure with high selectivity properties, functionalized nanofibers have been gaining increased interest during recent decades [1]. In the case when high selectivity is needed, chelating ligand functionalized nanofibers are good option for the removal of heavy metals and rare earth elements (REEs) from aqueous solutions [2–3]. Chelating ligands act as electron donors and form coordinative bonds to a metal cation called the central atom, and, in this way, can increased significantly selectivity.

In our study, we have synthesized polyacrylonitrile (PAN) nanofibers with 2-(2′-pyridyl)imidazole (pim) and 2-pyridine amidoxime (PyAMi) ligands for nickel and lead removal, respectively. Furthermore, we have also synthesized polystyrene (PS) and polyethylene terephthalate (PET) nanofibers with diglycolic anhydride ligand (DGA) and studied them for removal of the rare earth elements (REEs) Ce^{3+} and Nd^{3+} from aqueous solutions. All synthesized nanofibers were characterized for FTIR and BET specific surface areas, pore volumes, and average pore diameters. Chemical stabilities were studied in acidic conditions. Metals adsorption and binding kinetics were measured in batch system for all materials.

Metal adsorption capacities were in high level in all the materials. The case of PAN-pim, the nickel capacity at pH 5 was 0.8 mmol/g, whereas the lead capacity for PAN-PyAMI was at pH 6 0.025 mmol/g. In the case of REE removal, the binding capacities for PS-DGA and PET-DGA nanofibers for Ce^{3+} were 1.1 and 0.7 mmol/g, respectively and for Nd^{3+}, 2.3 and 0.5 mmol/g, respectively. The binding kinetics of PS-DGA and PET-DGA for Ce^{3+} and Nd^{3+} were relatively fast—equilibria were attained for both REE over 20 and 5 min, respectively. The chemical stabilities of PS-DGA and PET-DGAs were good in acidic conditions, and metals were successfully regenerated from the nanofibers and reused at least four adsorption–desorption cycles without the loss of significant metal adsorption capacities. The adsorption rate of nickel for PAN-pim was extremely fast; the adsorption equilibrium was attained after 1 minute. However, chemical stability was not good. In the case of PAN-PyAMI, neither chemical stability nor adsorption rate for lead removal were good.

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proceedings

Abstract

Synthesis and Characterization of Supported TiO_2 Based Nano Catalysts and Application for the Removal of Water Contaminants †

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Keywords: wastewater; drinking water; AOPs; photo catalysis; hydroxyl radical; corrosion; coatings; removal efficiency

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The occurrence of persistent organic contaminants such as pharmaceuticals, personal care products, pesticides, and organic dyes in water sources have been recognized as a major problem worldwide. Besides, the removal of these contaminants, particularly organic dyes, by conventional wastewater treatment processes such as physical, chemical, and biological methods have not produced satisfactory results. In order to comply with the environmental regulatory framework vis-a-vis improvement of water quality, cost effective, sustainable, and advanced treatment techniques need to be established. Among various advanced oxidation processes (AOPs), heterogeneous photocatalysts such as titanium dioxide (TiO_2) have been identified as a possible treatment method for water pollution remediation due to unique characteristics such as low cost, photochemical stability, and strong oxidizing power [1]. Nevertheless, post-filtration of the suspended TiO_2 particles after water treatment, high band gap energy, and high recombination of electron-hole pairs constitute serious disadvantages that limit their industrial applications [2]. In this study, various TiO_2 based-catalysts were synthesized by sol-gel method and calcined under N_2 at different temperatures, ramping rates, and holding times. The TiO_2 based were doped and co-doped with transition metal Ag (TiO_2, Ag-TiO_2) and non-metals C and N (C-TiO_2, C-N-TiO_2). The resulting catalysts were also immobilized by sol-gel dip coating on various supports including stainless steel (SS) and Ti meshes, Cr and Ti nitride and oxynitride anticorrosion coatings. The catalysts were characterized by numerous analytical techniques such as UV-vis/diffuse reflectance spectroscopy, XRD, HRSEM, HRTEM, EDS, SAED, FTIR, TGA-DSC, BET, and XPS. The photocatalytic activity of the prepared catalysts was evaluated upon the degradation of model dyes (methylene blue & orange II sodium salts) and micropollutants, such as bisphenol A (BPA) and 2-nitrophenol (2-NP), under UV and visible light at the applied conditions. The results showed that high pollutant removal efficiencies were achieved with supported C-N-TiO_2, C-TiO_2, Ag-TiO_2, and TiO_2, respectively. Likewise, excellent catalytic activities were achieved by combination of the prepared catalysts with other AOPs including dielectric barrier discharge (DBD) plasma system and hydro dynamic cavitation Jet loop. These studies clearly demonstrated that AOPs are environmentally safe and robust alternatives that can be

employed for water and wastewater treatment, while the synthesized nano materials could be used for various applications for environmental remediation, and perhaps for clean energy technologies.

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Abstract

Silane Primers as Adhesion Promotors for Coatings †

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Keywords: silane primers; sol-gel; silicone; adherence; polymer-metal assemblies

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Sol-gel processing is a soft-chemistry method to obtain ceramic materials at low temperatures starting from molecular precursors in solution. The precursors can be inorganic salts ($Al(NO_3)_3$, for example) but are mostly metal or silicon alcoxydes of a general formula $M(OR)_x$ with M = Si, Ti, Zr, Hf, Ce, Al, etc. The formation of a network of oxides from $M(OR)_x$ involves hydrolysis and condensation reactions. Condensation is a complex process that involves the formation of a bridging oxo group through the elimination of an alcohol (alcoxolation) or water (oxolation) molecule. The formation of bridging hydroxo groups through the elimination of a solvent molecule (olation) can also occur when the maximum coordination of the metal atom, N, is not satisfied in the alkoxide (i.e., N > z, the oxidation state of the metal). Silicon alcoxides, for which N = z, are thus not concerned by olation reactions. The development of inorganic sol-gel coatings has been driven by environmental and technical aspects: sol-gel coatings are non-carcinogenic, environmentally safe, stable, and strongly adherent on metal surfaces. The strong adherence to metal substrates has been related to the formation of covalent M-O-M' bonds (M = substrate and M' = Si, Ti, Zr, etc.) that are produced during the drying stage. The most promising applications of such coatings are their uses as thin adherence promoter layers for a subsequent organic coating. The brittleness of inorganic sol-gel coatings can be mitigated by the incorporation of an organic component into the dried film structure. Silica-based hybrids have been studied much more frequently than titania-based or zirconia-based hybrids. This is due to the fact that silicon can readily be covalently linked to the organic component through Si-C stable bonds. By using organoalkoxy silanes, $R_{1x}Si(OR_2)_{4-x}$ with x = 1 or 2, a silsesquioxane network built from $R_1SiO_{1.5}$ units(x = 1) or polysiloxane linear chains (x = 2) are obtained. The organic group R_1 can be non-reactive (for example methyl or phenyl) or reactive (for example amino, oxirane or methacryloyl groups in γ-aminopropyltriethoxysilane, γ-glycidyloxypropyltrimethoxysilane and γ-methacryloyloxypropyltriethoxysilane, respectively). The reactive group R_1 can attach to the polymer which is applied on the silane-treated metal. The organic component makes the gel network more flexible and, thus, less prone to cracking during heat treatment of the film. We will see in this presentation that γ-aminopropyltriethoxysilane, γ-APS, primers improve the wet durability of powder epoxy—steel joints that are prepared at high temperatures (around 200 °C). It was shown that a bonding between epoxy and silane occurred when the silane sol was prepared at natural pH conditions but not under acidic conditions. XPS and FTIR results revealed a partial oxidation of the amine head group of γ-APS to amide but a few amino functionalities remain to react with oxirane groups of epoxy resin and strengthen the epoxy/silane interphase. Silane-based primers can also be used to increase the adherence of silicone rubber/metal assemblies. In this case, PDMS reinforced with fumed silica is often incorporated to the primer formulation as film former and in order to

enhance the diffusion of the primer film into the silicone rubber matrix. We see that the nature and the amount of silica filler are decisive for the silicon-metal assembly to obtain a strong adherence.

Oral Presentation

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Abstract

Design, Synthesis, Molecular Docking and Antibacterial Screening of Some Quinolone Compounds †

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

Drugs belonging to the quinolone compounds are characterized by a quicker biological activity and a broad antibacterial spectrum [1–4]. Molecular, topological, and conformational characteristics on 3D quinolones optimized structure have been calculated using Spartan 14 Software. Molecular docking approach using CLC Drug Discovery Workbench 2.4 software have been realised to identify and visualize the most likely interaction ligand (quinolone) with the receptor protein. The quinolone compounds have been obtained by the Gould-Jacobs method. The compounds have been characterized by physical-chemical methods and by antimicrobial activity against Gram-positive and Gram-negative microorganisms. In this study, the DFT/B3LYP/6-311G* level of basis set has been used for the computation of molecular structure, vibrational frequencies, and energies of optimized structures. 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 quinolone compound in the active site of the protein-receptor (Figures 1 and 2). The protein-ligand complex has been realized based on the X-ray structure of *Bacillus cereus*, which was downloaded from the Protein Data Bank (PDB ID: 1VEN). In the present study, we have reported the synthesis of some quinolone compounds. The quinolones have been evaluated for their antibacterial activity against Gram-positive and Gram-negative microorganisms.

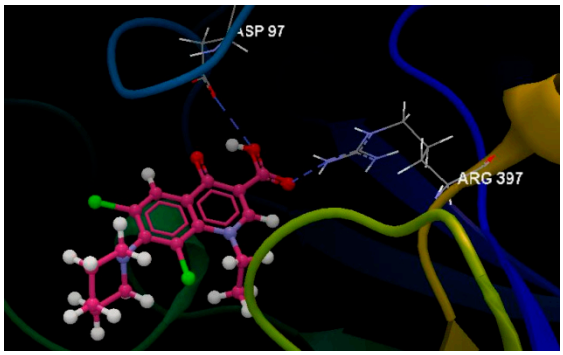

Figure 1. Docking pose of the compound 6ClPQ33.

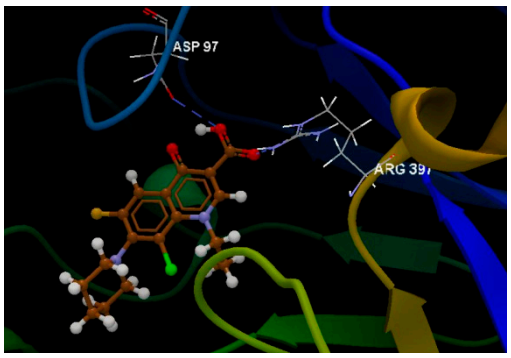

Figure 2. Docking pose of the compound FPQ33.

Structural modifications of this class of antimicrobial agents have afforded compounds with better activity aginst *Bacillus cereus*, *Bacillus subtilis*, *Salmonella typhimurium*, *Micrococcus luteus*.

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

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Abstract

Green Synthesized Silver Nanoparticles as Multifunctional Materials for the Degradation of Different Dyes †

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Keywords: silver nanoparticles; green synthesis; degradation; dyes

Silver nanoparticles, widely known for their antimicrobial, antioxidant, and antifungal properties, can be obtained using conventional or unconventional methods and have various applications in different scientific fields, including degradation of dyes from the textile industry [1,2]. This paper describes the one-pot green synthesis of silver nanoparticles (AgNPs) from three different plants (Sea buckthorn, Ramson, and Cornflower) and their potential use in the degradation of some azoic dyes. The three plants (Sea buckthorn, Ramson, and Cornflower) were used to prepare the aqueous extract at room temperature for 24 h. A qualitative and quantitative screening of bioactive components was carried out using standard analytical techniques, and the aqueous extracts were used for the green synthesis of AgNPs at room temperature and at 50 °C. In order to confirm the formation of the AgNPs, UV–Vis, FTIR, DLS, and SEM spectra were recorded. Also, their antioxidant activity was determined and their potential use in the degradation of some azoic dyes was investigated. The qualitative screening of phytochemicals revealed a positive response for saponins, carbohydrates, alkaloids, etc., making them an excellent natural material for the green synthesis of AgNPs. The UV–Vis spectra were recorded at different time intervals and exhibited peaks at 435 nm (Sea buckthorn), 442 nm (Ramson), and 452 nm (Cornflower). FTIR measurements allowed the determination of major functional groups present in the structure of the AgNPs (e.g., C=C, C=O, C–H, etc.).This paper presents the green synthesis of silver nanoparticles (AgNPs) from three different plants (Sea buckthorn, Ramson, and Cornflower) and their physical-chemical characterization using UV–Vis, FTIR, DLS, and SEM. Also, preliminary studies were carried out to investigate their potential use in the degradation of some azoic dyes.

Acknowledgments: This paper was prepared with the financial support of the project PN 19.23.03.01.04.

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proceedings

Abstract

Influence of Mesoporous Silica Functionalization and Pore Size on Resveratrol Release Profiles †

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Keywords: mesoporous silica; resveratrol; drug delivery; functionalization

Encapsulation of biologically active compounds in nanocarriers is a promising approach for controlling their release profiles and biological activity. Mesoporous silica nanoparticles (MSNs) are good candidates for developing drug delivery systems due to their biocompatibility, high porosity, and facile synthesis [1]. Moreover, the MSN surface properties can easily be tailored through functionalization with various organic groups [2]. SBA-15 and MCM-41 were obtained by sol–gel synthesis. The carriers were functionalized with 3-aminopropyl, 3-mercaptopropyl, cyanopropyl, isocyanatoethyl, phenyl, and carboxyl groups. Resveratrol was chosen as a model drug having low aqueous solubility, which limits its bioavailability. The carriers and resveratrol-loaded samples were characterized by small- and wide-angle X-ray diffraction, FT-IR spectroscopy, scanning electron microscopy, N_2 adsorption desorption isotherms, and thermal analysis. The resveratrol release profiles (Figure 1) were obtained in phosphate buffer solution (PBS) pH 6.8, at 37 °C and compared with the dissolution of biologically active compound in the same conditions. The experimental results were fitted with a theoretical kinetics model, consisting of biologically compound adsorption and desorption, followed by diffusion processes.

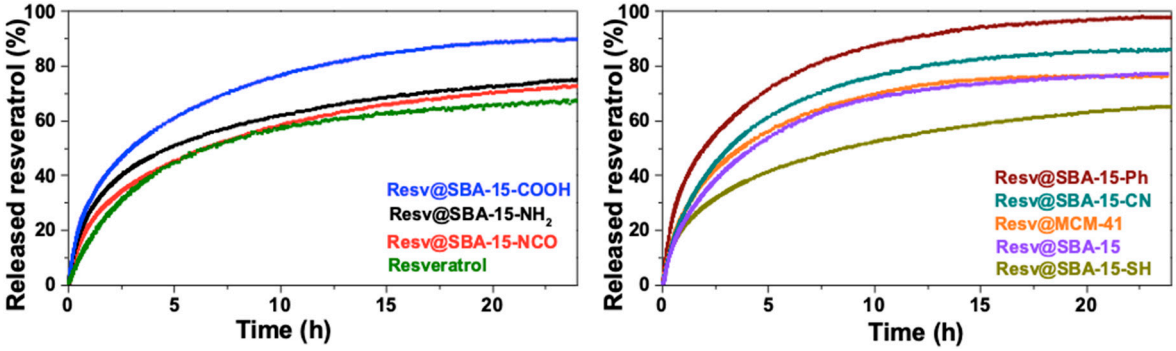

Figure 1. Resveratrol release from functionalized SBA-15 carriers in comparison with pristine silica with different pore size.

The resveratrol release profiles can be tailored by silica surface functionalization. Linking organic moieties on silica surface able to form strong hydrogen bonds, like carboxyl, isocyanatoethyl, or amine, it was possible to slow down the resveratrol sustained release. The best results in term of resveratrol enhanced solubility in PBS pH 6.8 were obtained for phenyl-functionalized SBA-15 carrier due to its hydrophobic nature.

Acknowledgments*:* The authors acknowledge the financial support from UEFISCDI funding program PCCDI 85/2018.

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Abstract

New Carbocyclic Nucleosides with a Constrained Bicyclo[2.2.1]Heptane Fragment as a Glycoside Moiety †

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Keywords: 1′homocarbonucleosides; 6-chloropurine; antiviral activity; Mitsunobu reaction; molecular docking

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Nucleosides with a norbornane fragment as sugar moiety (Figure 1) were found to have antiviral and anticancer activity [1]. Previously we obtained new carbocyclic nucleosides with an optically pure bicyclo[2.2.1]heptane fragment with antiviral activity against Influenza viruses and coxsackivirus B4 [2] similar to that of the most active norbornane nucleosides in this class of compounds. Now we present the synthesis of new 1′homocarbanucleosides, molecular docking, antiviral activity and correlation between the docking score and experimental found herpes simplex type-1 virus activity. Synthesis of the compounds started from an optically active intermediate in a sequence of reactions which conducted to a key 6-chloropurine intermediate.

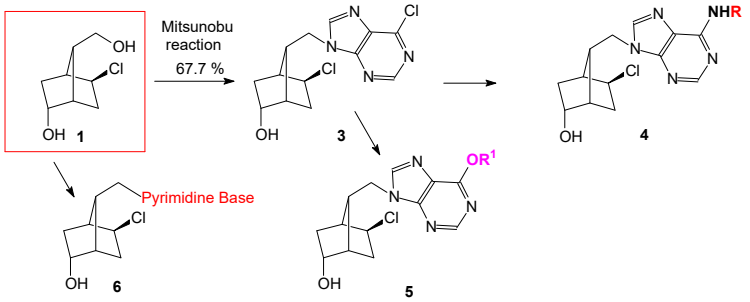

Figure 1. New carbocyclic nucleosides with a constrained norbornane scaffold as sugar moiety.

Molecular docking was performed on a professional soft CLC Drug Discovery Workbench Software. The protein-ligand complex was realized based on the X-ray structure of herpes simplex type-1 thymidine kinase (TK) in complex with acyclovir (AC2), which was downloaded from the Protein Data Bank (PDB ID: 2KI5). Antiviral activity against adeno-, herpes- and influenza viruses was done at Pasteur Institute of Epidemiology and Microbiology, Department of Virology, St. Petersburg, Russia and against enterovirus 71 (EV71), yellow fever and Chikungunya viruses, at Rega Institute, Laboratory of Virology and Chemotherapy, Leuven-Belgium, using published procedures. A total of 18 compounds were synthesized, fully characterized, and tested for their antiviral activity. Seven other synthesized compounds were not yet tested. A molecular docking study and the correlation between the experimental and predicted data were realized. Two compounds (**6j** and **6d**) had lower IC_{50} (15 ± 2 and 21 ± 4 μM) and one compound had IC_{50} similar to that of acyclovir (28 ± 4 μM) in experimental activity against herpes simplex type-1 virus [3] .

Acknowledgments: The funds were provided by PN 19-41 01 03.

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Abstract

High Temperature Nanocomposite Phase Change Materials Containing Mesoporous Silica Matrices †

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Keywords: phase change materials; mesoporous silica; molten salts; high temperature

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High temperature heat storage is an active field of research, especially for addressing the intermittency issues of solar power. Molten salts are used so far as sensible heat storage materials. Such materials can have greatly increased energy storage, if the solid-liquid phase transition is employed. However, the phase transition implies large changes in molar volume, leading to installation damage, leakage, and loss of storage. To alleviate this drawback, we proposed nanocomposites obtained by impregnating the salts into mesoporous silica, a porous matrix [1]. The resulting shape-stabilized phase change materials (ssPCMs) can be used for latent heat storage while preserving their solid shape. Mesoporous silica nanomaterials (MSN) were chosen as matrices because of their high thermal and chemical stability, large porosity, and monodisperse mesopore diameters [2]. The aim of the present study is to assess the influence of different textural properties of the MSN matrices (pore diameter, pore volume, surface area) on the thermal properties of the resulting nanocomposites. The ssPCMs obtained with molten nitrate eutectic show that 80% of the heat of fusion of pure salt can be attained for nanocomposites with 10% wt. silica. Alkaline earth halides are reactive towards the silica, leading to decreased heat storage. Salt eutectics with m.p. up to 520 °C could be used to obtain ssPCMs with heat of fusion values of up to 200 J/g. Shape-stabilized phase change materials containing mesoporous silica as matrix and molten salt eutectics can be obtained at high salt fraction. The nanocomposite shows good latent heat storage, up to ~80% of the pristine eutectic. Nanoconfinement effects can lead to a secondary phase with lower melting point than bulk (Figure 1). Larger pore diameters (≥9 nm) are required for salt nanoconfinement.

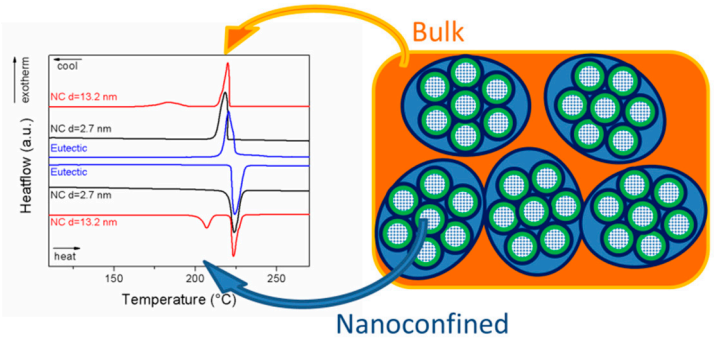

Figure 1. DSC data of molten salt eutectic and nanocomposites with mesoporous silica nanomaterials (MSN) with pore diameter of 2.7 and 13.2 nm (**left**), and schematic representation of salt distribution (**right**).

Acknowledgments: This work was supported by the Romanian Executive Agency for Higher Education, Research, Development and Innovation Funding (TE, No. 95/2018).

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Section 1

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Abstract

Influence of the Polymeric Matrix Type on the Optical Properties of YAG:Ce,Gd Phosphor †

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Keywords: YAG: Ce; Gd; PDMS; PMMA; epoxy resin; nanocomposite; white LED

The development of nanocomposites by incorporating YAG:Ce,Gd particles in different types of polymeric matrices aims to ensure the dispersion of phosphors in suspension medium to allow deposition on LED chips while maintaining luminescent properties or even improving them. Type of composite, uniformity, thickness, density of the deposited phosphor layer, concentration, distance to the blue chips, geometry, and so forth are important factors in order to obtain high-quality lighting sources. However, the biggest problem remains the agglomeration tendency of phosphor particles, regardless of the chosen matrix. Due to this inconvenience, problems can appear related to the control of the thickness of the deposited layer and the dispersion of phosphor in the matrix. Usually, a solution of polymer or oligomers containing nanoparticles is deposited on the chips, followed by a final heat treatment after which a polymerized and cross-linked composite film is obtained. The polymers used as matrix in the development of the devices must be transparent and not absorb in the visible field. For this purpose, we have studied the possibility of using epoxy resin, PDMS, and PMMA and their influence on the emissive properties of phosphor. The ex situ method used is based on the formation of a homogeneous mixture between YAG:Ce,Gd phosphor and the selected polymeric matrix. The structural characterization highlighted the incorporation of phosphor in the polymeric matrix while maintaining the structural YAG:Ce,Gd parameters. In the excitation PL spectra, no position variation of the bands was found, confirming that the polymers do not influence the excitation capacity of the composite. The emission spectra of the composites based on YAG:Ce,Gd polymers indicate a behavior similar to that of phosphor, confirming the existence of the same emission centers and maintaining the optical properties characteristic of phosphor in the polymeric matrix. The absence of absorption bands in the spectral domain above 600 nm confirms the maintenance of the spherical morphology of phosphor particles.

A decrease in the emission intensity was observed as a result of the lower refractive index of the polymer than of the phosphor and by the use of the substrate for the study of the optical properties. The decrease in emission intensity was found to be directly proportional to the increase of the thickness of the composite layer. In order to obtain composites with improved properties, we have found at least 5% phosphor concentration in the polymer matrix is sufficient. The obtained results

highlighted an increase in quantum yield of up to 79%. This observation is supported by the decrease in the agglomeration tendency.

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Abstract

Detection of Aflatoxin M1 Using a Dual Immunosensing Platform †

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Keywords: mycotoxins; dual detection; immune-sensitive platform

Determination of aflatoxin M1 in milk and dairy products is of great interest, due to its toxicity and negative effects exerted over the humans and animal's health when fed products contaminated with mycotoxins. Aflatoxin M1 (AFM1) represents the major hydroxylated metabolite of aflatoxin B1 (AFB1), which can be detected in the tissue and biological fluids of animals consuming contaminated food with AFB1. This metabolite is excreted in the milk produced by the mammary glands of the infected subjects [1].

Aflatoxin M1 is found in very low concentrations in milk and milk products, due to its high stability, even during the milkprocessing stages (pasteurization, UHT, etc.). It may be present in dairy products at even higher concentrations than in raw milk. Immunosensors represent a suitable alternative that has grown in the last decades in the development of sensitive, selective, simple and reliable systems for mycotoxin detection. The use of specific monoclonal antibodies or aptamers as bioreceptors, coupled with a physical transducer such as gold, carbon or graphite, leads to miniaturization of the systems and to improvement of the sensitivity, speed and low cost of analysis [2].

A combined electrochemical and optical immunosensitive platform has been developed based on an electrosensitive material obtained by incorporation of a monoclonal antibody specific to AFM1, into a polymeric film of 2,6–dihyroxynaphthalene and 2-(4-aminophenyl)ethylamine electropolymerized onto the gold working electrode on a glass support. This allows sensitive detection of aflatoxin M1 from complex liquid samples, based on quasi-simultaneous detection, electrochemical and surface plasmon resonance (SPR).

The principle of AFM1 detection from liquid samples using the combined dual detection platform is based on surface direct competition for the binding sites of the specific anti-AFM1 antibody immobilized in the polymeric film, between bioconjugate AFM1-HRP and target analyte AFM1. The immuno -recognition process is monitored indirectly, by electrochemical detection of the enzyme activity of horseradish peroxidase (HRP) used as marker in bioconjugate and, directly, by optic detection using surface plasmon resonance (SPR).

The results showed a good accuracy for AFM1 determination, with a dynamic range of quantification between 10 and 400 ppt, and a good correlation between SPR and electrochemical determination of AFM1, which indicates a high analytical performance of the developed dual detection platform.

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Abstract

Future Perspective for Incorporation and Removal of Chemical Agents from Contaminated Surfaces †

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Keywords: chemical decontamination; hydrogels; contaminants incorporation

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Decontamination for military purposes represents the process of removing/neutralizing of chemical, biological, radiological and nuclear (CBRN) agents so that they no longer represent a risk for personnel. Current research and development (R&D) is focused on developing a decontamination system/procedure that would overcome the limitation of classical systems (excessive labor and resource, massive water consumption, corrosive, toxic). In order to restore the combat effectiveness of equipment as soon as possible, we propose the decontamination solution with a water soluble hydrogel which will ensure the incorporation and removal of chemical agents from contaminated surfaces. The technical solution can be used to fix the contaminants in place in a safe manner until the operative situation allows the decontamination operations to be carried out [1].

The utilization is facile and it takes place in three simple steps: application, dry off and peel off. Another advantage represents the fact that can be used on a variety of surfaces: metal, concrete, wood, plastic, glass, etc.

Tests were performed according to the standard procedure on different support materials using nerve-type chemical warfare agents (CWA) simulant dimethyl methylphosphonate (DMMP) to the contamination norms stipulated in the NATO regulations. Different hydrogels with different compositions and drying times were used in order to study their ability to incorporate the contaminant.

The obtained results for the incorporation and removal of the chemical contaminants from the support materials were very good, achieving decontamination levels between 99.9–100%.

In agreement with the obtained results, we conclude that the tested hydrogel formulas have great potential for future use in the incorporation and decontamination of surfaces contaminated with CWA, using simple and safe operations (Figure 1).

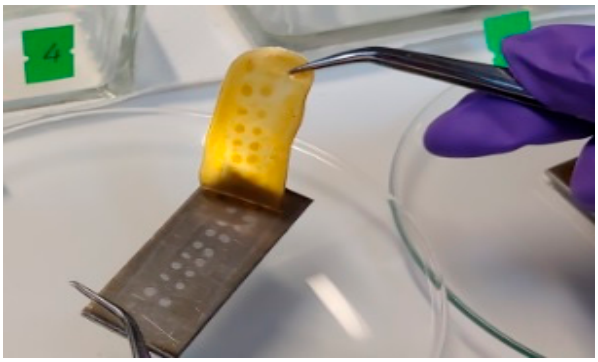

Figure 1. Decontamination of metal surface with hydrogel.

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Abstract

Cytotoxic Effects of Carbon Nanotubes and Cisplatin Conjugates on 3D Breast Cancer Cellular Models †

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Keywords: carbon nanotubes; MCTSs; cisplatin; cytotoxicity

Breast cancer represents one of the leading causes of death for which new strategies of treatment are intensively studied and tested. Single-walled carbon nanotubes (SWCNTs) represent promising tools in the treatment of cancer and can be used as transporters of drugs due to their unique properties [1]. Furthermore, advanced cellular models, such as multicellular tumor spheroids (MCTSs), are exploited for the study of cancer mechanisms. MCTSs represent 3D cellular structures composed by three layers of cells found in different stages of the cell cycle: the first one is characterized by proliferative cells, followed by cells in a quiescent state, and the last one in the spheroid's center is represented by necrotic cells [2]. In this context, we aimed to investigate the cytotoxic effects of SWCNTs loaded with cisplatin (CDDP) in breast cancer MCTSs.

SWCNTs were functionalized with carboxyl groups, resulting in SWCNT-COOH, which was mixed with dimethylformamide and CDDP to obtain the SWCNT-COOH-CDDP nanoconjugates. SWCNT-COOH-CDDP was characterized by inductively coupled plasma mass spectrometry, Fourier-transform infrared spectroscopy (FTIR), energy-dispersive X-ray spectroscopy (EDX), and Raman spectroscopy. MCTSs were generated from MDA-MB-231 breast cancer cells in Dulbecco's Modified Eagle Medium with 2.5% Matrigel, using Nunclon™ Sphera™ Microplates. On the second day of culture, MCTSs were treated with doses of 1, 4 μg/mL SWCNTs and 0.6, 2.52 μg/mL CDDP for 24 and 48 h. Untreated MCTSs were used as the control. The MCTSs' morphology was analyzed using optical microscopy while cellular viability was assessed through a fluorescence method, using LIVE/DEAD assay. Cell death was evaluated by analyzing the expression of pro-apoptotic (Bax) and autophagic (Beclin-1) proteins using the Western blot technique.

Our results indicated that the concentration of CDDP encapsulated in SWCNT-COOH is 192.82 μg/mL. Also, the EDX spectrum highlighted the presence of Pt ions in the SWCNT-COOH-CDDP sample while the FTIR results indicated a covalent bond between CDDP and SWCNT-COOH. The analysis of optical microscopy images indicated a reduction in the size of SWCNT-COOH-CDDP-treated MCTSs and the detachment of cells from the proliferative layer after 48 h, compared with the effects induced by free components, which presented high biocompatibility. Fluorescence images revealed the presence of a necrotic center surrounded by live cells in all tested conditions. However, when MCTSs were treated with 4 μg/mL SWCNT-COOH-CDDP, the detachment of cells from the edge was noticed, in correlation with optical microscopy images. The expression of the Bax protein increased after 24 and 48 h of

exposure to 4 μg/mL SWCNT-COOH-CDDP relative to the control but not in the presence of 1 μg/mL SWCNT-COOH-CDDP. In the same time, the expression of Beclin-1 was inhibited after 24 and 48 h of exposure with 1 μg/mL and 4 μg/mL SWCNT-COOH-CDDP, respectively. A slight increase of Beclin-1 expression was observed after the treatment of MCTSs with 4 μg/mL SWCNT-COOH-CDDP for 48 h. No significant changes were observed in the presence of 1 μg/mL SWCNT-COOH-CDDP after 48 h.

Considering the results of the present study, we conclude that SWCNT-COOH-CDDP nanoconjugates have the potential to induce significant morphological changes in MCTSs and to initiate apoptosis pathway through the activation of the Bax protein and the inhibition of the autophagy process.

Acknowledgments: This work was supported by a grant of Ministry of Research and Innovation, CNCS–UEFISCDI, project number PN-III-P2-2.1-PED-2016-0904, within PNCDI III.

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Abstract

Multifunctional Protective Coatings of RE-ZnO Nanocomposite Deposited on Metallic Alloys †

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Keywords: ZnO; epoxy resin; metallic alloys

The use of nanocomposite materials in various strategic industries has gained great extent due to the excellent protection ability on various substrates. In the manufacture of nanocomposites with multifunctional performances, it is necessary to take into account the selection of the main components (polymer matrix-RE and dispersed phase-ZnO), the characteristics and properties of each component, the compatibility and the impact of the interface between them, the synthesis technology, and the application domain. The study of substrates based on metallic alloys is a representative selection criterion, considering the compatibility between the nanocomposites and substrates, so that the whole assembly can be applied in many industrial sectors [1–3].

This paper focuses on the possibility of depositing RE-ZnO nanocomposites films on the surface of the alloy and examining the influence of the particles in the matrix and the effect of composite coating on the metal alloys. The incorporation of the ZnO nanoparticles into the epoxy resin was realized by ex-situ synthesis, and in order to increase the compatibility degree between the two components, the dispersion of the ZnO powder in the afferent matrix solvent was made in the beginning phase. The RE-ZnO samples were deposited on the aluminum alloy substrate, after its previous preparation, followed by the final heat treatment at 100 °C.

From the optical analysis of the nanocomposite film, a high degree of dispersion of the ZnO phase in RE and a good adhesion to the metal alloy substrate were found. The morphological analysis confirms the uniform relative distribution of the powder in the matrix, the particle size being about 35–80 nm. Structural analysis using FTIR and EDX highlights the total incorporation of ZnO nanoparticles into the RE matrix. The contact angle of the nanocomposite film indicates the improvement of the hydrophobic character by increasing the angle around 100 °C.

Based on the obtained results, the developed nanocomposites can be deposited by various substrates with applicability in different environmental fields.

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Abstract

Preparation and Characterization of Highly Porous Cellulosic Foams for Biomedical Applications †

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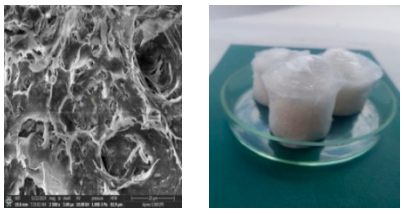
Keywords: nanocellulose; foams; biomedical application

Cellulose is the most abundant renewable biopolymer in nature, being the main constituent of plant cell walls [1]. Nanocellulose is a new class of biomaterial, with numerous biomedical applications due to its unique properties, such as biocompatibility, biodegradability, and good mechanical properties [2]. This study aimed to obtain 3D porous structures based on nanocellulose and PEG-based monomers/oligomers.

The obtained grafted cellulose aerogels were characterized by Brunauer-Emmett-TellerBET surface area analysis to observe the increased porosity and high specific area. Grafting of cellulose nanofibers is seen in the modification of the FT-IR spectrum by the appearance of new peaks and bands with high intensity. Due to these properties, the obtained cellulose composite aerogels (Figure 1) can be potentially used as scaffolds for tissue regeneration or as drug delivery systems.



(**a**) (**b**)

Figure 1. (**a**) SEM image of cellulose fiber coated with PEG-based monomers and (**b**) image of cellulose foams.

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Abstract

Composite Coatings Based on PLGA for Topical Treatment †

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Keywords: composite coatings; ibuprofen; degradation; drug release; cell viability

Different medical devices containing biologically active principles for cutaneous wound healing have been developed over time. Our aim was to propose new composite coatings based on poly(lactic-co-glycolic acid) (PLGA) embedded with ibuprofen (IBUP) as a potential device for topical application in wound healing.

PLGA-IBUP (2:1 and 10:1 wt. %) materials were obtained by combining dip coating and drop cast methods. IBUP release under dynamic biological simulated conditions (up to 30 days) was performed using a multichannel bioreactor and subsequent spectrophotometric analysis (265 and 274 nm absorption bands). Structural modifications of composite coatings were evaluated using scanning electron microscopy (SEM). Cell proliferation assay and fluorescence microscopy were used to investigate the viability and morphology of the human THP-1 cell line grown on polymeric coatings embedded with IBUP.

Mass losses of the composite coatings tested under a dynamic regime revealed a progressive increase in the degradation of the PLGA-IBUP structures after 30 days, with a mass loss of approximately 15%.

The SEM investigation revealed a slow and gradual degradation of copolymer and release of the therapeutic agent during the first 10 days. After 15 days, much larger swelling formations were present, with a severe degradation of the coating for the last evaluation interval (30 days). Cytotoxic effect was not observed for neither of the tested coatings on differentiated THP-1 cells grown for 24 h or 72 h as compared with the coverslip (control). The cells exhibited a typical round shape, similar to undifferentiated monocytes morphology when cultivated on either coverslips or PLGA-coated substrates. When the cells were grown on the PLGA-IBUP (2:1) or (10:1) samples, an increase in cell adhesion was observed as an adaptation of cells to surface characteristics. Morphological modifications induced by composite materials were not associated with an inflammatory response (absence of TNF-α release).

The physical, chemical, and biological characteristics of PLGA-IBUP composite coatings revealed their potential as medical devices to be used for topical treatment of skin injures.

Acknowledgments: This research received funding from the Romanian National Authority for Scientific Research (CNCS–UEFISCDI), under the projects TERAMED 63PCCDI/2018 and Structural and Functional Proteomics Research Program of the Institute of Biochemistry of the Romanian Academy.

proceedings

Abstract

Nanofibres Obtained by Electrospinning from Thermoplastic Elastomer and Graphene Composites †

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Keywords: nanofibres; graphene; thermoplastic elastomers; electrospinning

Graphene and its derivatives have attracted considerable attention in recent years as potential materials for various applications because of their unique physical-chemical properties [1]. The study aimed to obtain by electrospinning nanofibers using styrene-butadiene block-copolymers (SBS) and styrene-isoprene block-copolymers (SIS), as well as their composites with graphene, and to investigate their structural, thermal and mechanical properties. In the first step, styrene-butadiene block-copolymers (SBS) and styrene-isoprene block-copolymers (SIS) were obtained by anionic sequential polymerization. The reactions were carried out in cyclohexane solution through a three-stage process and were initiated with n-butyl lithium. In the second step, polymer composites were obtained, using the synthesized thermoplastic elastomers and graphene in tetrahydrofuran solution. The polymeric composites obtained from thermoplastic elastomers and graphene were used for the manufacture of nanofibers by electrospinning (Figure 1).

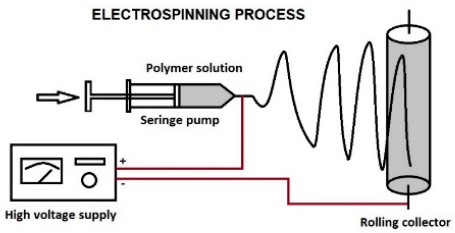

Figure 1. Electrospinning process scheme.

The polymer nanofibers obtained by electrospinning were characterized by ATR-FTIR analysis, Differential Scanning Calorimetry (DSC), and Thermo-gravimetric Analysis (TGA). The results indicated an improvement of thermal and chemical properties of nanofibers composites with graphene, compared to basic thermoplastic elastomers.

Acknowledgments: This paper was supported by a Nucleu Program conducted with MCI support, project no. PN.19.23.03.01.04, contract no. 23N/2019.

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Abstract

Studies on Obtaining Porous Hydroxyapatite Structures Using Porogen Agents of Natural Origin †

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Keywords: hydroxyapatite; starch; porosity; consolidation; heritage

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Hydroxyapatite is a calcium phosphate-based biomaterial utilized both in the medicine field (bone cement, scaffold, drug-delivery) and in the heritage field (stone conservation) [1]. On the other hand, starch is a natural biodegradable polymerconsisting of two polysaccharides present in the food industry [2,3]. In this research, we examined three main aspects: (i) the thermal synthesis of bovine bone-derived hydroxyapatite, (ii) the powder consolidation for obtaining HA/starch biocomposites, and (iii) the behavior of sacrificialporogen agent at sintering. Thermal processing of ceramic material started with deproteinization of bovine bone at 550 °C for 4 h followed by calcination at 800 °C for 6 h. Hydroxyapatite powder was mixed with 10, 25 vol. % starch and compacted by pressing at different press forces: 1tf, 3tf and 5tf (~1.5 MPa, 3.5 MPa, and 7.5 MPa). The consolidated parts were sintered at 1200 °C for 2 and 8 h. The porous structure resulted after starch removal during sintering. The sintered samples were characterized through SEM, EDS and FT-IR. The porosity was evaluated by using software dedicated to the characterization of SEM images. Chemical composition was evaluated using Energy Dispersive Spectroscopy (EDS) to determine the Ca/P atomic ratio. The results obtained from the FT-IR spectra confirms that starch removal does not affect existing hydroxyapatite compounds. We present conclusive data in Figure 1 relating to the different levels of porosity of final materials with a sintering time of 2 h. To be employable in the medical field, we reported the results obtained at the porosity rate of the cortical and cancellous bone [4]. The additions of starch increase the porosity and, by increasing the pressing force, the size of the pore decreases.Our future research will focus on the optimization of sintering methods through the management of process parameters and the selection of porogen agents for biomedical applications.

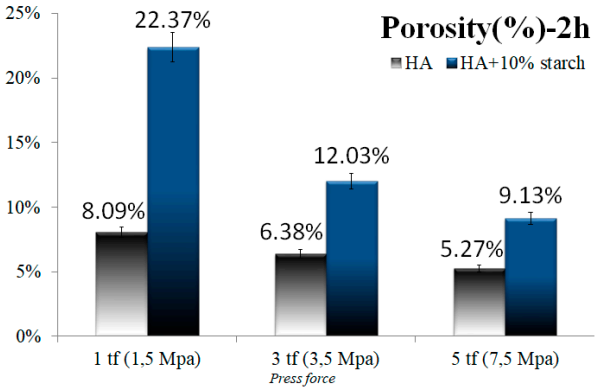

Figure 1. Determination of porosity at 2 h sintering maintenance.

Acknowledgments: This work was part of Denisa Loredana Copilu's Bachelor Thesis, "Studies on obtaining porous hydroxyapatite structures using porogen agents of natural origin," coordinated by Prof. F. Miculescu, Faculty of Materials Science and Engineering, University Politehnica of Bucharest, July/2019.

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Abstract

Evaluation of Photocatalysis Effect of Stainless Steel Mesh Coated with Nitrides, Oxynitrides and Transition Metals Cr and Ti on the Degradation of Orange II Dye †

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Keywords: wastewater; drinking water; advanced oxidation processes (AOPs); photocatalysis; hydroxyl radical; corrosion; coatings; removal efficiency

The increased detection of organic pollutants in drinking water and their resistance to degradation by wastewater treatment processes has motivated the development of more efficient, affordable and sustainable methods of purification of drinking water and wastewater. Advanced oxidation processes (AOPs), such as photocatalytic systems based on the production of powerful hydroxyl radicals, have been found to be efficient for water and wastewater remediation. Recently, semiconductor transition metals have been used as photocatalytic supports to minimise post-filtration of powder catalysts from the treated effluents and related costs. However, a few studies claim that exposure of metal supports such as stainless steel to an acidic environment for a prolonged time results in corrosion of the materials. Hence, coating of stainless steel photocatalytic supports with corrosion- resistant layers could be an alternative to overcome this limitation. In this study, the catalytic activity of Cr and Ti-based anticorrosion layers deposited on stainless steel meshes (coated by cathodic arc evaporation) was evaluated for the decolouration of 5 mg/L of orange II (O.II) dye solution that was exposed to UV light for 60 min. The absorbance of treated and untreated O.II samples was measured by UV-vis spectroscopy. The results showed that best dye decolouration was attained at pH 2.5 but all decolouration percentages were below 25%. On the other hand, slightly elevated decolouration of orange II dye was achieved with CrON, CrN/CrON, TiON and TiON/TiN coatings, respectively. The stability of anticorrosion coatings in an oxidative environment indicated that Cr and Ti nitride and oxynitride layers are effective and durable anticorrosion coatings. Nevertheless, their use as catalytic supports in photocatalytic systems, as well as their low removal of O.II dye, should be optimised to achieve high pollutant removal efficiencies.

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Abstract

Composites Based on Waste Printed Circuit Boards (WPCB) and Waste Polypropylene †

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Keywords: waste printed circuit boards (WPCB); waste polypropylene; elastomers; reinforced composites

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The high amount of plastics, which are durable, lightweight, and cheap materials, is one of the major current ecological concerns. The recycling of waste printed circuit boards (WPCB) has been an increasingly debated issue in the last two decades at government level and worldwide as they have a particularly harmful polluting effect (e.g., heavy metals and brominated compounds used as fire retardants) due to their non-biodegradability. WPCB recycling by blending with polypropylene waste (RPP) can be considered as a potential method with both technical and ecological implications. The research aimed to obtain impact-strength RPP composites using block-copolymers as impact modifiers and WCPB as the reinforcing agent. After the collection, the WPCB were ground into powder less than 1 mm size. The metallic parts (Cu) were removed by leaching and solvent evaporation. The waste polypropylene was collected from industrial injected boxes (density 0.96–0.99 g/cm^3; melt flow index at 190 °C and 5 kg of 6 g/10 min, tensile strength 2.06 MPa, elongation at break 2.83%, and IZOD impact strength at 23 °C of 6 kJ/m^2). As impact modifiers, a styrene-butadiene block-copolymer (SBS, Europrene 161 C) and a maleinized and hydrogenated block-polymer (SEBS-MA, Kraton FG 1901X) were used. The composites were obtained through melt compounding and the tensile and impact properties of the composites were determined. The composition influence on mechanical and impact properties of the RPP–elastomers–WPCB composites highlighted that impact strength improvement is controlled by elastomer domain size, their dispersion degree into the polyolefin matrix, and the compatibility between components. WCPB act as a reinforcing agent of the RPP matrix. Obtaining composites based on polyolefin waste and WPCB can be considered as a potential method for removing unused plastics from the environment. The new materials produced can be used for: different technical benchmarks for the construction industry, hangers, transport shuttles, and industrial containers, amongst other uses.

Acknowledgments: This paper was supported by a grant from the Romanian Ministry of Research and Innovation, CCCDI—UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0652/84 PCCDI/2018, within PNCDI III and by project no. PN.19.23.03.01.04, contract no. 23N/2019 within the Nucleu Program and 5PS/2019.

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Abstract

DSC Study of Cold Crystallization Process Characterizing the Stereocomplexed PLA Compounds †

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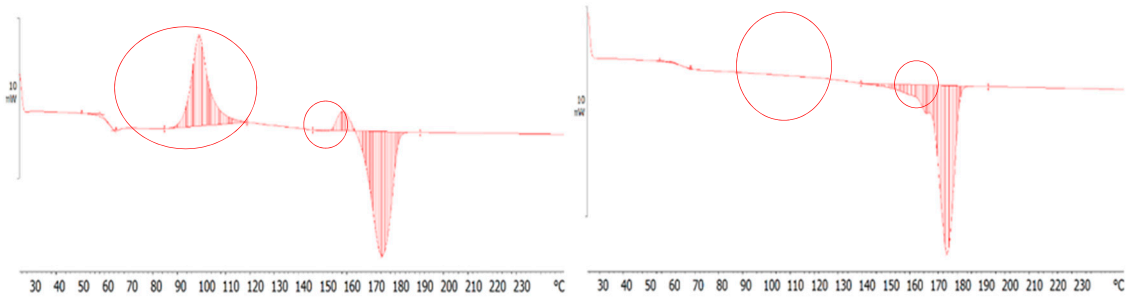
Keywords: PLA; DSC; stereocomplex; stereocomplexing; morphology; crystallization

The European strategy for plastics in a circular economy [1] underlines the importance of using renewable polymers for sustainable applications. The possibility of increasing the durability of the polylactic acid by stereocomplexing at melt compounding was studied. The purpose of the paper was to study the dependence of the cold crystallization processes on the Differential Scanning Calorimeter (DSC) cooling rate. Types of polylactic acid (PLA) with different molecular weights and dextro sequence content were stereocomplexed. To identify the dependence of the melting and crystallization characteristics on the type of polymers and DSC recording conditions, the compounds were studied, after the elimination of each compound's thermal history. The recordings were made on a DSC 3 Mettler Toledo device. On the DSC thermograms, besides the melting and crystallization processes, two additional exothermic ones were observed (Figure 1). According to [2], the two additional processes were attributed to the cold crystallization, which probably appeared because the polymers had no time to crystallize (too high of a cooling rate). In this situation, the crystallization continued over time. Another possible explanation can be related to defects of the new appeared crystals [2].



(**a**) (**b**)

Figure 1. (**a**) With cold crystallization (20 °C/min) and (**b**) Without cold crystallization (2 °C/min).

At a cooling rate of 20 °C/min, the crystals do not have enough time to be formed and, therefore, the resultant morphology is an amorphous type. At a 2 °C/min cooling rate the resultant morphology has a semi-crystalline architecture. The semi-crystalline phase content and the type of crystals depend

on the intensity of the stereocomplexation phenomenon. The nature of the new exothermal process observed on the DSC thermograms of the stereocomplexed PLA compounds will be clarified in the next experiments.

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proceedings

Abstract

Synthesis, Characterization, DFT Studies, and NLO Properties of Some Benzimidazole Compounds †

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Keywords: synthesis; benzimidazole; DFT; NLO properties; hyperpolarizability (β)

During the last decades, nonlinear optical (NLO) materials have played a significant role because of their various applications in medicine, molecular switches, luminescent materials, laser technology, spectroscopic and electrochemical sensors, data storage, microfabrication and imaging, modulation of optical signals, and telecommunication [1–3]. Organic materials are distinguished by the fact that they exhibit strong NLO properties [2–4]. Recent literature highlights the increased interest in organic materials in recent decades, as an alternative to their inorganic counterparts, and having several advantages, such as their low cost, low toxicity, ease of solution processability, flexibility for device fabrications [5], and modulation of their optical, electronic, and chemical properties by adapting their molecular structure. Organic commercial and synthetic materials were used for the synthesis of the compounds of interest. The second harmonic generation (SHG) capability of samples was measured by using a homemade experimental set-up. A series of benzimidazoles, potential candidates for NLO response, was synthesized. Compounds were characterized by elemental analysis, proton nuclear magnetic resonance spectra(^{1}H-NMR), mass spectra (MS), and Fourrier transform infrared (FTIR) spectra. The analysis of molecular structure and natural bond orbitals (NBOs) was performed using the GAMESS 2012 software. The molecular polarizability α, first-order hyperpolarizabilities β_{tot}, dipole μ_{tot}, and quadrupole (Q) moments were calculated. Our results show that the NLO response of such small, twisted molecules mainly depends on the dihedral angles of aromatic and heteroaromatic rings toward the transmitter group. We expect the structural parameters of these compounds to be favorable for ultrafast response times (i.e., femtoseconds applications). Benzimidazoles are organic compounds suitable for NLO applications, with several advantages: they are cheap and possess low toxicity and ease of solution processability. Density functional theory (DFT) calculations are very useful for the correlation between the NLO behavior of the compounds and their structure for the synthesis of new compounds with improved NLO properties.

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proceedings

Abstract

Physical Modification of PLA for Increasing Its Durability (Polarizing Light Microscopy Study) †

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Keywords: modified PLA; nucleation; reinforcing; morphology; order degree

The European Strategy for plastic materials in a circular economy underlines the importance of using renewable polymers for long-lasting applications. The purpose of the paper was to increase polylactic acid's (PLA) durability by controlling its crystalline structure [1–3].

The texture of the samples was analyzed in polarizing light with an Olympus BH-2 microscope, equipped with a THMS600 type heating system and a LINKAM TP92 temperature control system. The samples were studied during a heating/cooling cycle performed at a rate of 5 °C/min. The ATR-FTIR spectra needed for the chemical structure analysis was performed on a PerkinElmerSpectrum 100 instrument. The mechanical analysis was performed in a dynamic regime, on a PerkinElmer Diamond DMA instrument.

In the cooling stage of the neat PLA, the gradual formation of birefringent geometric shapes, next to which spherulites appeared, were observed. At 90 °C, fine birefringent texture was formed, similar in characteristics to those of semi-flexible or rigid polymers (Figure 1). PLA reinforced with nucleation agent presents birefringence at room temperature, indicating a highly ordered material. In the case of the polymer with nucleation and reinforcing agents, and because of their effects, a marked decrease in the mobility of the macromolecular chains was observed.

The investigations of morphological changes by FTIR analysis, optical microscopy, and mechanical properties in a dynamic regime prove the increase of the crystallization ability of the modified PLA due to the reinforcing agents.

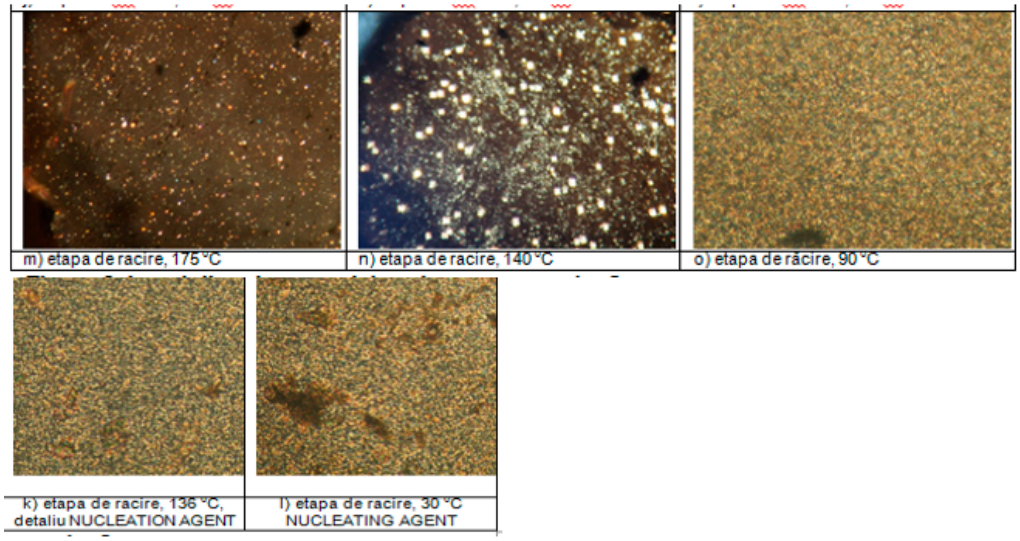

Figure 1. Polarized Light Microscopy (PLM) images of polylactic acid (PLA) without and with nucleation agent.

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Abstract

Composites of Styrene-Butadiene Block Copolymer Reinforced with Waste Printed Circuit Boards (WPCB) †

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Keywords: waste printed circuit boards (WPCB); styrene-butadiene block-copolymer; reinforced composites

The organic part of the waste printed circuit board (WPCB) contains mainly epoxy resin, fiberglass and brominated flame retardants, a composition that makes it quite difficult to reuse [1,2]. Therefore, WPCB has no economic value, becoming the final waste deposited in a waste storage space and a secondary pollutant of the environment. The mechanical recovery of the waste affects the ecosystem. The research aimed to reuse the WPCB powder as a reinforcing agent for styrene-butadiene block-copolymers, composites that can be used as masterbatch for the production of shoe soles that are injected directly onto the footwear. The reinforcing study was achieved using a star styrene-butadiene block-copolymer with 32% polystyrene, a molecular mass of 190000 g/mole and WPCB ground to less than 1 mm in size after the metal (Cu) was removed. The composites were obtained by adding 5–30% WPCB into the styrene-butadiene block-copolymer solution in THF, followed by centrifugal casting desolvation. To improve the processability by injection, the melting viscosity was reduced by extending the composites with 25% naphthenic-paraffin oil. The composites were characterized by mechanical (tensile) testing, and thermal (DSC, TGA) and dynamo-mechanical analysis. WPCB was found to be distributed in the continuous polybutadiene phase of SBS, acting as a non-reactive filler (continuous decrease in tensile strength and elongation at break with increasing WPCB dosage was observed). The increase in storage modulus and mechanical losses proportional to the ratio of WPCB confirms its reinforcing effect. The study established that WPCB can be recycled as SBS composites expanded with 25% naphthenic-paraffinic oil in a maximum proportion of 30% with mechanical properties suitable for obtaining shoe soles materials injected directly onto the footwear.

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Abstract

The Shape Memory Polymeric Materials and the Additive Manufacturing Technology as Promoter of the Future Smart Society †

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Keywords: synthesis; benzimidazole; DFT; NLO properties; hyperpolarizability (β)

Humans have progressed from the Stone Age, through the Bronze, Iron, and Steel Ages, into its current age, the Age of Polymers, which will be the material of choice [1].Considering the National Institute for Reasearch and Development in Chemistry and Petrochemistry's (ICECHIM) strategy, for the next decade, in the field of polymeric materials, the roll-up will present, in three parts, the role of the shape memory polymeric materials in the development of the future smart society, in correlation with the additive manufacturing technology that is on the verge of industrialization [2].

The first part of the roll-up will present the ICECHIM strategy regarding the research on structurated polymeric materials by classical, active, and intelligent types, which can be applied via classical technology or emerging technologies (3D and 4D printing)—Figure 1. The second part of the roll-up will present an overview of the two emerging technologies (3D and 4D printing) and their future evolution.The third part will be dedicated to the shape memory polymeric materials and their importance in the future development of society. They are the materials that respond to external stimuli by changing their shape and/or volume and/or color and/or physical properties—Figure 2 (e.g., glass transition temperature, deformation recovery speed, Young's modulus, stiffness—indicator of the tendency of an element to return to its original form, etc.)

ICECHIM has already begun the pursuit of achieving shape memory polymeric materials, the current state of the research being at the laboratory stage.

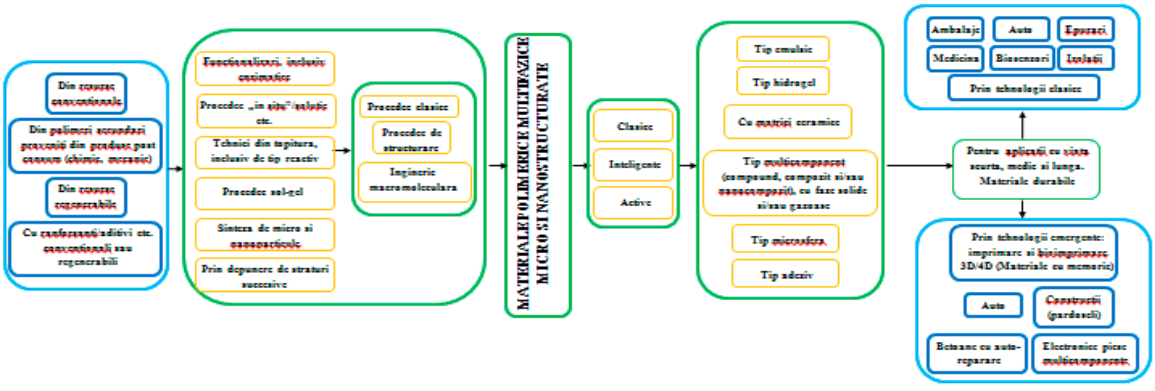

Figure 1. The ICECHIM strategy in the advanced polymeric materials domain.

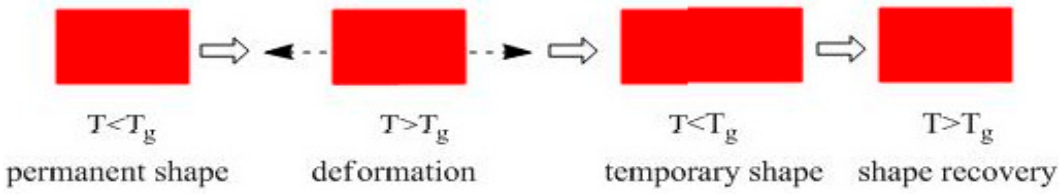

Figure 2. Physical process of shape recovery for a thermo-sensible material with memory shape**.**

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Abstract

Novel Coatings for Superhydrophobic/Superamphiphobic Surfaces with Tunable Morphology of Nanoparticles †

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Keywords: functional coatings; superhydrophobic; ZnO nanoparticles

Functional surfaces with special wettability properties are currently receiving a lot of attention due to their numerous potential applications, from water–oil separation strategies to self-cleaning and anti-icing or anti-corrosion coatings [1]. Both superhydrophobic and superomniphobic properties are based on the principle of roughness enhanced wettability. Among the methods proposed to fabricate coating materials with superhydrophobicity or superamphiphobicity, the most facile and easy scalable involves the embedding of nanoparticles (NPs) in filmogenic matrix with suitable chemical properties. In the present work, the influence of the morphology of nanopowders used to achieve the roughness of the coating was investigated. Functional materials have been prepared through the embedding of ZnO nanoparticles in organo-modified (Ormosil) silica matrix. Zinc oxide nanopowders with various sizes of nanocrystallites and different shapes (quasi- spherical, elipsoidal, rose-like, chrysanthemum-like 3D aggregates) were used to obtain nano- and micro-structure of the coating materials. ZnO nanoparticles were synthesized by using a simple ecofriendly hydrothermal synthesis in high-temperature/high-pressure conditions. Zinc precursor, composition of the solvent, concentration of the structuring agent added are parameters that allow fine tuning of size and morphology of the product.The nanoparticles obtained were characterized using various techniques such as dynamic light scattering, XRD, scanning electron microscopy (SEM). The functional materials were prepared by using the entrapment of ZnO nanoparticles in silica matrix obtained through sol–gel method. A model hydrophobic silica matrix was used prepared from a mixture of tetraethyl ortosilicate (TEOS) and organo-modified silane derivatives (octadecyl OTES and perfluorodecyltrichlorosilane, PFDTS) in various molar ratios, in order to obtain a filmogenic, transparent, and resistant coating. The wetting properties were investigated by using the contact angle method and the results have been discussed with the focus point on the morphological variation of the coatings assessed by SEM images.Superhydrophobic and superamphiphobic materials have been prepared using 3D nano and micro-structures formed by

using different ZnO nanoparticles with special morphologies. The NPs concentration and dispersing method is found to be critical to achieve "super" wetting properties.

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Abstract

Microbial Production of Polyhydroxyalkanoates from Structural Correlated Substrates †

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Keywords: biosynthesis; *mcl*-polyhydroxyalkanoates; *Pseudomonas* spp.; fatty acids; precursor

Polyhydroxyalcanoates (PHAs) are polyesters of aliphatic hydroxy acids. They have properties similar to petroleum-derived polymers and form a class of thermoplastic materials whose mechanical properties vary between elasticity similar to rubber and hardness comparable to crystalline textolite. These characteristics recommend PHAs to be used in various forms and in different areas [1–5]. PHAs are naturally produced by bacteria and accumulate in the form of granules in the cytoplasm, as an energy reserve, and carbon (C) atoms, in particular culture broth conditions. The aim of this work was to obtain medium chain length (co)polyhydroxyalkanoates (*mcl*-PHA) with controlled composition (containing monomers with 5–14 carbon atoms), through microbial biosynthesis, using *Pseudomonas* spp. strains (from the National Institute for Chemical-Pharmaceutical Research and Development (ICCF) culture collection of micro-organisms), by varying the carbon sources and the precursors. Continuing our previous studies on PHA production [6], in this work, assays were performed at the laboratory level with fermentation media seeded with inoculum cultures of strain *Pseudomonas putida* in a proportion of 10%. The influence on *mcl*-PHA production of glucose and citrate as carbon sources for strains development, as well as of octanoic (C8) and decanoic (C10) acids, as polymers precursors, were analyzed.

Bacterial strain: *Pseudomonas putida* (ICCF 391), inoculum culture: 24 h, 30 °C, 220 rpm, biosynthesis: Submerged fermentation in a medium containing mineral salts and Na-octanoate / Na-decanoate, at regular time intervals (0 and 24 h), in order to assure a constant precursor concentration (0.16% g/v), 10% inoculum culture; 48 h, 30 °C, 220 rpm, pH = 7. The precursors, sodium octanoate and sodium decanoate were added separately or together (in volume ratio 1:1) in the fermentation media.

The results showed the optimum conditions for metabolizing the fatty acids, and the ability of the microorganisms to easily and more productively metabolize the octanoic acid rather than decanoic acid. This behavior was proved in the experimental model of biosynthesis and down-stream processing, to obtain PHA containing predominantly C8 monomers or C10 monomers in different ratios.

Correlating the data obtained from several experiments in shake flasks, we can conclude the following: In case that all the precursor amount (octanoate) is used up during the fermentation (19.8–22.6 g), with an average conversion degree of total C in polymer of 32.5% which corresponds to 3.3–3.7 g/L dry bacterial biomass and to 1.7–1.9 g/L PHAs, represented predominantly by polyhydroxyoctanoate PHO (88%).

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Abstract

Synergistic Effects in Nanoparticle-Based Protective Coatings for Paper and Textiles †

Ludmila Otilia Cinteza [1,*], Adina Raducan [1], Petruţa Oancea [1], Lia Mara Ditu [1], Cristina Scomoroscenco [2], Elvira Alexandrescu [2], Cristina Lavinia Nistor [2], Cristian Petcu [2], Laura Chirilă [3] and Ioana Rodica Stănculescu [4]

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Keywords: multifunctional coatings; superhydrophobic; ZnO nanoparticles; Ag nanoparticles; chitosan

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Superhydrophobic materials have attracted considerable attention during the last decades, since they allow the facile transfer of special wettability properties on various surfaces. Protective coatings that ensure water repellency on asolid surface became the most common way for the treatment of stone or concrete buildings, metal devices, glass, textiles, etc. [1]. Most of these materials are nanohybrids consisting ofa filmogenic matrix with various nanoparticles as fillers, with the main role being to obtain a suitable roughness. In this work, a superhydrophobic coating based on a combination of ZnO and Ag nanoparticles embedded in a silica matrix was obtained and synergistic effects in antibacterial and other properties were investigated. Coating materials were prepared with various contents of ZnO and Ag nanoparticles embedded in an organo-modified (Ormosil) silica matrix. Ag nanoparticles were synthesized using a "green chemistry" method based on the reduction of silver ions in *Thymus vulgaris* extract. Zinc oxide nanoparticles were synthesized by using hydrothermal synthesis in high-temperature/high-pressure conditions, in the presence of surfactants as structuring agents. Commercially available normal-type paper and cotton textile were used as the model solid substrate to be functionalized. Ag and ZnO nanoparticles were characterized from the point of view of size, surface potential, crystallinity, and shape using dynamic light scattering, XRD, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The coating materials were prepared by adding various concentrations of Ag and of ZnO nanoparticles in a filmogenic silica matrix. The silica nanohybrid was obtained through the sol–gel method, and the deposition of coating material was performed by brushing or spraying onto a solid surface previously functionalized with chitosan. The contact angle of water on modified surfaces of both paper and textile materials wasin the range 150–1600, with sliding angle of less than 7°. A synergistic effect between ZnO and Ag nanoparticles was observed in terms of antibacterial activity, but no synergism with the chitosan was proved. Superhydrophobic multifunctional materials were obtained with reduced content of both Ag and ZnO nanoparticles. The coatings show

superior antibacterial activity due to the synergistic effect from the nanoparticulate components, together with UV-protection and self-cleaning properties.

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Abstract

Polymeric Nanofibers Manufactured by Electrospinning of Styrene-Ethylene-Butylene-Styrene (SEBS) Composites †

Bogdan Spurcaciu [1], Lorena Iancu [1,2,*], Mircea Filipescu [1], Rodica-Mariana Ion [1,2], Paul Ghioca [1], Ramona Grigorescu [1], Cristian Nicolae [1], Raluca Gabor [1], Maria Rapa [3] and Ecaterina Matei [3]

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Keywords: electrospinning; nanofibers; styrene-ethylene-butylene-styrene

The study aimed to synthesize nanofibers based on styrene-ethylene-butylene-styrene block-copolymers (SEBS) [1] and its composite derivatives, through the electrospinning (Figure 1) process [2]. Styrene-ethylene-butylene-styrene (SEBS) 1652 manufactured by Kraton was used as the basic polymer. This is a translucent thermoplastic elastomer, with a linear structure of triblock copolymer based on styrene and ethylene/butylene (SEBS), and with a Styrene/Rubber ratio of 30/70. Polymeric composites were synthesized in toluene solution, using SEBS and graphene at a gravimetric ratio of 80/20 and 90/10.

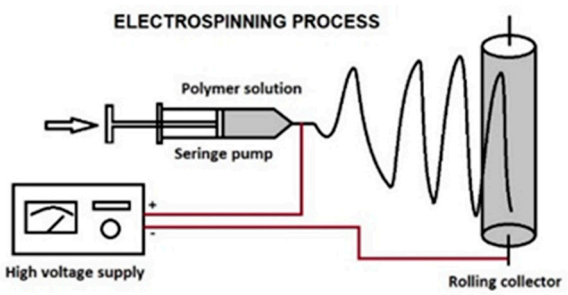

Figure 1. Electrospinning process scheme.

The composite materials based on SEBS and graphene, with a concentration of 20% polymer in toluene were used for the manufacture of nanofibers by electrospinning (Figure 2).

Figure 2. Electrospinnig equipment.

Nanofibers manufactured based on SEBS and SEBS with graphene composites were investigated by structural, thermal and chemical properties. The nanofibers based on SEBS and graphene obtained by electrospinning were characterized by ATR-FTIR analysis, Differential Scanning Calorimetry (DSC), Thermo-gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). The results indicated an improvement of thermal and chemical properties of nanofibers composites based on SEBS and graphene, compared to SEBS 1652 elastomer.

Acknowledgments*:* This paper was supported by a Nucleu Program conducted with MCI support, project no. PN.19.23.03.01.04, contract no. 23N/2019.

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Abstract

Effect of Different POSS Structures on Thermal and Morphological Properties of a Biodegradable Polyester †

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Keywords: poly(lactic acid); silica based nanofillers; thermal properties; atomic force microscopy

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The quest for materials with properties similar to those of engineering plastics but derived from renewable resources remains a continuous need of our time. Poly(lactic acid) (PLA) is a linear aliphatic thermoplastic polyester, intensively studied and currently used for various applications because of its biodegradability and availability on the market at a price close to polypropylene [1]. However, its slow crystallization rate, low thermal stability, and excessive brittleness are disadvantages that limit the wider applicability of PLA [2]. Extensive research has showed that an effective way to improve PLA properties is the addition of nanofillers. Because of their nanoscale dimensions, biocompatibility, recyclability, nonflammability, nonabrasive, and nonmigrating features, polyhedral oligomeric silsesquioxanes (POSS) could be an interesting choice as fillers for PLA [3]. The aim of this study was to evaluate the POSS influence on the thermal, morphological, and mechanical behavior of a poly(l-lactic acid) matrix (PLLA). POSS fillers (trisilanol-isooctyl polyhedral oligomeric silsesquioxanes—TSio-POSS, allyl-heptaisobutyl—ALib-POSS, and aminopropyl-heptaisobutyl polyhedral oligomeric silsesquioxane—APib-POSS) (Sigma-Aldrich) were incorporated into a PLLA matrix (4043D, NatureWorks Ingeo) by a melt compounding method. The morphological, thermal, mechanical, and surface properties of PLLA/POSS nanocomposites were evaluated by atomic force microscopy (AFM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and water contact angle measurements (CA). AFM analysis showed a more organized structure for the TSio-POSS nanocomposite, whereas some aggregates were detected mainly on the surface of the PLLA/ALib-POSS film. CA results indicated that POSS improved the hydrophobicity of the PLLA matrix, with the exception of the nanocomposite containing APib-POSS—probably due to the better incorporation of APib-POSS in the PLLA matrix, as also shown by AFM. The addition of POSS improved the thermal stability of the PLLA matrix, as demonstrated from the characteristic temperatures of the TG/DTG curves. A slight shift of T_m nanocomposites towards lower values was observed as a result of the plasticizing effect of POSS and good miscibility between PLLA and POSS.The downward shift of T_{cc} indicated that ALib and APib-POSS nanoparticles enhanced the nucleating activity and the rate of crystallization of the PLLA, which was also confirmed by the higher degree of crystallinity values. Incorporation of POSS led to a decrease of the storage modulus and increased PLLA flexibility, which was noticed in the glassy state, bellow T_g; beyond the $T_g$region, all the PLLA/POSS nanocomposites displayed higher storage modulus values as compared with neat PLLA. The loss modulus curves indicated that POSS addition decreases the melt viscosity of the corresponding PLLA

nanocomposites. The self-assembled POSS molecules were well dispersed in the PLLA matrix, as shown by AFM images. Furthermore, an increase in thermal stability was noticed, and both T_{on} and $T_{5\%}$ were modified, depending on the POSS type. Except for TSio-POSS, the fillers acted as plasticizers, lowering the E′ of the PLLA matrix in the glassy region and increasing the E″ above the glass transition temperature (T_g).

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Abstract

Innovative Sensing Platforms for Toxic Compounds Detection †

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Keywords: biogenic amines; nanomaterials; sensing platforms

Bioanalytical nanosystem based on an innovative hybrid nanomaterials have been developed for sensitive detection of some toxic compounds, such as biogenic amines and xenoestrogens from food and the environment. Both, active biogenic amines and xenoestrogens are chemical compounds found in food, environment and industry, having toxic effects on human and animal organisms. Biogenic amines represent a group of chemical compounds synthesized from amino acids, present in all eukaryotic cells, including cells of the nervous system (CNS). In the human body, they can have both positive and negative effects, depending on their origin, type, and dose. In nature, these compounds are found in plants, animals, and microorganisms [1,2]. Biogenic amines that occur as a result of chemical, biochemical, or microbial degradation processes, as well as in the catabolism of the body, have toxic effects (psychoactive and vasoconstrictor), and their presence in human nutrition is dangerous for human health [2]. Endocrine disruptors represent an exogenous substance or mixture of substances that possess properties leading to endocrine changes in an intact organism, by altering endocrine functions [3,4]. Miniaturized devices have been developed by modification of screen-printed carbon electrodes with hybrid nanocomposite material obtained by functionalizing carbon nanomaterials with metal nanoparticles (gold, silver, platinum). By incorporating these nanomaterials into conductive polymers, the catalytic activity has been considerably improved, allowing for a rapid transfer of electrons to the electrode surface due to the synergistic effects of the hybrid nanomaterial coupled with the excellent ability to mediate redox polymers. This nano-hybrid film provides a favorable micro-environment for immobilization of biomolecules (enzymes/peptides/aptamers), increasing the number of binding sites available for the detection of a specific chemical analyte.

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Abstract

Ternary Carbon-Based Nanocomposite as Sensing Layer for Resistive Humidity Sensor †

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Keywords: oxidized carbon nanohorns; graphene oxide; polyvinylpyrrolidone; relative humidity

Many principles and methods have been described in literature for measuring relative humidity (RH) and several types of materials have been employed as RH sensing layers [1,2]. This paper reports on the RH sensing response of a resistive sensor employing a sensing layer based on a ternary nanocomposite comprising single wall oxidized carbon nanohorns (SWCNHs)–graphene oxide–polyvinylpyrrolidone, at 1:1:1 w/w/w ratio.

The interdigitated (IDT) sensing structure was manufactured on a Si substrate (470 μm thickness) and covered by a SiO2 layer (1 μm thickness). The metal stripes of the IDT sensing structure were comprised of a Cr (10 nm thickness) and Au (100 nm thickness) stack, having 200 μm width. Six millimeters was the distance between the electrodes. A dispersion formed in water of a nanocomposite comprising oxidized SWCNTs (Figure 1)–graphene oxide–polyvinylpyrrolidone (at 1:1:1 w/w/w ratio) was deposited on the IDT structure using the drop casting method.

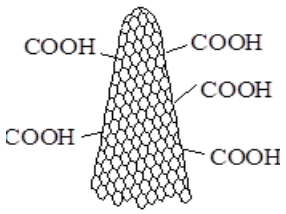

Figure 1. The structure of oxidized single wall oxidized carbon nanohorns (SWCNHs).

The RH detection capability of the structure was investigated by applying a current between two electrodes and measuring the resistance of the IDT, at different RH levels. Since oxidized SWCNTs and graphene oxide are p-type semiconductor materials, the interaction of the sensing layer with water molecules reduces the number of holes in the sensing material, thus increasing the sensor resistance (Figure 2). The performance of the sensor introduced by this paper was compared with

that of a commercially available Sensirion RH sensor, which was placed in the same humid nitrogen environment (Figure 2).

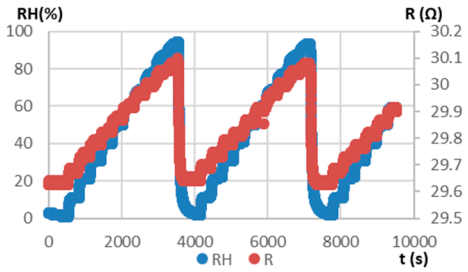

Figure 2. The output of the sensor (**red**), in time; RH variation (**blue curve**), as measured by a commercial, industrial sensor.

The IDT sensing structure introduced by this paper exhibits a linear response and good RH sensitivity when varying RH from 0% up to 90% in humid N2 environment. The sensor response time and stability are comparable to that exhibited by a commercially available Sensirion RH sensor.

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Section 2

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Extended Abstract

Embedding Polyphenols Extract from Grape Marc into Inorganic Supports with Enhanced Stability †

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Keywords: polyphenols extract; antioxidant activity; stability; mesoporous silica

Grape marc is a residue from the wine industry that contains a notable amount of polyphenols, which present antioxidant and anti-inflammatory properties [1]. Herein, we report the embedding of phenolic extract into mesoporous MCM-41-type silica matrices to enhance its stability with radical scavenger activity (RSA) preservation. As supports, pristine MCM-41 and mesoporous silica materials decorated with ZnO nanoparticles prepared by a reported procedure involving an ion exchange process between surfactant cations attached to the inner pore wall surfaces of silica and Zn^{2+} in a methanolic solution, which led to the formation of ZnO nanoparticles on silica surface during the material calcination [2]. As grape marc, Mamaia variety from Murfatlar (Romania) was used to prepare hydro-alcoholic phenolic extracts through conventional extraction (dry pomace marc weight/solvent = 1/6 w/v), which consisted of heating at reflux in three steps. The fractions from extraction were further analyzed separately and as overall extract.

The composition of polyphenolic extract was analyzed by reversed-phase high performance liquid chromatography with photometric diode array detector (HPLC-PDA) and spectrophotometric determination of total polyphenols (using Folin–Ciocalteu reagent), total flavonoids, and total anthocyanin monomeric pigments content. The radical scavenger activity (2,2-diphenyl-1-picrylhydrazyl-DPPH and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)-ABTS assays) of grape marc extracts was evaluated. Our recently reported method was used for RSA determination on solid samples by comparing the antioxidant activity of embedded extract with that of the corresponding support and extract (using the same amount as in the material containing embedded phytochemicals) [3]. The solid samples were characterized by FT-IR spectroscopy and nitrogen adsorption-desorption isotherms. The content of organic compounds into silica-type matrices was determined by thermal analysis (TG-DTA).

All supports presented high porosity and the ability to host a large amount of organic compounds (40–45% wt), making them suitable for extract encapsulation and the preservation of its beneficial effects.

The overall hydro-alcoholic extract from Mamaia grape pomace contained high polyphenolic content (27.50 ± 0.60 mg equivalent of gallic acid/g dry marc) and had a good antioxidant activity (264.55 ± 5.04 and 237.14 ± 5.47 g Trolox equivalent/g of extract determined by DPPH and ABTS assays, respectively).

The resulted materials obtained after the embedding of polyphenols showed an improved RSA in comparison to the corresponding extract, thus proving an enhanced stability, and hence preserving the beneficial effects of the phytochemicals. The toxicity of grape marc extract free and embedded in silica-type matrices was assessed on NIH 3T3 murine fibroblasts cell line. The proposed materials containing polyphenolic extract can be further used in the development of nutraceuticals.

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Extended Abstract

Biotechnological Studies Concerning the Ethanol Obtaining from Sugar Beet Molasses or from Hydrolyzed Corn Flour, in a Pilot Scale Fermentor†

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Keywords: ethanol obtaining; sugar beet molasses; hydrolyzed corn flour

This paper presents the obtained results concerning the screening of different yeast strains selected from different natural sources (such as wine manufacturing wastes) and their use in order to obtain a natural preparation containing pure distilled ethanol. After the first step of distillation, a level of 74.37 kg EtOH was obtained, with MeOH less than 0.02%, which means that this preparation can be used for human applications, like pharmaceutical or food industries, according to the literature data [1,2].

The screening of the yeast's development (mainly represented by strains of *Saccharomyces cerevisiae*, *Hansenula sp.*, *Candida scotii,* and *Candida robusta*) was carried out on a Sabouraud media first at a laboratory scale, and the better developed strains were then tested for their potential activity on a culture media containing sugar beet molasses 200 g/L (with 9.1% reducing sugar), KCl 0.8 g/L, KH_2PO_4 0.8 g/L, $NH_4H_2PO_4$ 0.8 g/L, and being sterilized for 30 min at 110 °C.

The optimal fermentation parameters for the laboratory researches were 400 mL culture media/ 750 mL capacity of the flasks, the temperature of 30 °C, and static culture conditions. For the case of using hydrolyzed corn flour first at a laboratory scale, the parameters were the following: flasks with 750 mL capacity containing 90 g corn flour (18% corn flour), 0.25 g $MgSO_4$ (0.05%), 2 g KH_2PO_4 (0.4%), 410 mL water, and 10 mL H_2SO_4 (2%). The chemical hydrolysis was then followed by a thermal process for 2 h at 125 °C. The parameters for the yeasts inoculum used in order to upgrade the researches to a pilot scale were: a specific bioreactor with 100 L capacity containing 80 L culture media composed of 24 kg sugar beet molasses (46% reducing sugar in molasses), 400 g KH_2PO_4, 400 g $(NH_4)_2SO_4$ (30 min of sterilization at 115 °C), pH 4.9, aeration 0.3 L/L/min, pressure 0.3 atm, temperature at 30 °C, and process with continued agitation. The parameters for the EtOH fermentation at a pilot level were the following: a metallic bioreactor with capacity of 2000 L containing 1700 L culture media composed of 380 kg sugar beet molasses, 500 g KH_2PO_4, 1.25 kg $(NH_4)_2SO_4$, sunflower oil 200 mL, sterilization of the medium during 30 min at 115 °C, pH 4.8 (corrected with H_2SO_4), aeration 0.1 L/L/min, pressure 0.1 atm, temperature at 30 °C, and process with agitation only for 5 min from 4 to 4 h.

After the first step of distillation, a level of 74.37 kg EtOH was obtained, with MeOH less than 0.02%, which means that this preparation can be used for human applications, like pharmaceutical or food industries.

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Extended Abstract

Chemical Composition and Antioxidant Activity of Some Widely Consumed Fruit Juices

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Keywords: antioxidant capacity; lemons; phenolic compounds; peppermint

Fruit juices are widely consumed due to their high content of vitamins (mainly vitamin C) and phenolic compounds, which act as natural antioxidants [1]. It is well known that phenolic compounds act as free radical scavengers and metal chelators, and that they increase the activity of the endogenous antioxidant defense system (catalase, superoxide-dismutase, glutathione peroxidase, etc.) [1]. The aim of our study was the phytochemical screening and evaluation of the antioxidant capacity of simple or mixed (with herbal products—dried ginger or fresh peppermint leaves—or other fruits—oranges or pomegranate) lemonade. The above mentioned herbal products and fruits have a wide variety of therapeutic properties, such as antibacterial, anti-inflammatory, hypolipidemic and hypoglycemic activities [2–4].

The samples consisted of fresh juices prepared using lemons only or lemons mixed with oranges, pomegranate, ginger or peppermint. The lemonades were encoded as follows: LS (simple lemonade), LP (pomegranate lemonade), LO (orange lemonade), LG (ginger lemonade), and LP (peppermint lemonade). Phytochemical screening was carried out based on qualitative (specific chemical reactions and thin-layer chromatography—TLC)) and quantitative (spectrophotometric determination of total phenolic content, phenolcarboxylic acids, flavones, and anthocyanidins) assays. The antioxidant activity was determined based on the scavenger capacity towards the 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical and was expressed as EC_{50} (the concentration of the tested lemonades, expressed in microliters, that provided 50% inhibition of the free radical activity). All analyzed lemonades were shown to be important sources of flavones, tannins, phenolcarboxylic acids, and proanthocyanidins; besides these compounds, LP also contains anthocyanidins. TLC analysis revealed the presence of caffeic acid in all analyzed lemonades, while rutin was present in LS, LG, and LP. Regarding the quantitative assays, the flavone content (expressed as rutin equivalents) decreased as follows: LP > LG > LS > LP. Peppermint (16.87 mg/mL) and pomegranate (12.12 mg/mL) lemonades had the highest content of phenolcarboxylic acids (expressed as caffeic acid equivalents). The total phenolic content (expressed as tannic acid equivalents) decreased as follows: LP > LR > LS > LG > LP. According to our results, pomegranate lemonade had the best antioxidant capacity.

The analyzed lemonades were shown to be important sources of bioactive compounds with antioxidant activity.

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Abstract

Qualitative Assessment of Beneficial Microorganisms

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Keywords: plant growth-promoting fungi; extracellular enzymes; keratinases; IAA

Modern agriculture needs various plant growth stimulant products. Biostimulants are a relatively new group of products with beneficial effects. They enhance plant nutrition and tolerance to the abiotic stress, and also improve the crop quality [1,2]. One type of biostimulant are microorganisms, including beneficial bacteria—mainly plant growth-promoting rhizobacteria (PGPRs), and beneficial fungi. The aim of this study was to screen fungal isolates—potential candidates for biostimulation of plant growth and the biocontrol of pathogens.

Several fungal strains belonging to *Hyphomycetes* were tested for characteristics representative for a beneficial microorganism: Production of extracellular enzymes (chitinases, cellulases, keratinases), phosphorus solubilization, siderophores and indole acetic acid (IAA) production. Also, the efficacy of tested strains as biocontrol agents against plant pathogens was achieved by antagonism, with double-culture method [3].

Positive results were obtained in the antagonism test. Two *Trichoderma* and one *Paecylomyces* isolates showed a significant inhibitory effect on pathogen growth. Production of lytic enzymes was more or less at the same level for all tested strains. It is important to highlight that the selected strains presented the ability to produce IAA, the most common plant hormone responsible for cell division and elongation as a response to various factors, such as light and the presence of pathogens etc.

The use of selected fungal isolates could be of practical interest for promoting plant growth and reducing nitrogen fertilizers. Further researches are required for an understanding of the action mechanisms of biostimulation on plants.

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Abstract

Antioxidant Activity and Phytochemical Compounds of *Capsicum annuum* L.

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Keywords: antioxidant activity; phytochemical compounds; *Capsicum annuum* L.

The benefits of *Capsicum annuum* L. are important for human health with its anti-inflammatory and analgesic properties in the case of stomach and back pain, muscle spasms, headaches, skin aging, peptic ulcers [1]. The aim of the present study was to characterize and investigate the antioxidant activity and phytochemical compounds [2] of three types (red, yellow, green) of hot pepper (*Capsicum annuum* L.) samples, using two methods of extract production (maceration and ultrasound).

In this research, we presented the results in the field of antioxidant activity and phytochemical analysis, using extracts obtained from three types of pepper native plants (red, yellow and green) extracted using two methods (maceration-M and ultrasound-U) in ethanol (EtOH) or methanol (MeOH) solvents. The sample extracts were studied using UV-VIS and TLC techniques. The antioxidant property was determined using DPPH method [3], Figure 1.

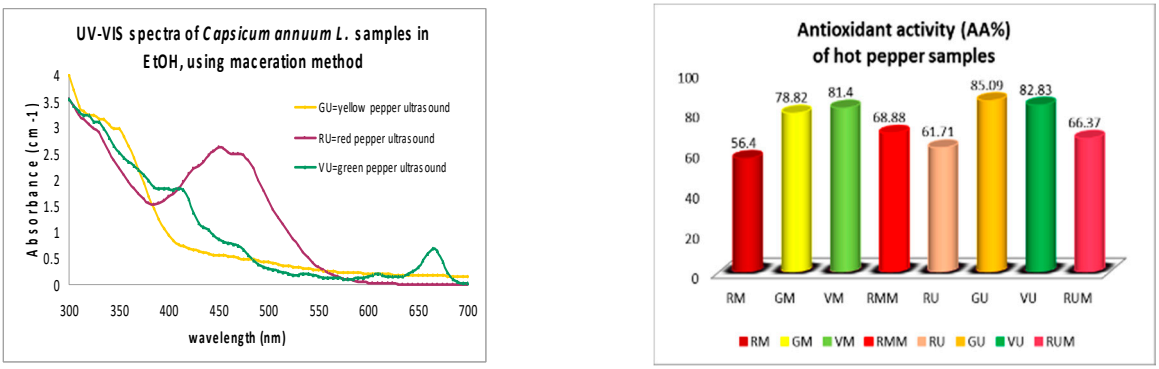

Figure 1. UV-VIS spectrum of *Capsicum annuum* L. and graph of the antioxidant activities (AA %) values for hot pepper samples.

For the maceration method in EtOH, the samples codifications are: GM—yellow hot pepper maceration in EtOH, VM –maceration in EtOH, RM—red hot pepper maceration in EtOH, RMM – red hot pepper maceration in MeOH. Ultrasound method: GU—ultrasound yellow hot pepper in EtOH, VU—ultrasound green hot pepper in EtOH, RU—ultrasound red hot pepper in EtOH, RUM—ultrasound red hot pepper in MeOH.

Red, yellow and green pepper extracts have a very high antioxidant activity (AA %), which denotes the benefits of the compounds existing in these vegetables. The ultrasound method revealed higher values compared to maceration. The color of the peppers is due to the presence of carotenoids, as demonstrated by the UV-VIS spectrum measurements. In the case of the yellow pepper extract (GM), the carotenoids are found in the range 325–425 nm. In red peppers (RM), β-carotenoid peak is found between 445–478 nm, which is more pronounced using ultrasound method. Hot pepper samples extracted in ethanol, using maceration method (RM, GM, VM), present higher values of flavonoids (TFC), compared to the samples extracted in the same solvent (ethanol), but using the ultrasound method (RU, GU, VU). In the case of terpenoids (TTpC), it was observed that the extracts of green pepper (VM and VU), obtained by both methods (M and U), have the highest values.

Acknowledgments: This work was supported by a NUCLEU Program, conducted with MCI support, project number PN.19.23.03.01.04.

Conflicts of Interest: Authors declare no conflict of interest.

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Extended Abstract

Identification of Valuable Bioactive Compounds in Underused Plant Parts of Industrial Hemp †

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Keywords: *Cannabis sativa* L.; HPTLC; terpenes; polyphenols

Cannabis sativa L. (hemp) is a unique versatile plant, which can provide high biomass quantities in a short time [1] and has been known since ancient times for its medicinal and textile uses [2]. Some biological activities of cannabinoids (the most studied class of hemp compounds) are known to be enhanced by the presence of terpenes and flavonoids in the extracts, due to a synergistic action [3]. The purpose of this research was to investigate the polyphenols and terpenes content of underused plant parts (root, hulled seeds, aerial parts, fiber, grist) of industrial hemp.

Hemp raw material was gifted by a grower from the northeastern area of Romania. The extracts from different plant parts (root, hulled seeds, aerial parts, fiber, grist) were prepared by (a) maceration with ethyl alcohol and (b) ultrasound extraction with ethyl alcohol 50%. The polyphenols and terpenes contents were evaluated by high performance thin-layer chromatography (HPTLC) using specific solvents systems [4].

Results showed a high content of flavonoid glycosides in the hydroalcoholic extract of hemp aerial parts. In the alcoholic extracts, aglycones were present in fiber and grist (Figure 1). As regards terpenes fingerprint (Figure 2), mostly dehulled seeds contain high amounts of important compounds.

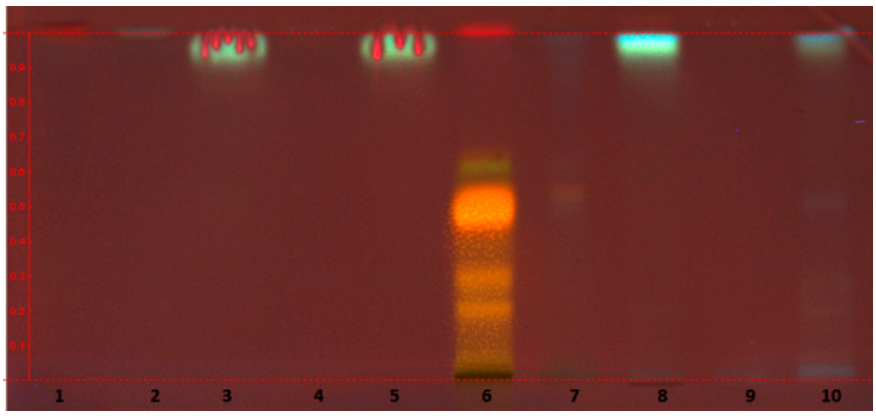

Figure 1. HPTLC fingerprint of polyphenols in hemp ethyl alcohol extracts (tracks 1—aerial parts, 2—root, 3—fiber, 4—dehulled seeds, 5—grist) and hydroalcoholic extracts (tracks 6—aerial parts, 7—root, 8—fiber, 9—dehulled seeds, 10—grist).

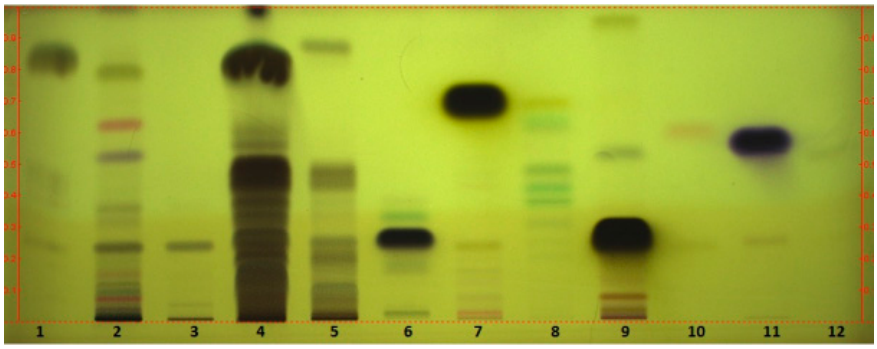

Figure 2. HPTLC fingerprint of terpenes in hemp ethyl alcohol extracts (tracks 1—fiber, 2—aerial parts, 3—root, 4—dehulled seeds, 5—grist) in comparison to reference compounds (tracks 6—terpineol, 7—geranyl acetate, 8—limonene, 9—geraniol, 10—thymol, 11—caryophyllene oxide, 12—beta-pinene).

Important bioactive compounds are present in the underused plant parts that could be converted into value-adding products for a complete valorization of industrial hemp.

Acknowledgments: This research was financially supported by the Ministry of Research and Innovation in the frame of the project PN.16.41.01.01/2018, CORE Program.

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Abstract

Optimization of Chitin Extraction from *Agaricus bisporus* Using a Taguchi Design †

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Keywords: chitin extraction; *Agaricus bisporus*; optimization; Taguchi Design

Edible mushrooms, e.g., *Agaricus bisporus* (*A. bisporus*), represents a well-known source of nutrients for humans because of their low calorie content and high content of proteins, carbohydrates, polyunsaturated fatty acids, phenolic compounds, dietary fibers, vitamins (B_1–B_3, B_5, B_6, B_9, B_{12}, C, D_2), minerals (Fe, Mg, P, K, Na, Zn), lectins, and other bioactive compounds. Their antioxidant, antimicrobial, dietary, and anti-allergenic content means they can be used for novel applications such as additives for food, nutraceuticals, or cleaning products [1]. The objective of this paper was to establish the optimal process parameters for chitin extraction from *A. bisporus* using an experimental Taguchi orthogonal array (OA) factorial designs under response surface methodology (RSM). A linear model with four independent variables (A = liquid/solid ratio, mL/g; B = extraction temperature, °C; C = extraction time, h; D = stirring speed, rpm) and three levels was used to maximize the relative extraction efficiency. The mushrooms were grinded and lyophilized. Conventional deproteinization and demineralization treatment with NaOH solution was used. Different volumes of NaOH solution were mixed with lyophilized *A. bisporus* in a round-bottomed flask with a reflux cooler for different extraction temperatures, times, and stirring speeds on a hot plate with magnetic stirrer. The extracted chitin was between 7.2% and 16%, where the minimum content obtained was for A = 100 mL/g, B = 100 °C, C = 4 h, and D = 900 rpm, and the maximum for A = 80 mL/g, B = 80 °C, C = 4 h, and D = 600 rpm. The polynomial equation coefficients were established using the Design-Expert® Software Version 11 (Stat-Ease, Inc. Minneapolis, MN, USA). The optimum chitin content was at A = 116.782 mL/g; B = 80.759 °C; C = 4.109 h, and D = 973.715 rpm, which is in accordance with the predicted values obtained using RSM. A positive influence on the chitin content was observed for the liquid/solid ratio (A), the extraction temperature (B), and the extraction time (C). The relevance of the regression analysis was determined using analysis of variance (ANOVA). This work could be a starting point in designing and optimizing new processes for higher valorization of chitin extraction.

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Conflicts: Authors declare no conflict of interest.

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Abstract

Pyrolysis of Sunflower Oil Mucilages for Fluxing Bitumen †

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Keywords: fluxing bitumen; pyrolysis; mucilages

The reduction of greenhouse gas emissions requires increasing the use of energy from renewable sources and reducing dependence on fossil fuels and energy imports, thus contributing to the security of energy supply. Pyrolysis has proven to be a promising technique for converting biomass into fuel.

The mucilages used in the experimental program came from the refining of sunflower oil. Mucilages were characterized by thermal analysis, determination of density, viscosity, and saponification index. Stable dispersions of mucilages were obtained with a nonionic polyoxyethylene 20 sorbitan monooleate surfactant (Tween80). The molybdenum catalyst was prepared using ammonium heptamolibdate as precursor. The pyrolysis of mucilages was performed in a laboratory continuous stainless steel tubular reactor heated in an oven with temperature control system and automatic feeding pump. The pyrolysis experimental test was carried out at atmospheric pressure and 500 °C temperature in the isothermal reaction zone. The composition of the liquid fraction resulting from the pyrolysis was determined by gas chromatography (GC–MS/MS triple quadAgilent 7890 A). A road bitumen D 50/70 penetration grade was selected for the preparation of fluidized bitumen with pyrolysis products. The homogenization of the mixture of road flux and bitumen was carried out in a 250 mL autoclave provided with an anchor-type stirrer and a thermostatic heating jacket.

Results: The stability test of the prepared emulsions was carried out for crude mucilage and mucilage emulsions with different concentrations of emulsifier. The recorded stability curves showed that the stability of the mucilage emulsions improved with the increase of the emulsifier concentration up to 3% wt. The chromatogram of liquid phase compositions separated during the catalytic pyrolysis process in the presence of Mo catalyst showed a high content of unsaturated fatty acids and a low content of saturated fatty acids and linear aliphatic hydrocarbons

The stabilization of the mucilage from the refining of vegetable oil was achieved by re-emulsifying it in the presence of a nonionic surfactant. The main processes in pyrolysis of mucilages are decarboxylation which results in linear hydrocarbons and solvolysis of the lecithins and glycerides present in the by-product fatty acids. The pyrolysis liquid fractions contain compounds with optimum polarity for solubilizing the bitumen and for stabilizing its colloidal

structure. The low volatility of these compounds does not adversely affect the aging characteristics of fluxed bitumen such as loss of mass and residual penetration.

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Conflicts: Authors declare no conflict of interest.

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Abstract

Carbonaceous Nanostructures Obtained by Hydrothermal Conversion of Biomass †

Marius Ghiurea [1], Stefan-Ovidiu Dima [1,*], Anca-Andreea Turcanu [2], Radu-Claudiu Fierascu [1], Cristian-Andi Nicolae [1], Bogdan Trica [1] and Florin Oancea [1]

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Keywords: carbonaceous nanostructures; hydrothermal carbonization; lignocellulosic biomass

By thermal treatment of biomass, different types of biochar can be produced, like carbon nanotubes (CNTs) and graphitic nanostructures, graphene, graphene oxide, or activated carbons, to name a few [1]. Their properties depend on the reaction conditions (temperature, pressure, reaction time, pH, and with or without catalysts), in addition to the type of biomass used [2,3]. Also, in the liquid phase, valuable chemicals like leuvulinic acid, furfural, 5-hydroxymethylfurfural can be obtained.

Lignocellulosic biomass (LCB) from corn stalks was mechanically grinded and subjected to hydrothermal conversion in water, under thermally generated pressure in a hermetic reactor, at different temperatures (140 °C, 180 °C, 200 °C, and 220 °C), and for different reaction times (2, 4, 6, 8, and 20 h). At the end of the hydrothermal reaction, solid and liquid phases were separated by filtration, and further analytically characterized using Fourier-Transform Infra-Red spectroscopy (FTIR), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and Thermo-Gravimetrical Analysis (TGA), respectively Gas-Chromatography coupled with Quadrupole Mass Spectrometry (GC-MS/MS), High_Performance Liquid Chromatography coupled with Time-of-Flight Mass Spectrometry (HPLC-TOF/MS), and Ultra-Violet Visible (UV-Vis) spectroscopy for the liquid phase.,.

Mild hydrothermal carbonization (140 °C, 180 °C, at 2, 4, and 6 h) led to a brownish, amorphous, lignin-rich solid phase, and a liquid phase containing aldehydes, organic acids, and polyphenolic compounds, while high temperature conditions led to a high content of black hydrothermal carbon with increased crystallinity (Figure 1), respectively furans, furfurals, and levulinic acid in the liquid phase.

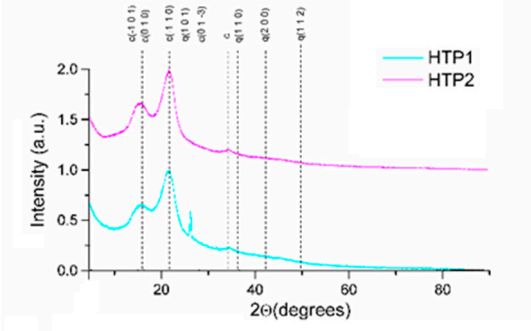

Figure 1. X-ray Diffraction analyses of the solid phase resulting from the hydrothermal conversion process, associated with the hydrothermally treated samples at 180 °C (HTP1) and at 200 °C (HTP2) samples.

Hydrothermal carbonization of LCB from corn stalks at higher temperatures and reaction times leads to nanostructured hydrothermal carbon, nanographitic, and nanowhiskers structures, with improved adsorption properties so this material can be recommended for use in the depollution of waste waters, for the abatement of volatile organic compounds (VOCs) from indoor spaces, and even for photovoltaics and nanoelectronics.

Acknowledgments: This work was supported by the Romanian Ministry for Research and Innovation through the National Authority for Scientific Research (ANCS) and Executive Unit for Financing Higher Education, Research, Development and Innovation (UEFISCDI) through the projects PN 16.31.01.01 contract No. 34N/2016, and PN.19.23.03.01 contract No. 23N/2019.

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Abstract

Chitosan Nanoparticles Stabilized with Gallic Acid, Never-Dried Bacterial Nanocellulose, and Alginate Have Biostimulant Potential for Plants †

Stefan-Ovidiu Dima [1,*], Anca-Andreea Turcanu [2], Sanda-Maria Doncea [1], Victor Faraon [1], Elena Radu [1], Angela Moraru [3], Bogdan Trica [1], Radu-Claudiu Fierascu [1] and Florin Oancea [1]

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Keywords: chitosan nanoparticles; gallic acid; ionotropic reticulation; plant biostimulant; bacterial cellulose

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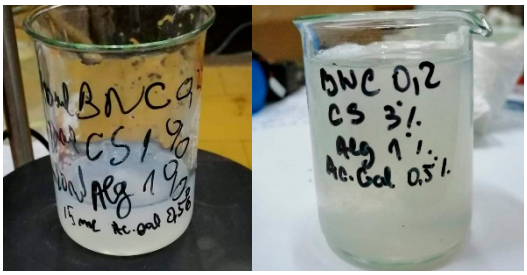
Current plant growth trends coupled with advanced analysis and in-field monitoring are oriented towards new agricultural inputs that protect and stimulate plant development. New nano-formulations sprays are being developed in order to help plants fight biotic and abiotic stress (i.e., osmoprotectants, biostimulants, biopesticides, or elicitors) [1]. The main categories of plant biostimulants include protein hydrolysates, polyamines, aminoacids, other N-containing compounds, seaweed extracts (alginate), botanicals, chitosan, other biopolymers, inorganic compounds (Si, Se), beneficial fungi, humic acids, fulvic acids, and beneficial bacteria [1,2].

A solution of 1% chitosan (CS) was prepared by dissolving it in 1% acetic acid. Further, it was mixed with 0.5% gallic acid that was dissolved in ethanol. The mixture was rigorously shaken using a vortex for 30 min, which allowed the gallic acid to act as an ionotropic crosslinker for chitosan. The nanodispersion was added in a 0.2% bacterial nanocellulose suspension, previously obtained by purification and microfluidization of Kombucha pellicles [3], the cellulosic nanofibrils having the role of a stabilizing net. Alginate was added as a 1% water solution due to its muco-adhesive properties and final stabilization role as a hydrogel containing crosslinked chitosan-gallic acidnanoparticles.

The viscosity of the system with 1% CS was lower, which allows us to recommend it for further spray-drying formulations. The system with 3% CS was homogeneous and more viscous, suggesting a possible application as soil amendment for soils depleted in nutrients. The prepared nanoformulations have potential biostimulant activity due to polyphenolic gallic acid, water retention-releasing characteristics of highly hydrophilic NDBNC, and plant nutrition properties through chitosan and alginate decomposition.



(**a**) (**b**)

Figure 1. (**a**) Preparation of chitosan: gallic acid nanoparticles by ionotropic reticulation. (**b**) Stabilization of CS-GA system in an NDBNC-Alginate hydrogel.

The NDBNC-alginate hydrogel contains gallic acid-chitosan dispersed nanoparticles that can be used in their concentrated form as biostimulant hydrogel that can beapplied on soil around plants roots, or in a 100x diluted form for foliar application. These biostimulant nanoformulations can be used for plant growth and protection during drought periods.

Acknowledgments: This work was supported by the Romanian Ministry for Research and Innovation and National Authority for Scientific Research (ANCS) and Executive Unit for Financing Higher Education, Research, Development and Innovation (UEFISCDI) through the project NEXT-STIM PN.19.23.01.03 contract no. 23N/2019.

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Abstract

Nanoemulsions Based on Biopolymers Loaded with Humic and Fulvic Acids Derived from Hydrothermally Treated Biomass †

Malina Desliu-Avram [1], Stefan-Ovidiu Dima [1,*], Anca-Andreea Turcanu [2], Elena Radu [1], Ana-Maria Stanciuc [3], Sanda-Maria Doncea [1], Angela Moraru [3], Irina Fierascu [1], Bogdan Trica [1]

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Keywords: nanoemulsions; humic and fulvic acids; nanocellulose; biostimulants; hydrothermal conversion

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Humic substances (HS) are complex systems widely spread in nature as a result of the humification process of biomass, although hardly quantifiable and understood. Various polyphenols are considered to be the main precursors of HS. HS are naturally synthetized in reactions involving hydrophilic, hydrophobic, ionic, and donor–acceptor intermolecular forces of different biomass-derived components, such as amino acids, carbohydrates, lignins, and pectines [1]. Humins, as macromolecular associations, and fulvic acids, as lower-molecular-weight compounds, present appealing properties that make them interesting for use in formulations with potential biostimulant effects for plants development [2].

Nanoemulsions were prepared by vigorously mixing on a magnetic plate a solution of 0.2% bacterial nanocellulose (BNC) previously obtained by purification and microfluidization [3], with 1% or 3% chitosan dissolved in 1% acetic acid, a 1% alginate solution, and a liquid phase containing humic and fulvic compounds obtained from un-catalyzed and catalyzed hydrothermal processes of lignocellulosic biomass. For catalyzed hydrothermal conversion (HTC) process, a Cu–Pd–Ce/γAl_2O_3 catalyst was used. The samples, as well as the liquid phase from the HTC process, were characterized by means of XRD, TGA, FTIR, and HPLC–FLD-MS.

HPLC–FLD-MS analyses performed on the liquid phase from the hydrothermal process of lignocellulosic biomass evidenced the presence of valuable compounds like high-molecular-weight humic acids (300–600 Da) and fulvic compounds, as shown in Figure 1.

The liquid phase resulting from the HTC process of lignocellulosic biomass (corn stalks) contained a huge number of organic compounds, including polyphenols, humic and fulvic acids, aldehydes, amino acids, and other small organic molecules with potential biostimulant properties for plant growth and protection against abiotic stress, such as drought and nutrients scarcity.

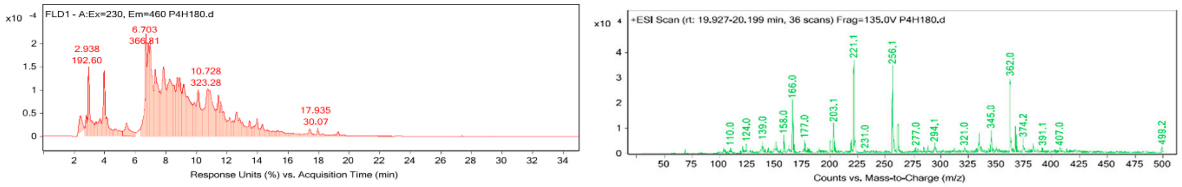

Figure 1. (**a**) HPLC-FLD-MS analyses of the liquid phase from the hydrothermal process and (**b**) MS spectrum of the humic components.

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Abstract

Preliminary Results on Aroma Compounds Recovery from Wine Lees †

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Keywords: wine lees; aroma compounds; hydrodistillation

Valorization of agro-industrial wastes and by-products to obtain new value-added products is one of the most important goals of the scientific research for the development of the sustainable bioeconomy. According to the statistics of The Food and Agriculture Organization (FAO) of the United Nations, grape is the largest fruit crop worldwide. Wine industry disposes large volumes of wastes which represent 20–30% of total wine production including wastewater and solid organic by-products as wine lees and grape pomace composed of stalks, skins and seeds [1]. Wine lees are the residue that forms at the bottom of the vessel containing wine during the storage, represent 2–6% of the total volume of wine produced and contain about 62.9% (w/w) water, 5.7% (w/w) ethanol and 31.4% (w/w) solids on a dry basis [2]. Biorefinery of wine lees produces mainly ethanol, antioxidants and tartaric acid. The solid fraction contains high concentrations of macronutrients, yeast cells with polyphenolic compounds and proteins [3]. Wine lees also contain natural essential oils with complex composition mainly fatty acid esters produced during the fermentative process, when metabolites from yeast after bioconversion of grape juice are released and contribute to wine flavor and aroma [4]. The purpose of present research is the wine lees valorization for the recovery of volatile compounds responsible for wine aroma, one of the most important indicators of wine quality and potential ingredients for new additives with various applications. Several preliminary experiments were performed using azeotrope distillation with Clevenger apparatus for light oil extraction. The most important aroma compounds known as "cognac oil" (C8-C12 fatty acid ethyl esters) were obtained from red wine lees by a cascade hydrodistillation process, identified and quantified to a 0.99% total concentration with GC-MS analysis.

Author Contributions: Authors declare no conflict of interest.

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Extended Abstract

Natural Bioproducts and Their Potential Preservative Properties in Food Industry †

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Keywords: *Plantaginaceae*; preservative properties; citrus fruits

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Phytosanitary products obtained from natural extracts represent an alternative, especially in the case of preservation of the products obtained from organic farming. The purpose of this work was to test the antifungal activity of three extracts obtained from a plant from *Plantaginaceae* family, obtained according to the methodology presented by Radu et al. [1]. The tests were performed in vitro on phytopathogenic fungi that cause alteration of the citrus fruits, such as *Penicillium sp*.; and *Aspergillus sp.* The methodology used was that of diffusive discs impregnated in sterile solutions containing 3% of the solid extract, dissolved into an inert solvent (respectively Dimethyl Sulfoxide) [2–4]. After inoculation with the tested microorganism and treatment with the analyzed phytoextract, the growth of microorganisms was monitored for two weeks. The obtained results showed that the tested extracts inhibit the development of the species of *Penicillium citrinum, Penicillium digitatum*, and *Aspergillus niger*. These effects have maintained for 72 hours in the case of the above microorganisms. After 2 weeks the antifungal effect of the analyzed extracts was reduced at 78.5% in the case of *Penicillium citrinum*, at 83.5% in the case of *Penicillium digitatum* and respectively at 57.9% in the case of Aspergillus niger. In conclusion, the best results are obtained at the treatment of *Penicillium* species which attack the citrus fruits, with studied plant extracts. Here is needed a deeper research, in order to develop a bioproducts from *Plantaginaceae* indigenous plants, with a role in protecting and preserving of citrus fruits.

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Extended Abstract

Extraction and Characterization of Glycosaminoglycans from Marine Snail *Rapana venosa* †

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Keywords: *Rapana venosa*; polysaccharides; hexoses; uronic acids; cell viability

Glycosaminoglycans (GAGs) are anionic straight chain polysaccharides with a wide range of applications in the pharmaceutical, cosmetic and food industries [1]. The aim of this study was to extract and to evaluate the chemical and biological characteristics of GAGs isolated from *Rapana venosa* collected from the Black Sea, in order to obtain valuable extracts for use in the biomedical field.

In this study, GAGs were obtained from snail soft tissue by chemical extraction, followed by ethanol precipitation. The extract obtained was analyzed in terms of total hexose [2], uronic acid and carbohydrate content [3]. Agarose gel electrophoresis was performed to separate the extract into the main types of GAG using chondroitin 4-sulfate sodium salt from bovine trachea (Sigma) as per commercial standards. In vitro cytotoxicity tests were conducted on NCTC clone L929 mouse fibroblasts cultivated in the presence of different concentrations of GAGs, in standard conditions, for 48 h. Cell viability was determined using MTT assay [4], while cell morphology was evaluated using Giemsa staining.

The extract obtained was rich in total hexoses, uronic acids and carbohydrates. The electrophoretic pattern revealed a single band at high molecular weight. Data obtained from in vitro studies showed that GAGs extract exhibited a good cytocompatibility up to the concentration of 3000 µg/mL after 48 h of cell exposure. Qualitative morphological observations of treated cells after Giemsa staining indicated the maintenance of a normal fibroblast phenotype, which has been correlated with the MTT quantitative results.

Rapana venosa represents a rich source of GAGs with high contents of hexoses, carbohydrates and uronic acids, which can be used for various applications in the biomedical field.

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Abstract

Bio-Oil Produced via Catalytic Pyrolysis of the Solid Digestates from Anaerobic Co-Digestion Plants †

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Keywords: bio-oil; catalytic pyrolysis; solid digestate

Digestate, the residue following anaerobic digestion, has attracted great attention recently as a potential feedstock for pyrolysis. Pyrolysis is regarded as a technology with great potential to treat wastes. Related studies have found over 91% of the digestate energy was transferred into products of bio-oil, solid, and gaseous [1]. Digestate pyrolysis oil shows promise as a biofuel source for engine applications [2]. However, related studies on the components of pyrolysis oil are still lacking.

In this context, the objective of this study was to investigate the pyrolysis process of the solid fraction from anaerobic co-digestion plants digestate in the presence of a nanostructured catalyst based on Mn, and the characterization of a bio-oil fraction produced in the pyrolysis process.

The digestate was obtained from anaerobic digestion in a laboratory. Composition analysis and thermogravimetric analysis were conducted. Experiments were undertaken to investigate the impact of the reaction temperature and pressure on the digestate pyrolysis, as well as characterizing the yield and quality of the bio-oil product. Further objectives were to propose the optimum reaction from digestate to bio-oil, and find a feasible foundation of the digestate decomposition mechanism for further utilization.

Experimental

The catalysts were obtained using a soft template method via the evaporation self-assembly (EISA) method, using salts of Mn precipitated in the presence of polymeric anti-agglomerates as Pluronic P123. The prepared catalysts were characterized by isothermal sorption measurements using a NOVA 2200e-Quantachrome Analyzer porosimeter (the specific surface was calculated from the linear portion of the adsorption isotherm using the B.E.T. equation), Fourier-transform infrared spectroscopy (Jasco FTIR-6300 with ATR Specac Golden Gate) and X-ray diffraction (XRD) analysis with X-ray diffractometer SmartLab (Rigaku). The acid strength distribution was performed by a method of thermal desorption of diethylamine on a Thermogravimetric Analyzer [3].

The experimental tests have been carried out in a laboratory-scale tubular reactor in inert gas. The tubular reactor made of stainless steel was heated in an electric furnace provided with a temperature control system. The solid digestate used as feedstock for pyrolysis were obtained from a laboratory biogas plant. The suspension obtained from the mixture of conditioned solid digestate, lipid fraction from algae biomass, and a catalyst in various mixed ratios was continuously fed into the reactor. A gas-liquid separator was used to separate the condensed liquids and gas products. The liquid and gas products were analyzed using a GC/MS Triple Quad Agilent Technology gas

chromatograph. The structural characterization of the resulted bio-char was made by textural analysis and determination of the ash content.

The catalyst characterization data indicates the obtaining of an amorphous hydrous nanostructured MnO_2. The results show that the amorphous hydrous nanoparticles with the mean particle size of 10–30 nm were obtained and the BET specific surface areas were 130 m^2/g.

The catalytic activity of synthesized MnO_2 nanoparticles was evaluated in the pyrolysis of anaerobic co-digestion plants digestate solid suspension. The reaction parameters studied for the pyrolysis process were: temperature 450–520 °C, atmospheric pressure, and catalyst concentration 1–10 wt.%. The obtained results showed that the catalyst concentration had an important effect over liquid yield. The liquid yield reached a maximum value at the pyrolysis temperature of 460 °C in the presence of 0.75 wt. % based on the feedstock amount. The analysis of the liquid fractions obtained on the nanostructured Mn catalysts highlights the presence of a large number of linear and branched aliphatic hydrocarbon components, unsaturated compounds, alcohols, carbonyl compounds, and carboxylic acids, with boiling temperatures ranging over a wide range. Meanwhile, the textural analysis of the separate coal from the catalytic pyrolysis reveals a low pore volume and implicitly a small specific surface, specific to the non-activated coal.

The nanostructured Mn catalyst was successfully obtained by a soft templating method using salts of Mn by precipitation in the presence of Pluronic P123. The pyrolysis of biogas solid digestate results shows that the yield and composition of the liquid fraction are dependent on the catalyst concentration and residence time.

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Abstract

Process Intensification on Circular Bioeconomy—A Practical Approach †

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Keywords: process intensification; microwave; ultrasounds; mecano(bio)chemistry; microfluidic chemistry; electrochemical upgrading; biogenic/natural nanoparticles; HPLC fingerprint analysis; IP protection

Bioeconomy, an area of smart specialization for Romania, is characterized by linear value chains. The sustainable closure of the loop of value chains involves the recovery of bioactive components from byproducts and a cascading/systemic approach for the revalorization of coproducts from one production cycle as resources for another production process. The recovered biologically active components are used for products highly required in the market, such as dietary supplements, cosmeceuticals, plant biostimulants, and bioplastic additives. The dietary supplements market exceeds the level of €200 million in Romania. Globally, it is projected to reach USD 194.63 billion by 2025, with a compound annual growth rate (CAGR) increasing to 7.8%. The cosmeceuticals market is the market with the fastest growth of all personal care products, with a potential global level of USD 85 billion by 2024, growing at a CAGR of 8.81%. Already, in Romania, the market for cosmeceuticals exceeds 10% from the total cosmetic product market of €1.7 billion. Plant biostimulants represent a new category of the products used as inputs in the plant cultivation technologies, USD 4.9 billion by 2025, at a CAGR of 11.24% during the forecast period, with an estimated growth rate of 11.24% per year by 2018, when it will exceed USD 4.9 billion at the global level. Despite the lack of specific regulation in Romania, the market of plant biostimulants (sold mainly together with fertilizers) exceeds €150 million. Biodegradable plastics will increase to USD 6.12 billion by 2023, at a CAGR of 15.1%. The high CAGR of these markets is related also to societal requirements. Plant biostimulants are increasing crop tolerance to abiotic stress, amplified by climatic changes. Totally biodegradable bioplastics represent one of the solutions for (micro)plastic ocean pollution. The development of the new (bio)process intended to close the loop in the bioeconomy value chains requires the intensification of the research and innovation on both laboratory and scale-up processes. Large-scale production also requires process intensification for higher productivity and profitability. Specific intellectual property aspects are arising from the implementation of the biomass pyramid value—e.g., the protection of the new utilizations for the products recovered from bioeconomy side-streams.

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Abstract

Extraction of Fungal Chitin Using Natural Deep Eutectic Solvents †

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Keywords: chitin; mushrooms; natural deep eutectic solvents

Chitin is considered the second most plentiful biopolymer in nature after cellulose, its main sources being crustaceous shells and cell walls of fungi [1]. Chitin has great economic value due to its various characteristics, such as biodegradability, biocompatibility, non-toxicity, and thermal stability, which offer many potential applications in different fields [2]. The extraction of chitin involves two preliminary steps including demineralization and deproteinization. They can be conducted by two methods, chemical or biological. The chemical method requires the use of acids and bases, while the biological method involves microorganisms. The conventional chemical extraction of chitin requires strong acids and alkali to eliminate minerals and proteins, but using these hazardous chemicals can deteriorate the physicochemical properties of this biopolymer, and consequently, its biological properties [3]. Natural deep eutectic solvents (NaDESs) have emerged as a promising alternative to classical methods for extraction of biopolymers and other biomolecules and offer the opportunity to preserve the exceptional qualities of chitin. The aim of this study was to investigate chitin extraction from *Agaricus bisporus* in several NaDESs. *Agaricus biosporus* was commercially purchased from a local supermarket, washed, cut, frozen the same day, and lyophilized before further treatments. Before chitin extraction, the mushrooms were depigmented with hydrogen peroxide, followed by demineralization and deproteinization with biocompatible acids such as citric acid, tartric acid, or ascorbic acid. A series of NaDESs were synthesized based on combinations between choline chloride, betaine chloride, guanidine, urea, and sorbitol, which were mixed at optimal molar ratio and heated at 50–80 °C until a homogeneous liquid was formed. The pretreated samples were dispersed in NaDESs with different mushroom/NaDESs ratios (1:5, 1:10, 1:20) and then the mixtures were heated at various times (2–12 h). After reaction, chitin and NaDESs were separated by centrifugation and the chitin was rinsed with distilled water and was lyophilized. The extracted chitin was analysed by a plethora of techniques such as FTIR and XRD spectroscopy, SEM, and TGA analysis which revealed a good quality chitin. This study could be a starting point for chitin extraction with NaDESs using Design of Experiments (DOE).

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Abstract

Improving the Shelf-Life of Fruits Using Chitosan and Chitosan-Based Glycodynamer Coatings †

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Keywords: chitosan; glycodynameric hydrogel; edible bioactive coating

The study aims to develop an edible bioactive coating in the form of a chitosan glycodynameric film, which is intended to protect fresh fruits (berry fruits, apples), during storage. A solution of 2% chitosan in acetic acid (0.7%), was cross-linked with 1% citral prepared in ethanol, generating a glycodynameric structure [1]. The citral solution was added to chitosan under continuous magnetic stirring at 55 °C. The glycodynameric feature (reversible/dynamic covalent bonds) is determined by the competition between the imine formation (amino groups of chitosan–aldehyde group of citral) with citral aliphatic side chains' self-organization into supramolecular layered architectures [2]. The resulted glycodynameric structures combine excellent mechanical properties with stimuli-controlled transitions [3]. Two types of film coating were applied on berry fruits, chitosan coating and glycodynamer coating. The fruits with and without coating, the chitosan and the glycodynameric films were characterized by FTIR spectroscopy. The decay of strawberries was reduced significantly when berries were either coated with chitosan (reference control) or with glycodynameric coating. The early signs of mold development on strawberries appeared after 9 days of storage at room temperature. Both the chitosan and the glycodynameric coating reduced the fungal decay, the glycodynamer being more efficient, probably due to the presence of citral. The FTIR spectral bands characteristic to chitosan and glycodynamer were observed on the surface of fruits, but the glycodynamer stability, in time, needs to be optimized. In conclusion, our study indicates that preservative coating based on glycodynamers has a potential to prolong storage life and control the fungal decay of fruits. Further studies with other fruits and different glycodynamers are needed.

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Abstract

Clean Technologies Combining Phytoremediation with Biofuel Production—Part II †

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Keywords: phytoremediation; biomass; biofuels

Within the CleanTech project, combined technologies are addressed in order to maximize the impact on process efficiency and environmental issues. In this paper, phytoremediation of soil with potential salt contamination [1,2] combined with the production of biomass for 2nd generation biofuels is the path used to fulfill the project's objectives. For this purpose, several plant species able to produce biomass for biofuels were tested using soil sampled from salt-affected land. Plant species were selected based on the potential to obtain low-lignin biomass for bioethanol synthesis.

For the laboratory study the seeds, provided by certified providers, were tested for direct germination in commercial peat (as reference) and soils with different initial salinity. In this paper, the results obtained using seeds of *Limonium sp.* are considered. Thermogravimetric (TGA) characterization of obtained biomass was performed in order to have a complete image of bio-components content and behavior.

Limonium sp. seeded on soil samples with different salinity (expressed in electrical conductivity, dS/m) did not germinate. Seedlings obtained from germinated seeds in commercial peat have shown good adaptability in different soil structures and salinity levels. Soil electrical conductivity (EC) before and after experimental tests are presented in Figure 1.

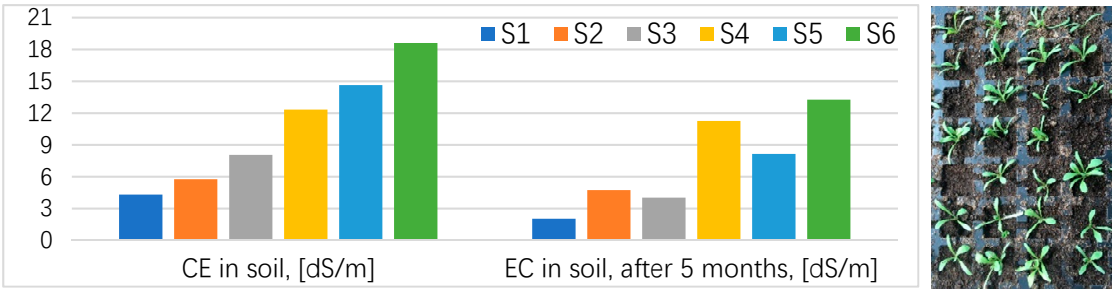

Figure 1. EC of tested soils before and after phytoremediation.

Limonium sp. has shown good salt removal capacity. The TGA analyses show that the salts tend to be deposited mainly in roots.

Acknowledgments: This work was supported by the Romanian competitiveness operational program through the knowledge transfer project CleanTech—POC - P40_308, SMIS: 105958 (http://cleantech.pub.ro/).

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Abstract

Plant Biostimulants Based on Selenium Nanoparticles Biosynthesized by *Trichoderma* Strains †

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Keywords: plant biostimulants; selenium nanoparticles; *Trichoderma* spp.; *Vigna radiata*

Biostimulants are a novel class of additives used to promote plant vigor and resistance to abiotic stress, such as desiccation. The most used biostimulants are humic and fulvic acids, seaweed extracts, and biopolymers, as well as beneficial bacterial and fungal strains [1]. One such beneficial fungal strain is *Trichoderma,* which exists in the soil and colonizes the root system and can enhance root proliferation [2]. *Trichoderma* spp. were shown to be able to bio-synthesize selenium nanoparticles (SeNPs) [3]. Selenium (Se) is known to have beneficial effects on plant and animal metabolism at low concentrations, being involved in protection against reactive oxygen species (ROS) in the form of selenoproteins [4]. Se can also act as a protective agent against the harmful effects of heavy metals [5]. Nevertheless, Se has a narrow physiological window, and the toxicity depends on Se species, SeNPs being much less toxic than Se salts [4].

The aim of this study was to develop and test a plant biostimulant based on SeNPs bio-synthesized by *Trichoderma* spp. by monitoring its effects on different stages of plant growth, as well as some biochemical markers of these effects. The tests were conducted on *Vigna radiata* seeds, which were germinated in aqueous solutions of SeNPs or Se selenite and compared to a control group that were germinated in water. The germinated seeds were planted in sterilized soil and grown in a lux-chamber. Post-harvest, the plant material was ground into a powder after freezing with liquid nitrogen, and small samples of this powder were used to assess lipid peroxidation and chlorophyll production of the plant tissue. SeNPs were found to be much less toxic than Se selenite and to protect the plants against phytopathogens.

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Abstract

Evaluation and Optimization of Polysaccharides and Ferulic Acid Solubility in NADES Using Surface Response Methodology †

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Keywords: ferulic acid; deep eutectic solvents; surface response methodology; polysaccharides

Response surface methodology (RSM) is an experimental approach composed of statistical and mathematical tools that aims to develop, improve and optimize a predictive model for a response (an output variable), which is influenced by several factors (input variables) [1]. RSM was developed in 1951 [2] to minimize the number and inaccuracy of physical experiments, and it has grown into modelling of numerical experiments. Using RSM in Design Expert® software, we aimed to evaluate and optimize the solubility of ferulic acid (FA) and polysaccharides such as microcrystalline cellulose (MCC) in two natural deep eutectic solvents (NADESs), ethaline and reline. For the optimization of the process, we used a two-level factorial model that suggested a total of 22 experiments, creating relevant combinations among three variable factors: ferulic acid concentration, polysaccharide concentration and NADES solution concentration. For each of them, an interval of variation was set, composed of a minimum value, a maximum and a medium one. After the preparation of NADES, the set samples were prepared, vortexed, ultrasonicated and centrifuged. The supernatant was acquired and used for UV-Vis spectroscopy, revealing the percentage of ferulic acid solubilized in the natural deep eutectic solvents. The sediment was analyzed by gravimetric methods to observe the polysaccharides' solubility in NADESs. In addition, FT-IR was used to observe the interactions between all the components. The ANOVA analysis tool contained by the software was employed to determine a polynomial equation that describes the variables' influence on the polysaccharides and FA solubility in NADESs, as well as their synergic effect. By processing the information, we obtained graphical and numerical results that showed a high correlation with the factorial model, exhibiting an adequate ratio between the variable factors in order to ensure the desired solubility in the case of ferulic acid and polysaccharides in natural deep eutectic solvents.

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Abstract

Innovative Method for Enhancing the Biological Activity of Honey †

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Keywords: ultrasound-assisted extraction; polyphenols; honey; antioxidant activity; antimicrobial activity; prebiotics

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Honey is a natural product composed of more than 80% sugars, the main constituents being fructose and glucose. It also contains a small amount of bioactive compounds, such as polyphenols, which provide the biological activity of honey [1]. The aim of this study was to obtain honey enriched in polyphenols, having enhanced biological properties. This was based on the solubilization of phenolic compounds extracted from propolis in honey. We present preliminary results on the biological (antioxidant, antimicrobial and prebiotic) activities of honey enriched in polyphenols.

The polyphenols were extracted from propolis by ultrasound-assisted extraction with 75% ethanol solution and the ratio of substrate to solvent at 1:5, for 30 minutes at room temperature. The extract was solubilized in honey in an ultrasonic bath, mixed thoroughly, and the polyphenols were left to diffuse overnight. Honey enriched with polyphenols from propolis was tested and compared with simple honey in terms of antioxidant, antimicrobial and prebiotic effect. The antioxidant activity (AOC) of the samples was assayed using three spectrophotometric methods: radical scavenging activity (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid, ABTS, and α, α-diphenyl-β-picrylhydrazyl, DPPH) and reducing antioxidant power (Cupric reducing antioxidant capacity CUPRAC). The total phenolic content (TPC) was determined with Folin–Ciocalteu. The dried extract of propolis was analyzed with Fourier transform infrared (FTIR) spectra to assess the chemical functional groups of the extract. Honey mixed with the dried extract of propolis showed an almost four-fold increase in TPC, which was also reflected in the antioxidant activity determined by ABTS and DPPH.

The antimicrobial activity of the sample was performed by determining the minimum inhibitory concentration (MIC) of the growth and adhesion capacity to an inert substrate. Quantitative analysis of adhesion to the inert substrate of *Salmonellaenterica* (Se) and *Bacillus cereus* (Bc) strains was performed by slim method using liquid medium (TSB) in 96-well plates using controls for sterility of the environment. The adherent biomass to the walls of a 96-well plate was evaluated by the micro-titration method that involves washing with physiological sterile water,

fixing with cold methanol, and staining with purple crystal. The optical density of the adhered biological material was visualized under a stereomicroscope. The adherent biomass was quantified by resuspending it in acetic acid and reading the absorbance at 490 nm. Honey enriched with polyphenol extract exhibited higher anti-adhesion compared to simple honey, but it showed higher inhibition of bacterial growth only in the case of *B. cereus*.

The prebiotic activity of the honey–extract mixture was evaluated on a strain of *Lactobacillus sp.* and compared to simple honey. Honey had a significant prebiotic effect by stimulating the growth of the *Lactobacillus sp.*, while the polyphenol extract did not influence the prebiotic effect of honey. Further parameters such as short-chain fatty acid production and lipid peroxidation in the cell membrane will be analyzed and the effect on other probiotic strains will be tested.

Our preliminary results show that one can increase the biological activity of honey by enriching it in bioactive compounds from other sources, the activity of which is preserved in honey.

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Abstract

Keratin Extraction from Wool and Feathers Using Natural Deep Eutectic Solvents †

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Keywords: keratin; wool; feathers; NaDES; agroeconomic value chain

The wool of Țurcana sheep, the Romanian national breed, has not been fully investigated and valorized up to now. This can be achieved by applying the approach of cascade processing and closing the loop for this value chain: lanolin and keratin are extracted from raw wool for the cosmetic industry, and the exhausted fibers can be used as agricultural fertilizers for new food crops. This work is focused on keratin extraction from two types of lateral agroeconomical flows: raw wool from Țurcana sheep and chicken feathers. The process is based on a pretreatment with dithiothreitol (DTT) or Na_2S [1,2] for breaking the disulfide crosslinks [3] and subsequent keratin extraction with a natural deep eutectic solvent (NaDES), reline (choline chloride:urea, 1:2 molar ratio).The extraction from chicken feathers gives at least ten times more keratin than from Țurcana wool. This can be explained by the differences in protein structure, β-sheets (feathers) being easier to denature than α-helix (wool). High concentration of Na_2S (0.5 M) completely dissolves both feathers and wool. At lower concentrations (0.05 M) of Na_2S or DTT applied during pretreatment, the keratin structures are only partially dissolved and the subsequent extraction with NaDES shows no difference between the Na_2S and DTT pretreatment. In conclusion, the pretreatment agent and its concentration, but also the keratin structure, have a significant influence on keratin extraction yield. The process for keratin extraction from Țurcana wool needs to be optimized, including by testing other NaDESs.

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Abstract

Biogas Production by Anaerobic Digestion Coupled with Wastewater Treatment †

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Keywords: biogas; anaerobic digestion; liquid digestate; microalgae; wastewater treatment

The aim of this paper is to present the laboratory scale installation for biogas production from indigenous feedstock coupled with treatment of the liquid digestate side flow by microalgae cultivation, developed for Complex Project 32PCCDI/2018. Besides the efficient production of biogas with high yield in methane, we also aim to prove the possibility of efficiently reducing nutrient content of liquid digestate, by growing microalgae on this side flow as an alternative to the specific nutrient rich medium currently used for cultivation.

Microalgae cultivation in wastewater is an integrative approach which offers a cost effective and eco-friendly method for sustainable production of valuable biomass, since it greatly reduces costs caused by the requirement of a large volume of fresh water, nutrients, and trace elements for its cultivation [1]. Liquid digestate, a side flow from biogas industries, is rich in nitrogen, phosphorus, micronutrients, and other organic compounds that can be used by microalgae growth, thus providing a cost effective way for liquid digestate treatment and biomass production for value-added products.

The anaerobic digestion process uses agricultural waste as feedstock: Cattle and poultry manure, silage maize, fodder beet and low quality potatoes. The digester has the capacity to process 30 L of substrate, calculated with a 10% dry matter content. The biogas obtained from this process is rich in methane, with a maximum of 73% methane. When the methane content of the biogas decreases significantly, part of the fermentation substrate (10%) is replaced daily by a fresh substrate portion, in order to maintain a high methane yield. The substrate replaced, the digestate, is further separated into liquid and solid digestate. The solid part is valued by pyrolysis to produce bio-char, bio-oil and bio-hydrogen, and the liquid digestate is processed to be used as nutrient medium for microalgae growth, thus adding value to this side flow from biogas production.

The cultivation process of microalgae on liquid digestate is conducted in an open pond with a volume of 30 L. The liquid digestate is diluted until a N and P concentration can sustain microalgae growth (too high concentration of these nutrients can be toxic to the microalgae strain). The open pond is inoculated with *Chlorella vulgaris* (AICB 329) microalgae strain, from ICECHIM's own strain collection. When the microalgae strain reaches the plateau state of growth, part of the microalgae suspension (10%) is replaced with a new portion of liquid digestate collected from the anaerobic digester and diluted accordingly, so as to maintain the necessary level of nutrients required for growth. The microalgae suspension is further concentrated by electro-flocculation and sedimentation,

the supernatant is separated and recycled in the process, and the concentrated microalgae suspension is further processed for obtaining value-added products.

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Abstract

Synthesis of Chitosan Based Bioflocculants and Their Use for Microalgae Harvesting †

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Keywords: chitosan; microalgae harvesting; bioflocculants

The aim of this paper was to study the harvesting of microalgae, specifically *Chlorella vulgaris* and *Nannochloris* sp., with chitosan based bioflocculants, synthesized from shrimp shell waste.

Microalgae harvesting remains one of the more expensive steps in microalgae cultivation, and is generally accomplished through chemical methods which involve inorganic and organic flocculants. Despite higher efficiency of chemical methods, their abundant use leads to contamination of both microalgae biomass and the growth medium, which is problematic further downstream for both the use of microalgae as feed for humans and animals, and also for the reuse of liquid medium. Chitosan has many advantages over commonly used flocculants for microalgae harvesting, as it is biodegradable and has no toxic effects on downstream applications [1,2].

The microalgae species which were used for these experiments, were grown in Bold Basal medium, respectively Zarouk medium, in a Sartorius PBR 25S photobioreactor with a capacity of 3 L. Chitosan powder obtained was mixed in three different acid solutions (citric acid, nitric acid and hydrochloric acid). For the determination of separation efficiency (SE): 5 ml of algal cells were placed in a 15 ml tube. Chitosan solution was added at different concentrations (0.25 g/L and 0.5 g/L) and mixed for 1 min. After mixing, the algal cells were allowed to settle down for 30 min. Samples of the supernatant were collected in order to measure the optical density at 680 nm by spectrophotometer.

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Abstract

Assessing the Impact of Low Level Laser Radiation on Microalgae Cultures †

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Keywords: microalgae; laser radiation; lipids

Laser radiation (LR) is generated by an optical quantum generator. This technical device emits light in a very narrow spectral range in the form of a directed high-coherent monochromatic polarized beam in the form of highly ordered electromagnetic one-color radiation in space and time [1]. The effects of lasers on biological systems has been used in medicine, agriculture, and biotechnology [2]. Microalgae biomasses have been considered promising renewable sources of raw material for biofuel production, as well as sources of valued nutrients in livestock feeds, dietary supplements, and in cosmetology. Microalgae have the capacity to change their functional composition based on growth conditions and stress factors. To date, there has been no experimental evidence relating microalgae *Nannochloris sp.* biomass accumulation and biomass composition under laser stress.

In this work, microalgae *Nannochloris sp*. was used to investigate the effect of two lasers (650 nm and 532 nm) on cell growth, lipid accumulation, and lipid composition. Different irradiation times (1, 5, 10, 15, and 20 min) for both laser wavelengths have been studied. The greatest increase in biomass was observed when 650 nm laser radiation was applied. The biomass accumulation increased with the exposure time. The maximum increase of the biomass was 30%, compared to the blank sample, and was obtained after 20 min of irradiation.

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Abstract

Antimicrobial Properties of Bionanomaterials Obtained from Vegetable Sources †

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Keywords: bionanomaterials; silver; vegetable extract; antimicrobial activity

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Antibiotic resistance of pathogenic microorganisms is a major problem of the 21st century. In this sense, finding alternatives to classical antibiotics is one way this problem can be solved. In this respect, we initiated research which aimed at the testing of bionanomaterials containing Ag^{+} or Au^{3+} ions and some vegetable extracts. The vegetable used for obtaining nanobiomaterials were the following: *Ranunculus ficaria* (AgNPrf, AuNPrf); *Allium ursinum* (AgNPau, AuNPau); *Hippophae rhanmoides* (AgNPhr AuNPhr); *Brassica oleracea* variety gongyloides, white and purple (AgNPbow, AgNPbop, AuNPbow AuNPbop); and *Cucurbita maxima*, Valenciano variety (AgNPcm, AuNPcm). Bionanomaterials were synthesized according to the methodology presented by Sorescu et al [1].

The antibacterial activity was evaluated using the disk-diffusion method [2], with microbial inoculum sown on the surface of Petri dishes. The obtained values were quantified compared to those obtained with the usual antibiotics [3–5]. Microorganisms used in biological tests were isolated in medical clinique from patients (*Escherichia coli, Bacillus subtilis*) or were purchased from DSMZ collection (*Candida rugosa*).

The results obtained indicated that the *Escherichia coli* present sensitivity to some bionanomaterials synthesized with Ag^{+}. From this point of view, good results are obtained for bionanomaterials AgNPhr, AgNPcm, and AgNPbop. In the case of the last two bioproducts, the inhibition diameters obtained are comparable with the antibiotic ampicillin.

The best results were observed in the case of the AgNPrf bioproduct, for which we obtained higher inhibition diameters, comparable with antibiotics such as: Ampicillin, Carbencilin, Ticarcillin, Cefazolin, Cefaclor, Nalidixic acid, Gentamicin, and Kanamicin.

In the case of bionanomaterials synthesized with Au^{3+}, the obtained results showed that these do not have biological activity on the studied microorganisms, except AuNPhr, where the occurrence of the resistance phenomenon (AuNPhr) is observed. It is important to mention the fact

that the phenomenon of resistance also appears in the case of nanomaterials with Ag^+, like AgNPau, Ag NPbow.

In conclusion, nanobiomaterials synthesized with Ag^+ and plant extracts have biological activity in the case of Gram-negative bacteria, the best results being obtained in the case of the bioproduct synthesized with *Ranunculus ficaria* extract.

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Conflicts of Interest: Authors declare no conflict of interest.

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Abstract

Extraction and Plastein Reaction of Bioactive Peptides from *Agaricus Bisporus* Mushrooms †

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Keywords: peptides; proteins; extraction; *Agaricus bisporus*; plastein; enzymes

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The common mushroom *Agaricus bisporus* has a high content of proteins and other bioactive compounds, which gives its high medicinal value [1]. The aim of this study was to generate enzymatic protein hydrolysate from *Agaricus bisporus* mushrooms, useful as bioactive peptides in different applications, such as obtaining plant biostimulant products or new generations of synbiotic formulations with prebiotics and probiotic microorganisms. In the past decades, attention has been drawn to the plastein reaction, which is a way for increasing nutritional value of proteins, but also for removing the bitterness of protein hydrolysates [2]. The mushrooms were lyophilized, and the powder was used for the extraction of proteins with enzymes, different buffer solutions, and different commercial, natural, deep eutectic solvents (NADESs) in order to optimize the extraction of proteins from *Agaricus bisporus* and to quantify the total amount of proteins extracted using the dye binding assay method (Bradford) or copper-based assays (Biuret, Lowry, BCA) against a bovine serum albumin (BSA) standard curve [3]. The molecular weights of the proteins were analyzed on sodium dodecyl sulfate (SDS) - Polyacrylamide Gel Electrophoresis (SDS-PAGE). The enzymatic hydrolysis of proteins was performed using a protease from *Bacillus licheniformis*, and the plastein was synthetized using the same enzyme to avoid extra proteolysis in the course of plastein reaction so as to increase plastein yield. Tangential ultrafiltration was used for purification and concentration of peptide samples. Synthetized plastein was analyzed using Dynamic Light Scattering (DLS) and SDS-PAGE.

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Abstract

The Ethaline Effect on Feruloyl Esterase Activity †

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Keywords: feruloyl esterase; ferulic acid; solubility; enzymatic activity; 4-nitrophenyl trans-ferulate; ethaline

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In recent years, extractions using natural deep eutectic solvents (NADESs) have attracted increasing attention, as these solvents represent an ecological, non-toxic and biodegradable alternative to conventional solvents, being easy to produce in laboratories [1]. Some studies showed that NADESs considerably increased the extractability of phenolic compounds compared to conventional methodology [1,2]. Another green extraction method is the enzymatic one, which can greatly increase the production of phenolic compounds together with other extraction methods [3]. The purpose of this study was to investigate and optimize the activity of feruloyl esterase (FAE) and the solubility of ferulic acid (FA) in ethaline. The FA solubility was tested at different ethaline concentrations (5%–90%) by the spectrophotometrical method (λ = 320 nm). The enzyme activity of FAE was optimized by varying the pH values, and the substrate (4-nitrophenyl trans-ferulates) and enzyme (feruloyl esterase) concentrations. After optimizing these parameters, the effect of different concentrations of ethaline (10%–45%) on the enzymatic activity was determined. The optimal pH value for the reaction was 7. The enzyme was still active in ethaline, but the initial velocity was decreased at higher ethaline concentrations, probably due to higher viscosity which decreased the diffusion. The solubility of FA decreased with the decrease in ethaline concentration, but it was soluble enough for FA extractions from biomass, even at ethaline concentrations below 50%. In conclusion, FAE can be combined with ethaline at certain concentrations to improve FA extractions from biomass.

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Extended Abstract

Bio-Fluxing Agent for Bitumen Road Based on Pyrolysis Bio-Oil †

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Keywords: bitumen; bio-fluxing agents; pyrolysis

Bio-oil is the liquid fraction obtained from the pyrolysis process and is an important source of both energy and valuable commodity chemicals. The liquid is composed of a water phase (containing diverse oxygenated hydrocarbons) and an organic tar phase containing a complex mixture of several hundreds of organic compounds such as acids, alcohols, aldehydes, esters, ketones, and phenols [1].

The pyrolysis-derived bio-oils from different biomass have different compositions but the basic properties for bio-oil usage as fuel substitute are heating value, viscosity, density, and stability. The oxygen content of biomass bio-oils is higher than that of fossil oil and, consequently, they have higher reactivity and lower stability than fossil fuels and cannot be used in their present form as transportation fuels [2]. Thus, there is an urgent need to develop new approaches to utilize these oils as sources of fuel additives or extenders. In this context, creating blends of bio-oil with other transportation fuels could be a viable short-term alternative to utilize an important fraction of these oils [3].

The objectives of this research were (a) conditioning of blends from bio-oil and lipid fraction, and (b) evaluation of bio-oil/lipids blends in order to obtain components for fuels and/or ecological additives for road bitumen. The bio-oil used in this study was obtained from the slow pyrolysis of biogas solid digestate. The physical and chemical properties of the pyrolysis oil/lipids/diesel blends were evaluated in accordance with the corresponding specification. **Acknowledgments:** In this section you can acknowledge any support given which is not covered by the author contribution or funding sections. This may include administrative and technical support, or donations in kind (e.g., materials used for experiments).

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Abstract

NPK Fertilizers' Coatings Using Biodegradable By-Products from the Agro-Food Industry †

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Keywords: NPK fertilizers; keratin hydrolysate; coating; agro-food by-products

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At national and international level, mixed complex fertilizers are obtained using physical mixing of different sources of macroelements and/or microelements, which are grinded and granulated together using different granulation technologies, such as, for example, on a fluidized bed [1,2] or a pan or drum granulator [1,2]. The main macroelements present in commercial fertilizers are N, P_2O_5, and K_2O, and these macroelements can be supplied using many sources [3]. In order to improve the absorption of nutrients by plants, granulated fertilizers can be coated with different chemical or bio-based materials, thus creating a slow release of nutrients, in accordance with plant absorption capability [4]. For these purposes, were used some biodegradable coating materials, consisting in fractions of keratin hydrolysates, in order to delay macroelements leaching in soil and also as an important source of biostimulating material for plants.

There are many sources for biodegradable coating materials, however including huge amounts of feathers and wool that remain after primary processing og raw materials [5].

I. Granulation: Some usual NPK formulations were prepared using a pan (disc) granulator (Figure 1). As raw materials were used urea (N source), monoammonium phosphate (N and P source) and potassium sulfate or chloride (K source). As a binder, several substances were tested, based on raw materials water solutions and also includind small amounts of PVA (polyvinylic alcohol) or HEC (hydroxiethyl cellulose) solution, a polysaccharide solution etc.

Figure 1. Disc granulator.

II. Coating: The coating of NPK granules was made on the same rotating pan granulator, using an aqueous solution containing a keratin hydrolysate solution and small amounts of PVA. This hydrolysate was previously obtained mainly from poultry feathers. Analogously, the NPK formulations were also coated with the same keratin hydrolysate by using a lab-scale fluidized bed granulator (the Würster method) (Figure 2).

Figure 2. Fluidized bed granulator.

Granules with a 2–4 mm average diameter were obtained for three NPK formulations using a rotating pan granulator, operated at various working parameters (rotation speed, inclination to the horizontal axis, granulation time). After drying at room temperature, the granules were coated using two coating equipments. The coating, in both cases, was uniform (Figure 3). The SEM analysis showed that a compact and uniform coating layer was obtained for both methods.

Figure 3. NPK granules before and after coating.

Complexe NPK fertilizer compositions were successfully granulated using a lab scale rotating pan granulator, and the main fraction of granules having a 2–4 mm diameter was coated with an aqueous solution containing a keratin hydrolysate solution, using two coating equipments, a rotating pan granulator and using a GLATT fluidized bed granulator. The differences between the 2 methods rely on the different working parameters. For the method using the fluidized bed granulator, raw material losses was observed, that can be diminished by adjusting the working parameters

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Extended Abstract

Clean Technologies Combining Phytoremediation with Biofuel Production—Part 1 †

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Keywords: soil salinity; soil sampling; chloride; phytoremediation

One of the major problems that has been faced by the oil upstream industry is related to soil contamination caused by oilfield water pollution [1]. An efficient method of saline soil decontamination is phytoremediation. Halophytes (salt-tolerant plants) are ideal candidates for the phytoextraction of salt from soil [2]. The evaluation of the efficiency of the phytoremediation process was performed by monitoring the salinity of the soil during the life cycle of plants [3].

Initially, the contamination of the soil with reservoir water was evaluated in terms of salinity and hydrocarbon content. For this purpose, samples were collected using the grid method from the entire surface of the land, roughly 2000 m^2, on three depths (0–30 cm, 30–60 cm, 60–90 cm). The chloride concentration in the soil was determined using ion chromatography.

Depending on the distribution of the chloride concentration in the soil, in the next stage, the land was divided into six lots from which average soil samples were taken from a 0–60 cm depth.

From analyses initially carried out on soil samples taken from the entire surface of the land, the results showed that the soil was contaminated only with salt water, not with hydrocarbons. Based on the results obtained the modeling of chloride concentration distribution on the soil surface was undertaken. This is shown in Figure 1.

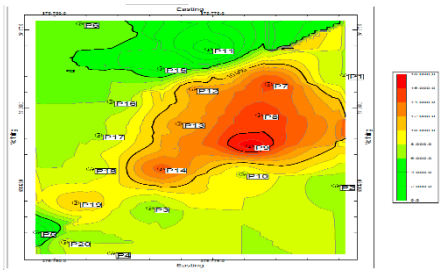

Figure 1. Modeling of the chloride concentration distribution on the soil surface.

Based on the analysis of soil samples taken from the six lots, a 3D graphic representation of the chloride concentration is presented as shown in Figure 2.

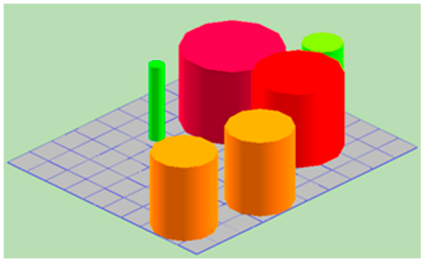

Figure 2. A 3D model of chloride concentration distribution on the six lots.

These lots are periodically monitored to determine the efficiency of phytoremediation using different types of plants. Both soil samples and plants grown on the selected six lots will be analyzed.

The efficiency of the phytoremediation process of a strongly salted soil is monitored, during the life cycle of the plants, by analyzing the average soil samples taken from the selected six lots.

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Abstract

Rapeseeds a Rich Source of Polyunsaturated Fatty Acids †

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Keywords: rapeseed; transesterification; molecular distillation

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In human diet, polyunsaturated fatty acids (PUFA), have an essential role in optimal brain functions and stroke prevention, specially, omega-3 fatty acids, e.g., 9,12,15-linolenic acid (ALA, 18:3), 5,8,11,14,17-eicosapentaenoic acid (EPA, 20:5), and 4,7,10,13,16,19-docosahexaenoic acid (DHA, 22:6). The rich sources in this type of acids are vegetable seeds like rapeseed, hemp, flax, camelina, and ocean fish oils.

Global rapeseed production has had a sustained growth over the last years. Rapeseed is primarily grown for meal and its oil, which can be further processed.

In this context, due to their rich content in polyunsaturated fatty acids (PUFA), rapeseed oils can be transformed in their alkyl esters by transesterification, through one or two stages.

PUFA have been prepared by extraction of triglycerides from seeds, followed by transesterification with ethanol over basic catalysts and purification. A few homogeneous and heterogeneous catalysts will be tested.

The analysis of polyunsaturated fatty acid ethyl esters was performed using GC-MS/MS TRIPLE QUAD (Agilent 7890 A).

Fatty acid ethyl esters have been synthesized in order to be enriched in PUFA by molecular distillation.

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Conflicts: Authors declare no conflict of interest.

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Extended Abstract

Gemmotherapy—Modern Medicine

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Keywords: gemmotherapy; buds; cellular division; disease

1. Introduction

Gemmotherapy, also known as phytoembryotherapy, is a modern homeopathic method of biotherapeutic drainage using the extracts of various trees and shrubs. The raw material of the buds, emerging shoots, seeds, rootlets and sap is taken at the peak time of the plant's annual germination.

2. Materials and Methods

Plants are harvested in the spring, throughout the period of cellular division and plant growth. During this stage they contain the highest concentration of active growth factor hormones, auxins and gibberellins. These specific hormonal agents contain valuable informative matter required for the drainage of various organs and tissues at the cellular level.

3. Results

In order to extract the embryonic substance from the fresh buds, the complex remedies are macerated for increased patient compliance.

Gemmotherapy is very popular in European countries such as France, Belgium, Italy and Germany, as well as in some areas of Eastern Europe.

4. Conclusions

It works great for skin conditions, seasonal allergies, chronic ENTs, asthma, UTIs, migraines, digestive disturbances, sleep difficulties, menstrual irregularities, fertility issues, high blood pressure and many more.

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Abstract

Effect of Temperature and Composition on Viscosity of Different Formulation of Ethyl Levulinate/Diesel Fuel/Biodiesel †

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Keywords: ethyl levulinate; diesel fuel; viscosity

Alkyl esters of levulinic acid have significant potential as blend components in diesel formulations. Compared with biodiesel, esters of levulinic acid have high oxidative stability, good low temperature properties and do not have a tendency for gum formation [1]. Different formulations of alkyl levulinates and biodiesel has been studied as transportation fuels in order to improve emissions of nitrogen oxides in high compression diesel engines. Moreover, technological initiatives are being taken to use ethyl levulinate as a 100% biodegradable neat fuel in the near future [2]. Consequently, the development of new routes for the production of levulinates from bio-based platform molecules has attracted ever more attention [1].

Viscosity is a key properties of automotive and aircraft fuels, because influences the lubrication properties as well as the combustion properties of the fuel. Low viscosities lead to poor lubrication, which can cause excessive wear and leakage. Meanwhile, a higher viscosity generates an obstruction for hoses or poor atomization of the fluid, leading to poor combustion and an increase in exhaust gas emissions [3].

The objective of this paper is to evaluate the effect of ethyl levulinate addition over fuel viscosity. The viscosity of different formulation of ethyl levulinate/diesel fuel/biodiesel was determined at temperature range 30–80 °C. The ethyl levulinate and biodiesel tested were synthesized in our laboratory. The Artificial Neural Network (ANN) was used as a modelling tool, for understanding the correlation between temperature and viscosity property of fuel mixtures. Several architectures were tested until a good match between the ANN's predictions and the experimental data was found.

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Conflicts: Authors declare no conflict of interest.

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Abstract

SeparationMethods of the Eggshell Membranes from Eggshell †

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Keywords: eggshell; eggshell membrane; separating methods

As a result of the technological processes of the egg industry, there are tons of egg shells, which raise environmental problems and costs for their management. For a superior valorization to obtain active principles with high biological and economic value, it is necessary to separate eggshell membranes from eggshells. Therefore, eco-friendly and efficient processes have been developed. The complete separation of membranes and shells increases the value of the resulting products. Several methods are known for obtaining the shell membrane [1].

Manual detachment of membranes is the simplest procedure. The detached membranes dried in the oven at 30 °C for 30 min, then ground and kept in the freezer.

Separation with dilute acids (acetic acid, hydrochloric acid, EDTA, sulfuric acid) dissolves the calcium carbonate of the shell and the membranes are recovered, washed with deionized water to remove the remaining acids and dry at room temperature or in the oven. Separation using acids is an efficient technique, but FTIR analyzes revealed the modification of the absorption bands corresponding to the organic structure of the membranes in the presence of HCl and EDTA-Na2 solutions. The acetic acid solution does not alter the chemical composition of the organic structure of the membranes [2].

Separation by flotation with dissolved air is a recently developed method, which has a high efficiency rate. The pressurized water is saturated with dissolved air and is pumped into a flotation basin. The air bubbles formed are microscopic and have the role of dragging the suspended matter towards the floating surface. The process takes two hours and allows the recovery of 96% of the membranes and 99% of the calcium carbonate present [3].

Separation of the membranes from the eggshells by microwave treatment is based on the fact that the membranes have a higher water content than the shells and absorb more energy from the electromagnetic waves, which leads to a differentiated heating of the two components followed by the expansion of the membranes, weakening of physical connections between shells and membranes and separation [4].

Another technique of separation is the passage of fragments of eggshells through a series of drills in aqueous environment heated by steam, the separation taking place in a cyclone. This process is used commercially [5].

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Conflicts of Interest: Authors declare no conflict of interest.

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Extended Abstract

Isolation and Characterization of Kefiran Exopolysaccharides from Romanian Kefir Grains †

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Published: 21 October 2019

Keywords: exopolysaccharides; kefiran; kefir; cytotoxicity; anti-tumoral

Kefiran is the water-soluble branched glucogalactan from kefir grains and it contains D-galactose and D-glucose units in approximately equal quantities [1]. These bacterial exopolysaccharides, because of their status as probiotics for the bacteria that generated them, will become a category of biopolymers that offer new perspectives in the development of products with health and safety benefits [2]. The aim of our study was to obtain kefiran from a Romanian kefir artisanal culture and to characterize it physicochemically and biologically, in order to evaluate its potential as a nutraceutical.

The extraction of kefiran was performed by alcohol precipitation and the evaluation of the total carbohydrates and hexoses content was done by spectrophotometric methods, while the major carbohydrates were identified by 1H-NMR, and glucose and galactose were quantified by HPLC methods. Structural observations on kefiran extract were performed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Cytotoxicity and anti-tumoral activity were tested with normal fibroblasts (NCTC clone L929) and epithelial tumoral (HT-29) cell cultures, cultivated in the presence of kefiran, in standard conditions, for 24 and 72 h.

Structural analyses revealed that the kefiran is composed of a hexasaccharide repeating unit, sugar composition analysis confirmed the previously reported values [3]. Ultrastructural and morphological analysis showed a fibrillar structure of kefiran (by TEM) and a compact structure with a homogenous matrix and smooth surface (by SEM), specific to polymeric materials. In the presence of kefiran concentrations ranging from 50 to 2700 mg/L, an antitumoral effect was observed at 72 h, while the cytotoxic effect was registered for concentrations that exceeded 500 mg/L.

These results demonstrated that kefiran extract presented valuable properties and confirmed its potential use in nutraceutical and biological applications.

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Section 3

proceedings

Abstract

The Germination of Spores and Gametophyte Development in Ferns under Extracts Influence †

Liliana Cristina Soare [1], Irina Fierăscu [2], Radu Claudiu Fierăscu [2], Codruța Mihaela Dobrescu [1], Alina Păunescu [1], Anca Nicoleta Șuțan [1] and Oana Alexandra Drăghiceanu [1,*]

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Published: 12 October 2019

Keywords: spores; gametophytes; ferns; extracts

The aim of this study was to establish the influence of ferns extracts (*Asplenium scolopendrium* and *Dryopteris filix-mas*) on spore germination and gametophyte development in two *Dryopteris* species.

The extracts were obtained from *Asplenium scolopendrium* (EA) and *Dryopteris filix-mas* (ED) leaves. Some variants contained, beside the extracts, Ag nanoparticles (EAN, EDN) [1,2]. Variants with alcohol were also tested (HA). For each variant, dilutions were made (1:10, 1:100).

The percentage of germinated spores decreased after extracts exposure (Figures 1 and 2). In variants with AgNPs, no germination was observed regardless of extract, dilution or species. In the variants with alcohol, the germination of spores was significantly inhibited compared with the control (C, Figure 3) at the smallest dilution, in both species (Figure 4). The lack of the spore's rhizoid affected the gametophyte development (Figure 5).

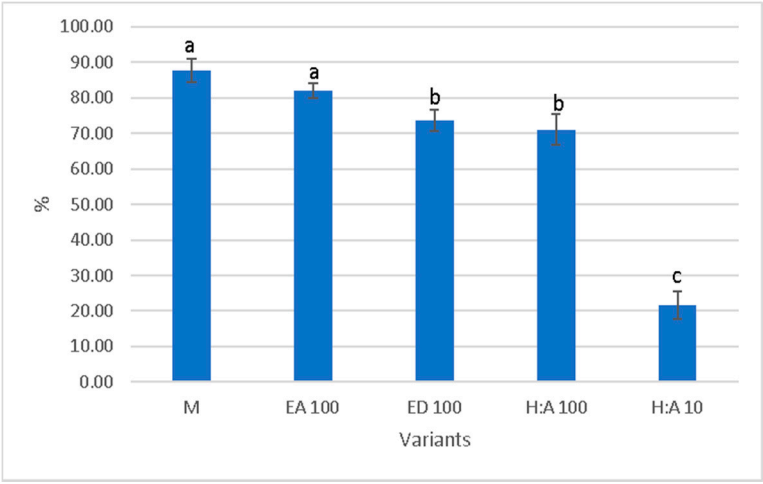

Figure 1. The influence of extracts on spore germination in *Dryopteris affinis*.

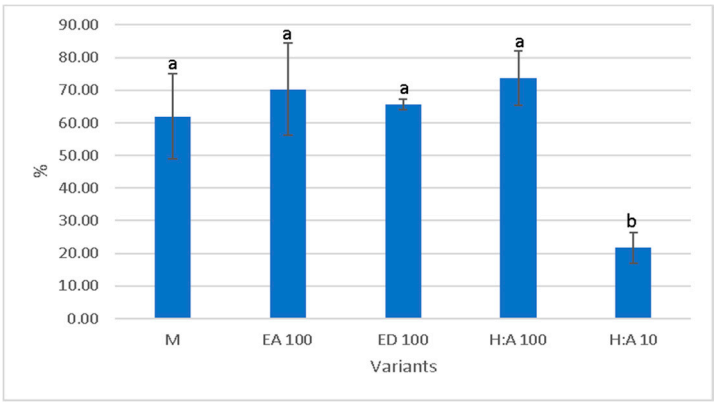

Figure 2. The influence of extracts on spore germination in *Dryopteris filix-mas*.

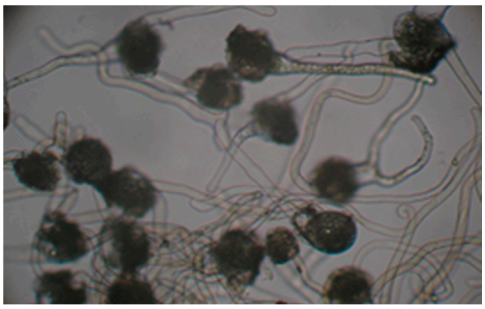

Figure 3. *Dryopteris affinis*—germinated spores: Control, ×100.

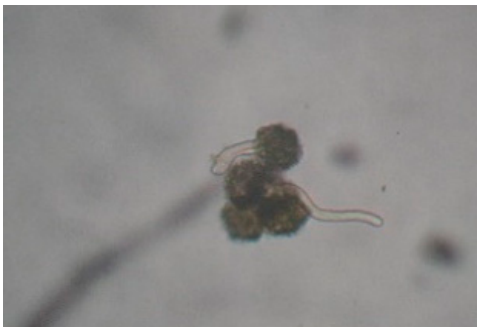

Figure 4. *Dryopteris filix-mas*—germinated spores: HA 1:10 variant, ×100.

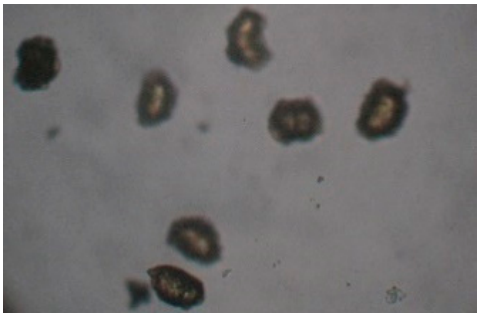

Figure 5. *Dryopteris affinis*—ungerminated spores EAN variant (100), ×100.

Overall, the ferns extracts had a negative influence on ferns spores by reducing the germination percentage and by inhibiting gametophyte development in both species.

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Abstract

Large Scale Production of a Nanomaterial-Based Formulation for Horticultural Applications †

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Keywords: phytosynthesized nanoparticles; antifungal; horticultural crops

Worldwide agricultural production is permanently threatened by the numerous fungi and phytopathogenic bacteria. These diseases are known to be caused by pathogens, such as fungi, molds, oomycetes, bacteria and viruses. Many of them, usually related to the climatic conditions, have dramatic consequences, leading to yield losses of crops, which can have a profound and sometimes catastrophic impact on the agricultural economy, especially when the disease reaches epidemic status.

Plasmopara viticola, responsible for the appearance of grapevine downy mildew is very common in our country and can lead to production losses of up to 80%. The disease attacks the grapevine on all the aerial organs such as leaves, flowers, bunches, shoots and grapes (Figure 1). Current treatments, based on synthetic biocides (inorganic copper salts, copper hydroxides, different organic compounds, etc.) have been used for long periods of time, and the pathogens have developed resistance. Modern fungicides have good efficiency, but they accumulate in plant organs, and are toxic for human consumption.

Due to concerns about the impact on human health and the environment, there is a growing demand for chemical pesticides to be replaced by ecological alternatives. In this respect, for the treatment of this disease, our group proposed a nanomaterial-based recipe, with no impact on the environment or human health, obtained from photosynthesized silver nanoparticles, using natural extracts. The large-scale production was achieved in 50 L reactors. The nanomaterials were characterized using UV-Vis spectrometry and X-ray diffraction, while the efficiency of the formulations was tested in greenhouse experiments.

Figure 1. Grapevine affected by downy mildew.

The tested materials proved to be a very efficient antimicrobial agents, even when compared with commercial products.

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Abstract

Adsorption of Dyes from Aqueous Solutions Using Apatitic Materials †

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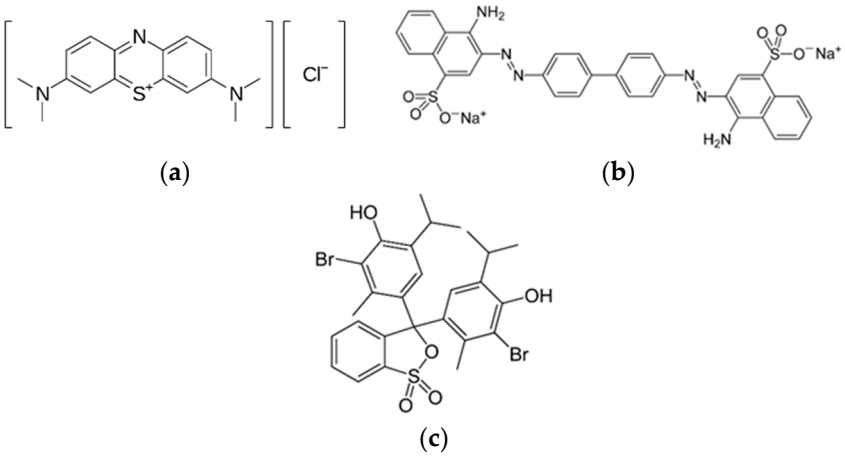
Keywords: apatitic materials; adsorption; dyes

Hydroxyapatite is a calcium phosphate biomaterial that is widely used to treat polluted water, soil, and air, due to its adsorption capacity [1]. Methylene blue (MB) (Figure 1a), a cationic dye, is frequently used in the leather industry for dyeing and printing. This dye is toxic to both humans and animals [2]. Bromothymol blue (BTB) (Figure 1c) is a sulfonphthalein dye, being one of the most widely used indicators to distinguish the acidity, alkalinity, or neutralization of an aqueous solution. Its removal from the environment is important due to the presence of azo groups from the dye component [3]. Congo red (Figure 1b) comes from the textile, printing, dying, paper, and plastic industries. This type of dye is toxic to most organisms, being suspected of carcinogenic and mutagenic effect [4].



(**a**) (**b**) (**c**)

Figure 1. Dyes used for the adsorption studies: Methylene blue (**a**), Congo red (**b**), and bromothymol blue (**c**).

The adsorption capacity of three apatitic materials were tested against the described dyes. The adsorption studies were performed by HPLC, while FTIR studies were conducted on the solids after the adsorption experiments.

In conclusion, the tested apatitic materials shown good adsorption capacities for the tested dyes.

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Abstract

Decorated Apatitic Materials: Synthesis, Characterization, and Potential Application †

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Keywords: apatitic materials; decorated apatites; antimicrobial; cytotoxicity; phytotoxicity

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The literature provides us several examples of apatitic materials in whose structure the calcium ions are substituted by different metals, which are remarkable for their applicability in heritage conservation, bioremediation, and biomedicine [1–4]. According to the desired properties, several methods were developed to obtain these apatitic materials. The decoration of the apatitic structure with metal and metal oxide nanoparticles is far less studied, even though it provides the development of more economical materials, using mild reaction parameters [2].

Hydroxyapatite was prepared according to a recipe developed before in the laboratory [4]. For the incorporation of copper in the hydroxyapatite's structure, we studied two approaches: the decoration of hydroxyapatite with metal nanoparticles and metal oxide nanoparticles. The copper nanoparticles were obtained using a modified Turkevich method [2]. The decoration of the apatitic materials was achieved post-synthesis, using metallic oxide nanoparticles and metallic ions.

To confirm the nanoparticles' synthesis, the obtained materials were subjected to UV–Vis spectroscopy. The X-ray fluorescence, X-ray diffraction, FTIR spectroscopy, transmission electron microscopy, and thermal analysis were performed to confirm the obtainment of the decorated apatitic materials. In order to evaluate their potential applications, we studied their antimicrobial, phytotoxic, and cytotoxic effects.

Two types of apatitic materials decorated with copper and copper oxide nanoparticles were obtained; the developed materials were analytically characterized, and their potential application was proven by the antimicrobial, cytotoxic, and phytotoxic assays.

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Abstract

Isolation of *Plasmopara viticola* from Grapevine Leaves †

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Keywords: *Plasmopara viticola*; grapevine; isolation; biofungicides

In order to test some biofungicides, the isolation of *Plasmopara viticola* was carried out. *Plasmopara viticola* is a fungus that causes the grapevine downy mildew disease [1,2].

The fungus strain was cultivated onto potato dextrose agar (abbreviated "PDA") from Sigma-Aldrich with next composition: agar, 15 g/L, dextrose, 20 g/L, and potato extract, 4 g/L. A chloramphenicol antibiotic was used to avoid bacterial contamination. Experiences were effectuated with samples (leaves) from the National Research and Development Institute for Biotechnology in Horticulture Stefanesti, Arges.

Morphological observations (Figure 1) were taken based on colony, conidia and conidiophore morphology, and other morphological characters [3].

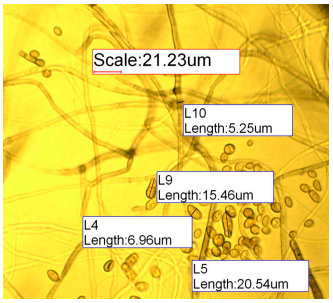

Figure 1. *Plasmopara viticola* (microscope view)—sporangiophores and sporangia. Identification according to [2,3].

Plasmopara viticola was isolated from infected grapevine leaves and grown on the potato dextrose agar culture medium with the goal to test some biofungicides.

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Abstract

Non-Invasive Treatment Based on Nanomaterials for Cultural Heritage Objects †

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Keywords: apatitic materials; antimicrobial; cultural heritage conservation

Cultural heritage objects suffer from different reasons for degradation, which are often irreversible. They represent the link between the past and the future, and it is our duty to protect them. Among different support materials, leather and paper are the most sensitive materials, due to their organic support, and improper storage conditions can lead to severe damage due to bacterial degradation.

In previous studies, our research group revealed the presence of several species, such as *Aspergillus* sp. (*Aspergillus clavatus* and *Aspergillus ochraceus*), *Penicillium* sp., *Fusarium* sp. (*Fusarium expansum* and *Fusarium flavum*), *Alternaria* sp. (*Alternaria rudis*) and *Rhisopus* sp. (*Rhizopus stolonifera*) on selected paper artefacts from the XIXth century [1]. This study demonstrated that even if at visual evaluation, the samples do not appear to be infested, they are damaged at the microscopical level by different bioteriogens. In this context, the necessity of safe treatment methods conducted us to the use of non-invasive treatments, based on nanomaterials, to protect the cultural heritage materials.

For this study, recipes based on synthesized nanostructures were developed in order to be used as pulverizable solutions for obtaining a protective antimicrobial layer. The solutions were tested for efficiency using old natural leather (from historical book covers), new natural leather (lamb, calf, and goat, tanned with vegetable tannins) and old parchment (sheep leather) (Figure 1).

(**a**) (**b**) (**c**)

Figure 1. Aspects of the samples treated with the proposed recipe: Old leather book cover (**a**); new leather (**b**); and parchment (**c**).

The tested nano-recipes showed good antimicrobial properties, accompanied by a slight discoloration of the treated materials, with no deposits of solids visible on the surface of the samples.

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Abstract

Surface Consolidation of Model Stone Samples with Carbonated Hydroxyapatite †

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Keywords: carbonated hydroxyapatite; metallic derivatives; nano-consolidants; stone consolidation

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Recently, numerous studies have been carried out on various materials with potential applications in the preservation and restoration of cultural heritage objects. Among the studied materials, special attention has been given to hydroxyapatite (HAp) regarding its use as a consolidating agent for various types of artifacts: stone, paper, and wood [1]. The selection of CHAp as a potential material for the protection and consolidation of carbonate stones was based on its low solubility and slow dissolution rate.

Carbonated hydroxyapatite (CHAp) and its metallic derivatives, Me-CHAp (Me=Ag, Sr), as very fine and uniform-sized powder, have been obtained by the nanoemulsion technique and characterized by Raman spectroscopy, thermogravimetric analysis (TGA) and transmission electronic microscopy (TEM). The surfaces of some model stones were consolidated with CHAp and Me-CHAp applied by brushing, immersion and spraying, Figure 1 and colorimetric tests have been correlated with water drop absorption, water repellency, penetration of water measurements and compressive strength.

Some model stones have been treated with these consolidants, and the effectiveness of CHAp and Me-CHAp as inorganic stone consolidants was tested.

The application method and the type of carbonated hydroxyapatite play a very important role in determining the final effects of the consolidating treatment. Based on the obtained results, these consolidants were selected for application on some monument surfaces.

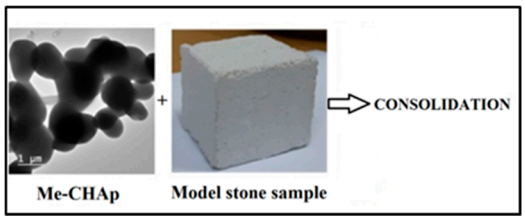

Figure 1. Model stone sample treated with metallic carbonated hydroxyapatite (Me-CHAp).

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Abstract

Photocatalytic Degradation of Direct Orange Dye under Solar Light †

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Keywords: direct orange; dye; ferrite nanoparticles; photo-degradation

As the development of the textile industry has progressed, intense concerns have been focused on the contamination of the environment caused by dye pollutants, which can cause severe environmental pollution and health problems due to their variety, toxicity, and persistence characteristics. Therefore, in recent years, the degradation of dyes in industrial wastewaters has generated considerable attention due to the huge volume of production, slow biodegradation, low discoloration, and high toxicity [1]. This study was undertaken to determine the feasibility of oxidation processes in the treatment of textile dyes. Direct Orange 26 (DO-26) is an azo dye with potential ecotoxicity to exposed organisms [2]. Effective degradation of the DO-26 was studied by photocatalytic degradation under direct solar light.

The photocatalysts used in the study were TiO_2, ferrite nanoparticles-$CoFe_2O_4$ and Fenton reagent. After the solutions were prepared, they were exposed to sunlight, between 2 h and 11 h in a Pyrex reactor of a cylindrical shape. Then, their maximum absorption at 495 nm and 519 nm (λ_{max}) was recorded at specific times by a UV–Vis spectrophotometer.

Exposure of DO-26 under direct solar light in the presence of the catalysts caused important discoloration of the dye solution in a reasonably time. Conversely, the exposure of the DO-26 to solar light without catalysts did not cause any noticeable discoloration. It can be observed that in the first 2 h, the absorbance of all DO-26 containing photocatalysts significantly decreased (Figure 1). For DO- 26+50%$CoFe_2O_4$+50%TiO_2+Fenton and DO-26+TiO_2+Fenton, a tendency of decrease in absorbance after 11 h could still be observed.

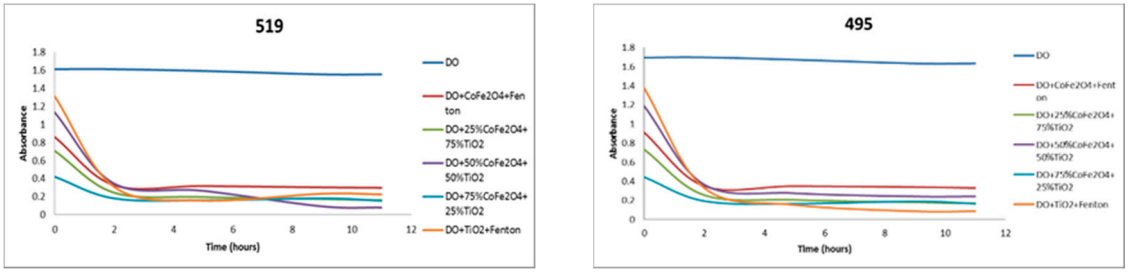

Figure 1. Photo-degradation of DO-26 under direct solar light.

This work demonstrates that these new materials are effective catalysts for the destruction of the industrial dye Direct Orange 26 (DO-26) under solar irradiation.

Acknowledgments: This work was supported by a NUCLEU Program, conducted with MCI support, project number PN.19.23.03.01.04.

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Abstract

Elemental and Corrosion Investigations Performed on Coins from 20th Century †

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Keywords: coins; corrosion; electrochemistry; elemental analysis

Corrosion represents the transformation process of metallic surfaces, caused by the influence of the contact medium. Coins are not exempt from the undesired effect of corrosion. This process progressively alters their aspect, shape, and resistance until their numismatic and historical value is lost. Coins that commonly contain non-noble metals like iron are more susceptible to corrosion. Thus, modern coins undergo an electroplating process with more corrosion-resistant metals [1]. The aims of this study are to identify the elemental composition of coins from the 20th century and to submit them to an artificial electrochemical corrosion process.

The elemental composition of samples was analyzed by wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) with a Supermini200-Rigaku Benchtop (elements ranging from ^{8}O to ^{92}U). Detection limit: 1 ppm–10 ppb; accuracy < 0.1–0.5%. The artificial rate of corrosion was electrochemically analyzed by the Tafel extrapolarization technique. For this process, a Voltalab PGZ 100 was used with an electrochemical cell consisting of three electrodes (the coin as the working electrode, Ag/AgCl as the reference electrode, and an auxiliary Pt electrode).

Results: X-ray fluorescence spectroscopy results for the 1966 M1 coin (Figure 1) revealed that the major chemical elements found were nickel (88.9%), followed by iron (2.88%). The usual corrosive chemical elements, like sulfur (0.38%) and chlorine (0.32%), were minor elements, indicating good anticorrosive protection of the electroplated layer. Electrochemical corrosion rate results for the same sample revealed a corrosion speed value of 1.55 μm/year (Figure 2).

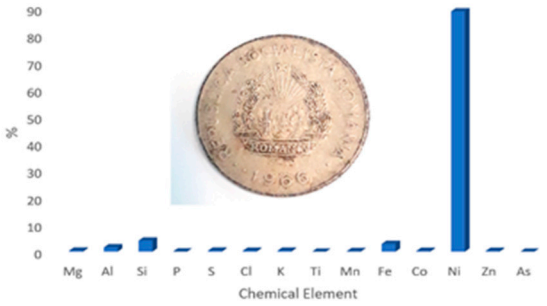

Figure 1. Elemental analysis of the coin.

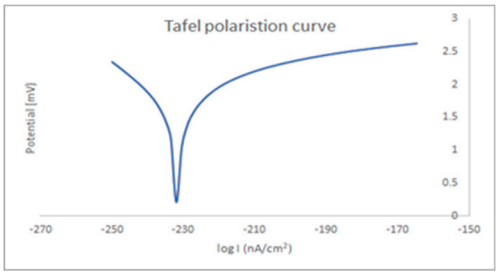

Figure 2. Tafel polarization curve of the coin.

Fluorescence spectroscopy is a non-destructive and sensitive technique for studying the elemental composition of coins, revealing all the metallic chemical elements used in the production of coins, and other chemical elements that can cause irreversible negative effects on coins. Electrochemical corrosion provides relevant information about the corrosion speed of metals in an electrically conductive medium.

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Abstract

Use of Vegetal Resources and Nanotechnology for Improving Horticultural Products—BIOHORTINOV (Year 2) †

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Keywords: vegetal resources; nanotechnology; horticulture

Within the international symposium PRIOCHEM XV, partner INCDCP-ICECHIM has organized the second workshop "Use of vegetal resources and nanotechnology for improving horticultural products" of the complex project "Increasing the bioeconomic research institutional capacity for the innovative exploitation of the indigenous vegetal resources, in order to obtain horticultural products with high added value".

The participants, members of the consortium, will address technical progress of the complex project in its second year of implementation, focusing on the research project lead by INCDCP-ICECHIM, "Development of vegetal extracts and innovative phytosynthesized nanostructured mixtures with phytotherapeutic applications to reduce biocenotic stress in horticultural crops", and the degree of the fulfillment of the assumed objectives and indicators.

At this workshop, the following representatives of the consortium partners will participate: University of Pitesti, Research Institute for Fruit Growing Pitesti (Maracineni), the National Institute for Research & Development for Biotechnology in Horticulture Stefanesti, Politehnica University of Bucharest, National R & D Institute for Welding and Material Testing (ISIM Timisoara).

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Abstract

Protection and Promotion of Romanian Cultural Heritage–RO-CHER (Year 2) †

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Keywords: Romanian cultural heritage; complex project; multidisciplinary approach

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As part of the International Symposium PRIOCHEM XV, the partner INCDCP-ICECHIM has organized the workshop entitled, "Protection and promotion of Romanian Cultural Heritage" as a consortium working meeting for the complex project, "Multidisciplinary complex project for monitoring, conservation, protection, and promotion of the Romanian cultural heritage" (RO-CHER).

The participants, members of the consortium, will address the technical progress of the complex project in its second year of implementation, with focus on the research project lead by INCDCP-ICECHIM, "Nanotechnology–an innovative approach with development of materials and techniques for safeguarding the cultural heritage", and the degree of fulfillment of the assumed objectives and indicators.

At this workshop, participating representatives of the consortium partners will include: the Romanian Space Agency (ROSA), the Museum of Dacian and Roman Civilization Deva (MCDR), the National Museum of the Union Alba Iulia (MNUAI), the University of Agronomic Sciences and Veterinary Medicine of Bucharest (USAMVB), and the National Institute for Research and Development in Chemistry and Petrochemistry–ICECHIM Bucharest (INCDCP-ICECHIM).

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Abstract

Romanian Traditional Buildings—Conservation of a National Legacy †

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Keywords: traditional buildings state; conservation and restoration strategies

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The International Symposium PRIOCHEM XV host a workshop entitled "Romanian traditional buildings—conservation of a national legacy" within the sectorial project "Innovative methods and techniques for evaluating conservation–restoration interventions and monitoring the conservation status of traditional constructions in Romania", organized by partner INCDCP-ICECHIM. Representatives from public authorities, museum specialists, other RDI organizations, NGOs, representatives of the Ministry of Research and Innovation, and Ministry of Culture and National Identity are welcome to attend.

The project's main goal is to ensure and implement in practice the means of and methods for evaluating the quality of materials and interventions, monitoring in time the environmental, microclimate, and anthropic risk factors and the state of conservation of Romanian traditional buildings, based on advanced scientific techniques and taking into account the principles of restoration.

The contribution of the partner INCDCP-ICECHIM (workshop organizer) to the project is related to the assessment of the present situation of the cultural heritage buildings in the rural area, their construction materials, as well as the identification and systematization of the correlations between the physicochemical properties of the monuments from the Romanian heritage subjected to the study and their current state. This will be realized through the analysis of support materials, using physicochemical and microbiological methods.

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Abstract

Biopolymeric-Hydrothermal Carbon Beads for Decontamination of Polluted Waters †

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Keywords: biopolymers; hydrothermal carbon; alginate; decontamination; metal ions

In the field of water depollution, considerable attention in past years was given to bio-based and biodegradable compounds from renewable resources, generically termed "biomass" [1]. Biomass represents the sum of raw materials from which one can produce bio-substances like alginate (from brown algae), chitosan (from shellfish), starch, cellulose, and also hydrothermal carbon (HTC). Sodium alginate is an extract from the walls of brown algae cells, used in the food industry and for body care products as an emulsifier, due to its viscosity [2]. HTC can be produced from lignocellulosic biomass by hydrothermal conversion in water, catalytic or non-catalytic, under thermally generated pressure in a hermetic reactor at temperatures ranging from 140 to 280 °C and different reaction times.

A 2% alginate solution was prepared by dissolving the alginate in water at 90 °C, under vigorous stirring. HTC was produced by hydrothermal treatment of lignocellulosic biomass from corn stalks at 200 °C, for 20 h. Then, 3% HTC (Figure 1b) was added to the alginate solution and homogenized for 1 h, and the obtained mixture was loaded in an automatic syringe and dripped with 180 mL/h flow in a $CaCl_2$ bath for ionotropic reticulation. The beads of alginate (Figure 1a) and of alginate with HTC (Figure 1c) were washed to remove Cl^- ions and dried afterwards in an oven at 60 °C for 24h. The beads were characterized by means of SEM-EDS, XRD, zeta potential, and batch adsorption experiments of Mn^{2+}, evaluated with Atomic Adsorption Spectroscopy (AAS).

(**a**) (**b**) (**c**)

Figure 1. (**a**) Alginate beads; (**b**) Hydrothermal carbon (HTC) from corn stalks; (**c**) Alginate/HTC beads.

For comparison, simple alginate beads were also prepared and tested in the adsorption of metal ions from synthetic water solutions. A quantity of 0.5 g beads were added in batch adsorption experiments to 40 mL aqueous solution of 1 mg/L $Mn(NO_3)_2$. Alginate-only beads presented a maximum adsorption efficiency of approximately 76% after 60 min, while the alginate/HTC beads presented a maximum adsorption efficiency of approximately 83% after 45 min.

By adding hydrothermal carbon to the alginate beads, a more efficient adsorbent was obtained for the removal of metal ions from polluted waters, Mn^{2+} for this case, with an increased adsorption capacity, while maintaining the biodegradability, renewability, and low cost of bioadsorbents.

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Abstract

Models of Environmental Impact Assessment of Emerging Technologies from Chemical and Cement Industry †

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Keywords: chemical industry; cement industry; greenhouse gases

Industry is a major source of global greenhouse gas emissions. The global industrial sector accounts for approximately 47% of energy-related carbon dioxide emissions, and significant quantities of additional greenhouse gases (GESs) are released as industrial process gases, such as CH_4, N_2O, and fluorinated gases (hydrofluorocarbons-HFC, perfluorocarbons-PFC, and Sulphur hexafluoride - SF6), with the latter emissions being concentrated in the chemical industry [1]. Additionally, the cement industry is one of the major contributors for greenhouse gas (GHG) emissions, specifically CO_2 emissions [2]. Regarding CO_2 emissions, the global emissions of CO_2 reached approximately 28.3 gigatons (Gt) in 2005, of which the cement industry generated approximately 1.8 Gt CO_2, indicating that the cement industry contributed approximately 6% of the total global CO_2 emissions [2]. In the EU-28, CO_2 accounted for over 94% of CO_2-equivalent GES emissions in the industrial sector, in 2012 [3].

In this context, models of environmental impact assessment of emerging technologies are critical to promote sustainable chemical production, and can provide policy makers with useful insights for the future. Increasing demand for energy and more severe environmental problems is a consequence of the globalization of industry and the increasing population. In this context, development of emerging technologies for different industries is necessary for a "cleaner future" and a decrease in energy consumption.

For models of environmental impact assessment, many parameters must be taken in consideration. Starting from the stage of RD&D (Research, Development, and Deployment) to the final product manufacturing, evaluations must be performed in order to fulfill the greenhouse gas emission (GES) reduction goals.

In this review paper, the advantages and drawbacks for some models of environmental impact assessment are briefly described, which can be used in the technologies emerging from different industries.

Life Cycle Assessment is the most commonly used approach for evaluating both conventional and emerging technologies in the chemical industry, but sometimes can present major drawbacks due to variations in parameters, when the laboratory model is scaled to the pilot model and further to industry [4]. In this case, the pass from one scale to another is the subject of the mathematical or computing simulations [5]. Emerging technologies are also evaluated through the economic input–output analysis, offering an average value of all products included in one sector [6]. Other models developed by different authors like Fault Tree Analysis, Failure Mode Effect Analysis, and Hazard

and Operability Study could also be considered [7]. These methods could be used as part of the process design procedure, especially in operation phases but they can only approach single aspects of the chemical processes.

In conclusion, the study found that the use of these models can offer the possibility to improve the processes, in a given timeframe, in order to reduce environmental footprints. Additionally, a decrease of different costs can be performed, leading to an enhancement in the decision-making related to future developments in emerging technologies.

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Abstract

Overview of the Materials Used for the Conservation/Restoration of Traditional Buildings †

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Keywords: traditional buildings; conservation; restoration; commercial materials

The restoration and conservation of traditional buildings (Figure 1) represents an important topic, both at an international and national level. The selection of the materials used for preserving the heritage constructions must be made using a complex approach, using both the literature data regarding the properties of such materials and physico-chemical analyses of the support materials.

The present paper aims to review the recent progress regarding the development and application of traditional/modern materials used for the restoration and conservation of traditional buildings, both at an international and national level.

Several authors and reports all over the world present the use of classical and innovative recipes for the restoration and conservation of buildings, including lime mortar prepared by traditional techniques, or composite materials based on organic and inorganic fibers incorporated in polymeric matrixes applied to the surface of masonry [1]. Some authors suggest the reinterpretation of old construction materials, by incorporating additives such as animal glue, nopal, or olive oil to obtain lime mortars compatible with traditional buildings [2], while others present the damages induced to the heritage buildings when not all elements are considered (including the social value of the building) [3]. A constant of all the studied works is that the proper material for the restoration is always selected after extensive laboratory testing, including characterization of the support material, the restoration material and their interaction [4].

Figure 1. Example of a Romanian traditional building [5].

For the selection of the proper materials for the restoration and conservation of traditional buildings, the first step of a truly scientific approach is represented by the analytical characterization of the materials (both support materials and restoration material), as well as their interaction. Those studies should usually be conducted in a trans-disciplinary manner, including specialists from different areas, such materials science, architecture, civil engineering, and cultural heritage.

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Abstract

Determination of Sulphates in Model Stones and Stones from Corvins' Castle †

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Keywords: stones; sulphates; Corvins' Castle; protection of cultural heritage

Stone monuments represent a big part of the world's cultural heritage. The deterioration of stone monuments is caused by a wide range of factors. Depending on the source of ions, various salts can be contained in building or decorative stones [1]. The most common salts are chlorides, nitrates, and sulphates. The possible sulphate sources include groundwater, seawater, and atmospheric pollution.

In this paper, we determined the sulphate content from model stones made of plaster mortar and mortar for construction and from stones from Corvins' Castle. The model stones were first dried at room temperature and at 100, 200, 300, and 400 degrees Celsius, respectively. In the first stage, the extraction of water-soluble substances was carried out. A quantity of 2 g of sample was added over 200 mL distilled water and then stirred at room temperature for 1 h. The solution was further filtered and the sulphates obtained from the aqueous extract were determined using hydrochloric acid and barium chloride. A barium sulphate precipitate was obtained, which was further calcinated at 800 degrees Celsius for 1 h. Finally, the amount of sulphates present in the sample was calculated.

The content of sulphates was determined from model stones (dried at different temperatures) and from the samples from Corvins' Castle. It can be seen that the model stones dried at 200 degrees Celsius had the largest amount of sulphates. The lowest content of sulphates was in the model stones dried at 100 degrees (Figure 1). Regarding the samples from the Corvins' Castle, the New Gate tower had an insignificant amount of sulphates, while the Deserted tower had the largest amount of sulphates (Figure 2). This could be due to the fact that in history, some restorers and conservators used noncompatible materials (e.g., cement), which are responsible for the generated sulphates.

A large quantity of sulphates was found in the samples from Corvins' Castle compared to the model stones. The presence of sulphate anions may be linked to the presence of the cement used in restoration.

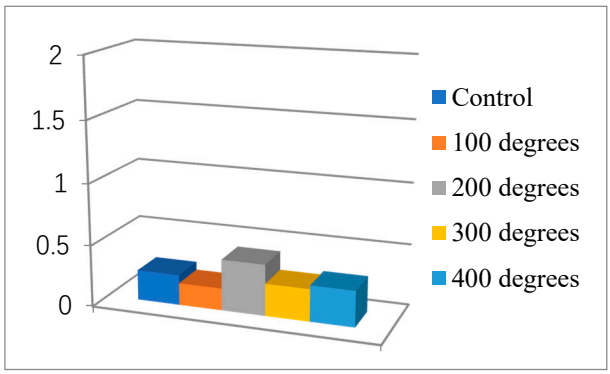

Figure 1. Percentage of sulphates in model stones.

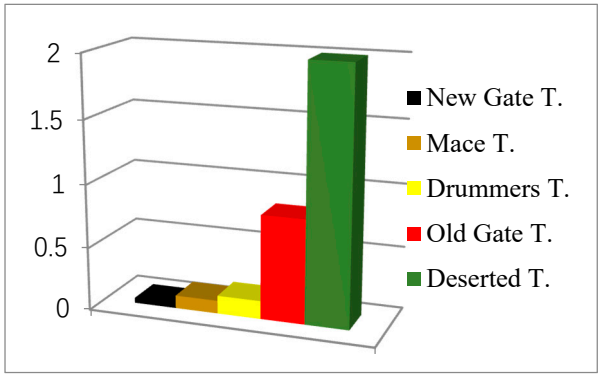

Figure 2. Percentage of sulphates in samples from Corvins' Castle.

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Abstract

Electrical Resistivity and Moisture Content Measurements for Some Concrete Samples †

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Keywords: electrical resistivity measurements; concrete moisture content; concrete permeability

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The aim of this study was to assess the properties of some concrete samples according to their moisture content and, thus, permeability. There are different causes of deterioration of reinforced concrete structures, such as corrosion of reinforcement bars due to carbonation or chloride ingress, freezing and thawing action, sulfate attack, alkali aggregate reaction, and so forth [1].

Studies have shown that resistivity can be directly correlated with chloride diffusion rate. On-site mapping of the resistivity of a concrete structure will identify the most permeable areas. These areas are more likely to be susceptible to chloride penetration [2].

Resistivity measurements may be used on site to determine premature drying of concrete. This application is particularly important, as premature drying can lead to structural weakening [3].

Here, the electrical resistivity of concrete samples was measured using a Resipod Proceq with a 50 mm probe spacing model at room temperature in an indoor climate. Four types of samples were used for measurement: a simple concrete one, concrete with nails, concrete with thick wire (steel), and concrete with thin wire.

Empirical studies have shown that resistivity is directly linked to the likelihood of corrosion. When the electrical resistivity of concrete is low, the likelihood of corrosion increases. When the electrical resistivity is high, the likelihood of corrosion decreases. Figure 1 shows that electrical resistivity values were between 4 and 50 kΩcm, corresponding to a moderate risk of corrosion for most measurements and a high risk of corrosion for six of the measurements. Figure 2 shows the capillarity measurements for the same samples, which provide a better understanding of the water penetration phenomenon occurring inside the concrete.

The obtained results can be used for mapping out areas of various wetness and dryness degrees and assessing which areas of the concrete samples are more likely to be permeable. Identifying these particular areas is necessary because they are more likely to be susceptible to chloride penetration, leading to a more pronounced structural degradation of the concrete.

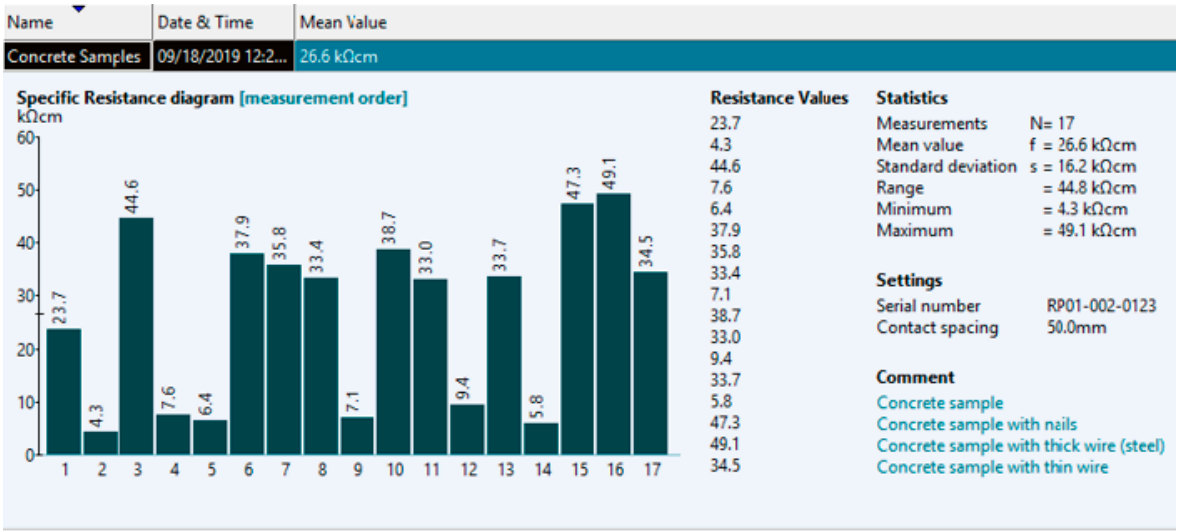

Figure 1. Electrical resistivity measurements of concrete samples.

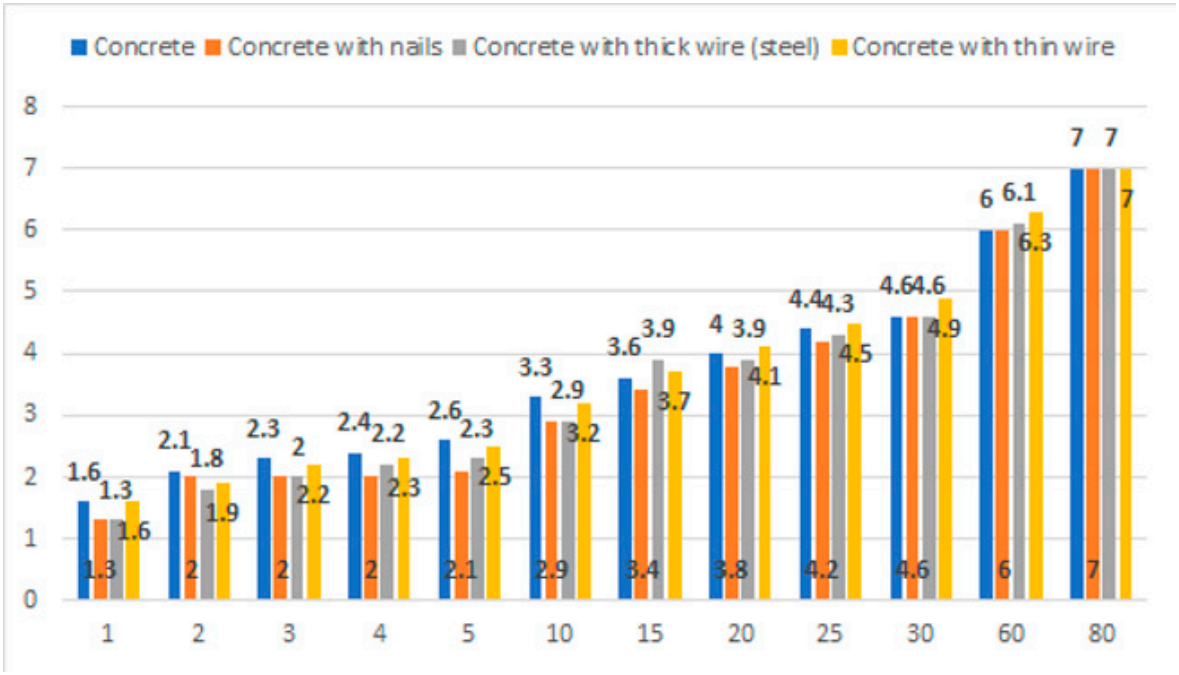

Figure 2. Capillarity.

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Abstract

Trends in Hybrid Nanocoatings †

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Keywords: coatings; metallic nanoparticles; inorganic nanoparticles; antimicrobial; environmentally friendly synthesis; plant extract

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The aim of the present work was to prepare intelligent materials for coatings with advanced protection properties against development of biofilms and deposition on stone, paper and metal surfaces.

Coatings based on metallic and/or inorganic nanoparticles were prepared by sol-gel process and via supercritical CO_2 in order to achieve manufacturing processes with minimum energy consumption and the least polluting.

The obtained materials were tested both in terms of antibacterial properties, as well as structurally (FTIR, XRD) and morphologically (SEM, TEM).

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Abstract

Investigation of Chromatic Parameters of Some Samples from Constanta Casino †

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Keywords: chromatic parameters; cultural heritage; Constanta Casino

Cultural monuments are subject to a degrading phenomenon induced by several factors, such as pollution, temperature, and humidity variations [1,2]. In the last years, several studies have been carried out in order to investigate the main factors involved in the degradation of art components and historical monuments. An example of a historical monument is Constanta Casino, which was built in 1909 and opened in 1910. It was designed by Swiss-Romanian architect Daniel Renard in the Art Nouveau style [3]. Although a landmark of the Black Sea shore, the building was abandoned from 2000s, and is currently in a very bad shape.

This study presents the archaeometric investigation of stained-glass window samples collected from Constanta Casino (named P9-P19). In order to understand the manufacturing and weathering/deterioration processes of these artifacts, color measurements were recorded. The differences in L*, a*, and b* and the total color differences ΔE*ab were calculated. The CIELab (CIE 1986) chromatic parameters were chosen for the study, i.e., chromatic coordinates a* and b*, with the following significance: coordinate a* ranges in value from +60 (red) to −60 (green) and b* from +60 (yellow) to −60 (blue).

The chromaticity coordinates presented in Figure 1 indicate the change in color of the samples. It can be observed that all the positive Δa values suggest the presence of red pigments, while all the positive Δb values suggest the presence of yellow pigments in the samples. P9-P13, P16, P18, and P19 show different tones of green shades, and P14, P15, and P17 show dark tones: black, blue and brown.

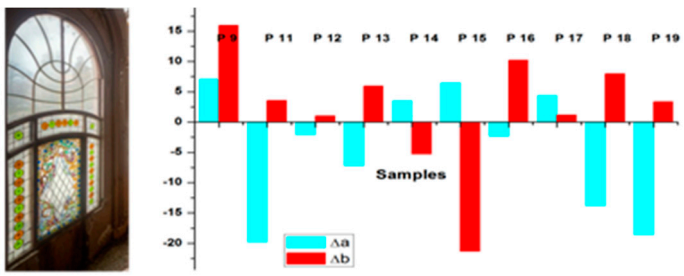

Figure 1. Image of stained-glass windows (**left**) and chromatic coordinates (**right**) of samples from Constanta Casino.

These colorimetric determinations on stained-glass windows demonstrate the presence of some pigments with different shades in the green-red-yellow area, useful for further conservation procedures.

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Abstract

The Influence of Solvents on the Stability of Carbonated Hydroxyapatite †

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Keywords: hydroxyapatite; solvents; stability of consolidants

Hydroxyapatite is an inorganic consolidant used in the restoration of cultural heritage. For this reason, the study of the effects of different agents on hydroxyapatite is paramount [1,2]. In this paper, the effect of solvents (isopropyl and tert-Butyl alcohol) was investigated by measuring the stability of absorbance over time.

To this end, solutions containing water and alcohol in different proportions were prepared, starting from the binary solutions containing water: Alcohol (0–100%) with a constant mass of hydroxyapatite added, and the absorbance was measured over a period of time at a fixed wavelength, λ = 600 nm.

For this study, a JK-VS-721N visible spectrophotometer was used to measure the absorbance of 11 solutions containing water (0–100%) and isopropyl alcohol or tert-Butyl alcohol (0–100%) and hydroxyapatite.

For a hydroxyapatite suspension to be effective as a consolidant, the sedimentation rate of this solution should be as low as possible so that the respective suspension is homogeneous when applied to a stone surface [3]. In our case, with hydroxyapatite in the binary water mixture: Alcohol (60–40%) has the lowest sedimentation rate, thus being the most efficient solution for applying on the stone surface (Figure 1).

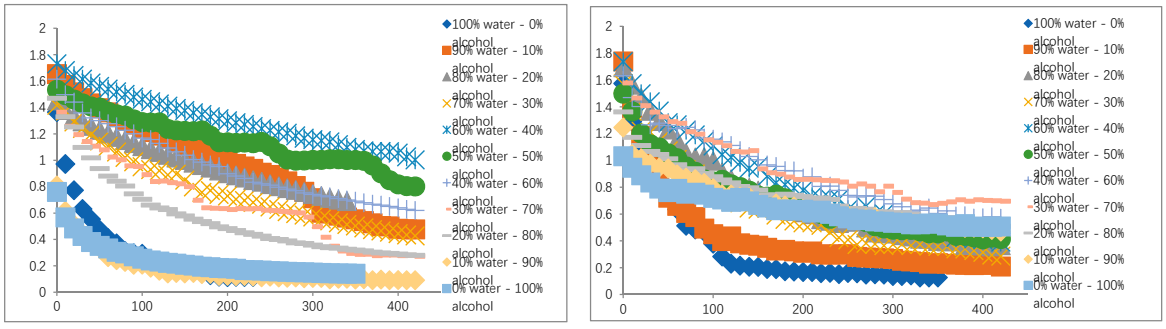

Figure 1. Absorbance variation in time for solutions containing water/isopropyl alcohol (left) and water/tert-Butyl alcohol (right).

In the case of hydroxyapatite in the binary water mixture: Alcohol (60–40%) has the lowest sedimentation rate, being the most efficient solution for application on the stone surface.

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Abstract

Evaluation of Peroxide-Based Compositions Containing Amino Acid Surfactants †

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Keywords: amino acid surfactants; surface active properties; environmental impact

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Chemical warfare agents are a real threat to the security of mankind and efforts are constantly being made to counteract their effects by developing new formulations and technologies [1,2]. At the same time, there is a need to reduce the environmental impact of decontamination formulations. In surfactant-based decontamination formulations which include reactive compounds, the role of surfactants is to solubilize the sparingly soluble chemical warfare agents and catalyze their decontamination. In this work, we studied the stability in oxidizing agents and also in hard water, saline solutions and seawater formulations which contain amino acid surfactants [3], such as sodium lauroyl sarcosinate surfactant with low environmental impact made from renewable feedstock. The stability of formulations containing hydrogen peroxide was evaluated by the proportion of active oxygen remaining after variable lengths of time. The foamability and foam stability were assessed using the Ross-Miles method. The influence of water hardness and water salinity on the surface properties of surfactants were investigated by surface tension measurements performed on a KSV tensiometer Sigma 700 model, using the Du Nouy ring method. This study helps to expand the range of environmentally friendly surfactants that can be used in decontamination formulations of chemical warfare agents in land or maritime applications.

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Abstract

FTIR Analysis Both for Degradation and Treatment with Nanoparticles of Historical Paper †

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Keywords: cellulose; degradation; treated historical paper; hydroxyapatite; FTIR methods

Cellulose destruction reactions consist of a series of physico-chemical phenomena, which cause the shortening of macromolecular chains. These reactions occur with the cleavage of the cellulose chains and thus with the decrease of the average degree of their polymerization. They can be caused by both internal and external factors.

The transformations due to internal causes are due to a series of elements related to the molecular, secondary or tertiary structure of cellulose, such as: the existence of defects in the supra-molecular structure, causing the formation of so-called "weak points", or the existence of some internal stresses in the cellulose fiber structure, which occur during repeated drying processes. Degradation reactions can also be caused by the filler compounds existing in historical paper [1].

Destruction reactions resulting from external causes occur under the action of multiple factors: light, temperature, humidity, air pollutants, biological pollutants, mechanical forces, etc. [1].

Historical book papers from the nineteenth to the twentieth centuries, without heritage value, cellulose, ethyl cellulose and carboxymethyl cellulose standards were analyzed. The FTIR spectra were registered on a Perkin Elmer GX spectrometer, both in transmission and attenuated total reflection ATR, spectroscopy analytical techniques.

The restoration and conservation of artifacts with nanomaterials is a new and insufficiently explored area.

Globally in the last 20 years, particles of Ca or Mg hydroxide nanomaterials have been applied in non-aqueous dispersions to cellulose-based artefacts, with the idea of achieving deacidification. However, these complexes have the disadvantage of having an overly strong alkaline character [2,3].

This study is based on the use of hydroxyapatite (HA) as a historical paper conservation material. The similar structure of HA with that of the phosphates found in the paper, either as fillers or as impurities accompanying the component materials of the paper, has led to the certain conclusion that there is a perfect compatibility between this material of conservation and restoration and the paper support [4,5].

FTIR methods have been applied for the study of degraded paper as well as for historical paper treated with HA. To assign the FTIR absorption bands in the historical paper samples, different standards were used, including cellulose, ethyl cellulose and carboxymethyl cellulose standards.

After treating the historical paper samples with HA, they were subjected to FTIR analysis, and the next step was a comparison between the treated and untreated samples.

It is very difficult to establish the existence of FTIR differences between the untreated historical paper and the one treated with HA nanoparticles—on the one hand due to the very small amount of HA deposits, and on the other hand due to the perfect similarity between the treatment material and

the phosphates already existing in the paper. However, upon careful examination, small differences were noted between the untreated and treated papers.

Acknowledgments: This work was supported by an NUCLEU Program, conducted with MCI support, project number P.N.19.23.01.03.

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Abstract

Contributions to the Interpretation of Mass Spectrum of Octaethoxycyclotetrasiloxane: Linked Scansand Isotopic Effects †

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Keywords: octaethoxycyclotetrasiloxane; mass spectrum; linked scans; M+1; M+2 isotopic effects

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The aim of this article is the study of the fragmentation reactions of octaethoxycyclotetrasiloxane (CTET) initiated by electronic impact in the ionization chamber of a double focusing mass spectrometer. Octaethoxycyclotetrasiloxane as tetraethoxysilane (TEOS) tetramer, with structural formula $(C_2H_5O)_8Si_4O_4$ and molecular weight M = 536, is obtained in sol-gel process by hydrolysis–condensation reactions. The stereochemistry-optimized formula of CTET by MOPAC 7 program (computer program used in computational chemistry) is shown in Figure 1.

Mass spectrum of an organic substance such as octaethoxycyclotetrasiloxane obtained in sol-gel process is the result of a series of unimolecular consecutive and competitive chemical reactions, which constitutes a pattern of fragmentation (Figure 2a,b; integral spectrum and 250–540 amu, respectively).

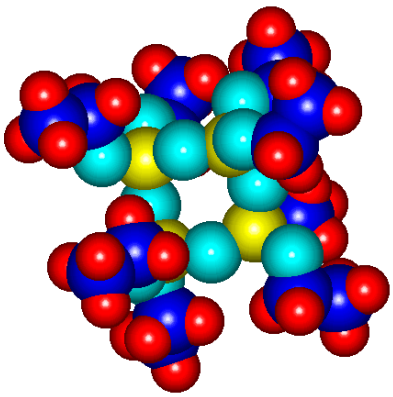

Figure 1. Legend: Si: yellow, O: cyan, C: blue, and H: red.

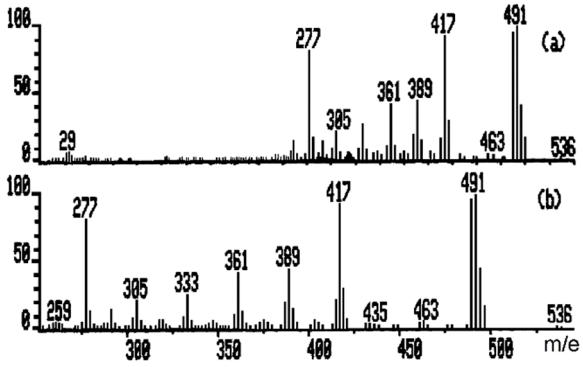

Figure 2. Mass spectrum of octaethoxycyclotetrasiloxane (integral spectrum and 250–540 amu).

The experimental data for this paper were obtained on a GC-MS tandem produced by VG-Analytical, England. The working conditions for 70-SE, VG Analytical double focusing mass spectrometer are as follows. B/E linked scan: This method of scanning allows for obtaining daughter ions m_2^+ from a preset precursor ion m_1^+; $(B/E)(1-E)^{1/2}$ linked scan: It is used to obtain ions which lose small molecules with a preset mass (e.g., ethanol, ethylene, water, etc.).

The TEOS tetramer fraction, separated and identified by GC-MS, is at the center of the oligomer distribution of the reaction mixture TEOS:H_2O:EtOH in acid catalysis; these molecular species have high stability and are very important for the characterization of the sol-gel process in the transition from solution to gel.

The reaction pathway from m/e 536 to m/e 277 in the mass spectrum of the CTET can be highlighted by linked scans. Figure 3 shows the linked scan B/E(1-E)1/2 for the elimination of ethylene (Figure 3a) and ethanol (Figure 3b) and the linked scan B/E for the daughter ions of the ions with m/e 536 (Figure 3c), m/e 463 (Figure 3d), m/e 435 (Figure 3e), m/e 417 (Figure 3f), and m/e 333 (Figure 3g) for successive eliminations of ethylene. Based on experimental data mentioned above, we can write the reactions for obtaining the fragmentation ion m/e 277 according to equations presented in Figure 4.

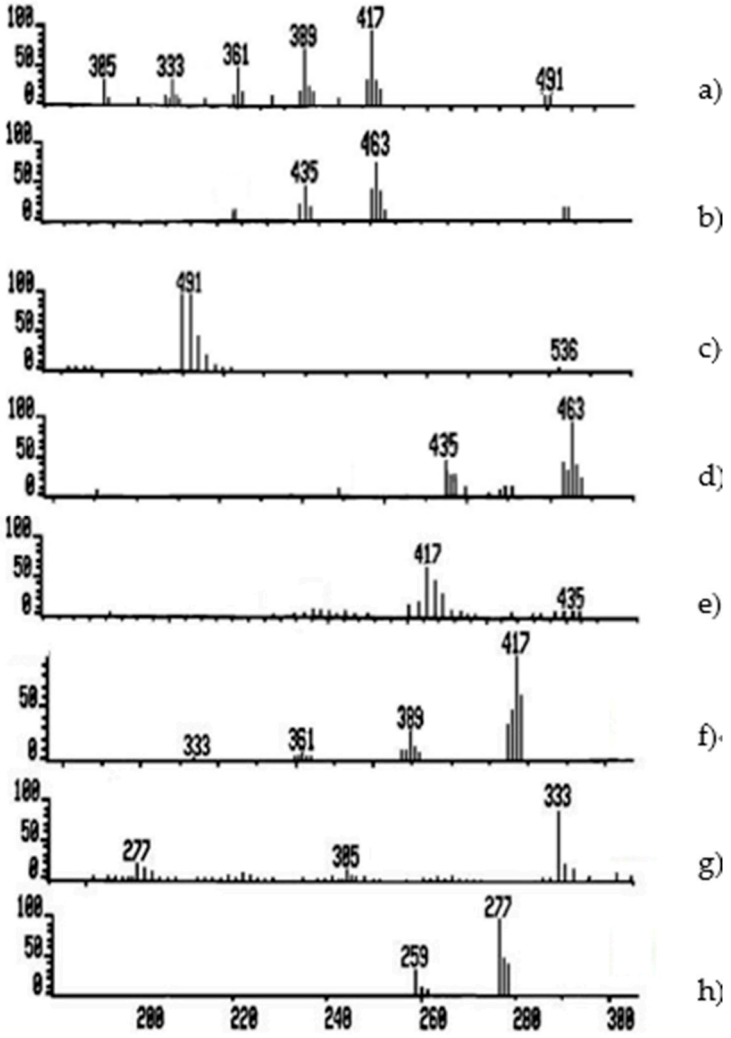

Figure 3. The linked scan B/E(1-E)1/2 for the elimination of ethylene (**a**) and ethanol (**b**) and the linked scan B/E for the daughter ions (**c**–**h**).

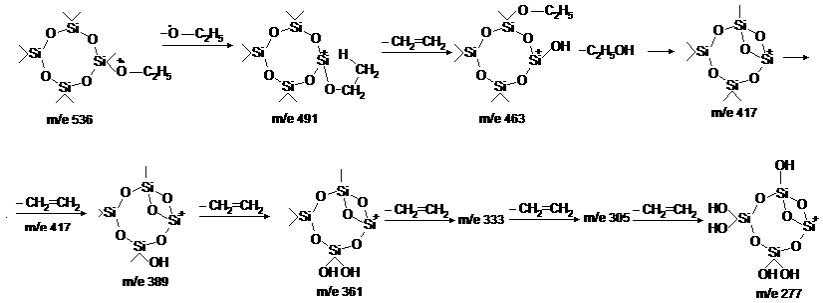

Figure 4. The reactions for obtaining the fragmentation ion m/e 277 from molecular ion at m/e 536.

The m/e ion 277 with the ionic formula $H_5O_{10}Si_4$ is characteristic ion for bicyclic, cyclic, branched, cyclic, branched, and linear tetramers and can be used to identify and measure the TEOS tetramer fraction. The existence of this ion is argued by the M+1 and M+2 isotopic effects for the molecular species of tetramers of TEOS [1–3]. There is a good agreement between the experimental values for the ion with m/e 277 and intensity 76.0% (14,3% and 11.8%) in the mass spectrum of CTET and those calculated theoretically by MS Interpreter software (15.5% and 12.6%) [4].

The reaction path from m/e 536 to m/e 277 in the mass spectrum of the CTET is obtained experimentally by the B/E and $B/E(1-E)^{1/2}$ linked scans. Thus, there can be written the fragmentation pathways for the primary event (ethoxy group removal) and successive eliminations of six ethylene and ethanol. The existence of this ion is confirmed by the M+1 and M+2 isotopic effects.

Acknowledgments: This work was supported by a NUCLEU Program, conducted with MCI support, project number P.N.19.23.01.03.

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Abstract

Energetic Efficiency Biogas Plants Improvement by Integrated System: Biogas–Microalgae–Biofuels in Frame of Biorefinery Concept (Algal Biogas Concept Energy) †

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Keywords: biogas; biomass; microalgae

Algal Biogas Concept Energy (2018–2021) is a national project financed by PN III Program, PN-III-P1-1.2-PCCDI-2017; Program 1—Development of national CD system; Subprogram 1.2—Institutional performance, complex projects developed in CDI consortia.

The complex project proposes the development and demonstration of innovative technologies to optimize the biogas plants by integrating the open ponds for microalgae cultivation using the digestate resulted from anaerobic digestion as a culture medium. The integral valorization of microalgae biomass consists in: obtaining of algal extracts (for co-digestion), lipid fraction (for biofuels), and spent biomass (co-digestion substrate); advanced separation and valorization of biogas by carbon dioxide conversion to bio-methane; biorefining of the solid digestate and lipid fractions obtained from algal biomass into biochar, fuel components, bitumen fluxes, bio-hydrogen, and liquefiable gaseous fractions. The results of this project will be: a demonstrated technology at TRL 6 level within the biogas–microalgae integrated and an experimental stand for the evaluation of bio-methane and liquefied gaseous hydrocarbons combustion efficiency and emission control. In order to achieve the main goals of the project, the project involves six partners.

The main objectives of the project:

1. Development of innovative technologies for the optimization of biogas plants functioning, by integration of open systems for mixotrophic cultivation of microalgae that use the liquid digestate resulted from anaerobic fermentation as a nutrient source and that produce algal extracts (fito-catalysts for co-fermentation process), lipid fraction (biofuel production), and spent algal biomass (as substrate for co-digestion);
2. Advanced valorization of biogas resulted by carbon dioxide conversion to bio-methane;
3. Processing, by bio-refining, of the solid digestate and lipid fractions from algal biomass for obtaining bio-coal, fuel components, bitumen fluxers, and liquefiable gaseous fractions;
4. Elaboration of an integrated demonstrative installation (experimental pilot), biogas–microalgae, for demonstration of optimized co-digestion technology functionality and for ensuring the instruction of research personnel from the consortium partner institutions; the experimental pilot installation will be placed at the headquarters of Partner 3—INCDCSZ, Brasov, andactivity conducted within Project 1—coordinated by ICPE-CA;
5. Settingup an experimental stand for combustors, with gaseous fuels for characterization of the obtained liquefiable gaseous hydrocarbons; the stand will serve equally for research within the project, for research personnel training, and for analyses required for economic partners that

want to characterize gaseous fuels, taking into account that there is no such laboratory existent at this moment in Romania; the experimental stand will be set up at Partner 5—UT, Iasi headquarters.

Acknowledgments: This work was supported by PN III Program, PN-III-P1-1.2-PCCDI-2017; Program 1—Development of national CD system; Subprogram 1.2—Institutional performance, complex projects developed in CDI consortia, Contract 32PCCDI/2018.

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Abstract

Multifunctional Metal-Oxide-Nanopowder-Polymer Composite Coatings for Stone Built Heritage Conservation †

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Keywords: historic stone protection; multifunctional coatings; sol-gel; metal-oxide-polymer composites

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Multifunctional composite coatings composed of metal oxide nanoparticles dispersed in polymer matrices are an innovative solution for stone heritage protection, specifically designed to be stable, durable, transparent (should not alter color), easy to apply, nontoxic, removable, hydrophobic, and permeable to allow stone transpiration. Sol-gel metal oxide nanopowders have photocatalytic and antimicrobial proprieties that act against environmental pollutants and biodegradation [1,2]. The protective coatings we propose in this work combine the hydrophobicity of sodium polyacrylate with the antimicrobial effect (even in the absence of light) and compatibility of MgO and TiO_2 eco-friendly nanopowders.

MgO (pure phase periclase) and TiO_2 (pure phase anatase) nanopowders were synthesized by the sol-gel route [3]. Aqueous dispersions of hydrophobically modified polymer ($NaPAC_{16}$, polyacrylic acid sodium salt) and MgO/TiO_2 nanopowders were deposited for testing on glass slides (through a layer-by-layer dip-coating technique) and stone fragments imitating mosaic stone from the fourth century AD Roman Mosaic Edifice, Constanta, Romania (through immersion).

The powder size and morphology were investigated by scanning electron microscopy (SEM), while the coating surface characteristics were evaluated by optical profilometry measurements. Photocatalytic activity measurements indicated highly efficient degradation of methyl orange dye under UV irradiation. Hydrophobic properties were confirmed by contact angle measurements, while the inhibition of microbial growth was shown by microbiology testing using *Aspergillus niger* cultures under illumination and in darkness conditions. Colorimetric tests indicated that the applied coatings do not induce perceivable changes in color hue and lightness.

Our study shows that MgO(TiO_2)/$NaPAC_{16}$ composite coatings are highly suitable for historic stone protection due to their demonstrated transparency, hydrophobicity, antimicrobial, and photocatalytic self-cleaning properties. A possible synergistic effect between the two oxide nanopowders is also suggested.

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Abstract

Restoration Materials Compatible with Heritage Wall Paintings †

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Keywords: lime-based mortar; hydraulic lime; fresco painting; wooden church; masonry monuments

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The conservation-restoration interventions at historical monuments in Romania require materials that respond both to the general requirements set out in the International Charters on the conservation and restoration of heritage, and to the specific conditions of the country: compatibility with the nature and characteristics of the constituent elements of the historical monuments, reversibility, and resistance to environmental factors. Failure to comply with the above principles has favored, in the past, the application in the works of conservation-restoration some inadequate materials, with excessive hardness and impermeability, with negative consequences on the state of preservation of historical monuments. The restoration materials presented in the paper were made on the basis of the information obtained through the physical and chemical characterization using specific investigation techniques (, X-ray diffraction, scanning electron microscopy coupled with energy dispersive X-ray analysis, Fourier transform infrared spectroscopy, chemical analysis) of the mortars taken from historical monuments. The characteristics of the new materials are compared with those of other similar materials used in the restoration work.

The materials based on hydrated lime or hydraulic lime, with and without pozzolana addition have been characterized from a chemical, physical-mechanical, and durability (frost-defrost and crystallization of soluble salts resistance) point of view.

For the materials made, we obtained characteristics that recommend them in the works of conservation-restoration of the mural paintings:

- do not contain the chemical components of cement degradation (tricalcium aluminate, sulphates);
- allow the exchange of humidity, having good water vapor permeability;
- good resistance to thermal variation;
- mechanical resistance compatible with the original;
- good resistance to biodeterioration.

The materials made were tested on support-models (reproducing the original techniques) and experimentally in situ, on different masonry or wood monuments. Materials containing hydraulic lime or pozzolana addition play a special role in restoration because they allow the execution of work on monuments located under severe microclimate conditions (permanent excessive humidity or large variations in temperature and humidity).

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Abstract

Antibiotic Incidence, Distribution and Resistance in Wastewaters †

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Keywords: antibiotic distribution and incidence; antibiotic resistance; antibiotic resistance genes; waste water treatment plants

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In 2016, the population-weighted average consumption of antibiotics from the European Union (EU) and European Economic Area (EEA) for systemic use in the hospital sector was 2.1 defined daily doses (DDD) per 1000 inhabitants per day. Consumption ranged from 1.0 (Netherlands) to 2.9 (Malta) DDD per 1000 inhabitants per day.

Although Romania is in the top of EU countries in terms of antibiotic resistance rates with Bulgaria, Croatia, Cyprus, Estonia, Hungary, Latvia, Lithuania, Malta, Romania, and Slovakia, the prevalence of nosocomial pathogens and resistance genes to associated antibiotics (RGAAs) in natural or polluted aquatic environments are not documented nationally. Furthermore, the effects of wastewater discharges from the hospital on the prevalence and characteristics of nosocomial pathogens are not studied in Romania.

The purpose of this study is to evaluate the incidence of antibiotics or metabolites and to correlate with the antibiotic resistance (AR) and antibiotic resistance genes (ARGs) occurrence and dynamics associated with aquatic environments characterized by a high level selective pressure (especially hospital, poultry waste water, urban and pharmaceutical waste water treatment plants—WWTPs). This research will assess the incidence and distribution of the antibiotics in wastewaters, will correlate them with antibiotic resistance and the impact on the aquatic environment.

Acknowledgments: The present work was possible due to the EU-funding grant POSCCE-A2O2.2.1-2013-1, Project No. 638/12.03.2014, code SMIS-CSNR 48652. The financial contribution received from the national project Antibiotic Resistance in Wastewater: Transmission Risks for Employees and Residents around Waste Water Treatment Plants is highly acknowledged.

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Abstract

Evaluation of Harmful Factors of Municipal Solid Waste in Order to Be Valorized in Industrial Application †

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Keywords: municipal solid waste; heavy metals; building materials; environment

Municipal waste disposal is an issue that is important to the management of any urban area. Cities without a functioning waste-disposal plan face the risk of diseases running rampant and economic activity grinding to a halt [1]. The safety and acceptability of many widely-used solid waste management practices are a serious concern from a public health perspective. The quantity and composition of municipal solid waste (MSW) varies from place to place, and bears a rather consistent correlation with the average standard of living. Waste recovery is one of the objectives of the national strategy. One method of recovery is the valorization of waste to produce fuel, while others suggest its incorporation into building materials [2–4].

The paper presents the chemical analysis and heavy metal composition of solid municipal waste for quantification of harmful compounds. Samples were obtained from a historical Romanian municipal solid waste disposal site.

Samples collected from 30 points were characterized from a heavy metal and corrosive agent (Cl^-) content point of view. Specifically, analyses for determination of the calorific value, ash content and oxidic composition were carried out. In addition, determination of the heavy metal content (mercury, cadmium, cobalt, chromium, copper, manganese, nickel, lead, styrene, thallium, vanadium and zinc) was performed using graphite oven atomic absorption spectrometry, and a NovAA 400 hydride generator. To determine the calorific value of the waste, an IKA WERKE-type calorimetric pump was used. The chlorine content (considered a corrosive agent) and oxide composition of the ash was determined by wet chemistry.

The results obtained showed that:

- the content of heavy metals had a wide range of variation, with different domains depending on the type of element
- the minimum content of Cl determined was 0.68% and the maximum value recorded was 2.01%
- the limits of variation for the lower calorific value were 3281–5790 kcal/kg, while the higher calorific value varied in the range 590–5880 kcal/kg
- in the case of ash, there was quite a wide variation in the limits of its oxide chemical composition

Based on the complex characterization of the collected waste samples, and considering the wide range of variation in the values determined for each characteristic presented, it can be concluded that the deposited material was not homogeneous.

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Abstract

Histopathological Alteration on Marsh Frog Skin Induced by the Action of Dual Gold 960EC Herbicide†

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Keywords: skin; marsh frog; Dual Gold 960EC

The aim of this study was to establish the influence of Dual Gold 960EC herbicide upon skin structure in marsh frog (*Pelophylax ridibundus*).

The sublethal concentration used in the experiments was 2.5–10-3 mg metolachlor/g body weight, respectively, 0.0026×10-3 ml Dual Gold/g body weight, administered to *Pelophylax ridibundus* specimens by intraperitoneal injection, 1 injection every 2 days for 3 weeks.

The histopathology of the tegument determined by the action of the Dual Gold 960EC herbicide on *Pelophylax ridibundus* specimens describes the presence of a stratified covering epithelium, consisting of 7–8 cell layers, as a result of the increase in the number of layers made up of horn cells (Figure 1). The cells of the superficial layer retain their nuclei, but show an exfoliation tendency. The cells of the basal layer are tall and cylindrical, with elongated nuclei that divide themselves continuously, in order to ensure the regeneration of the epithelium. In the dermis, immediately below the epidermis, the presence of melanophores is observed. These present a small amount of melanin. The mucous glands are large, hypertrophied and formed by secretory cells that are in full activity (Figure 1).

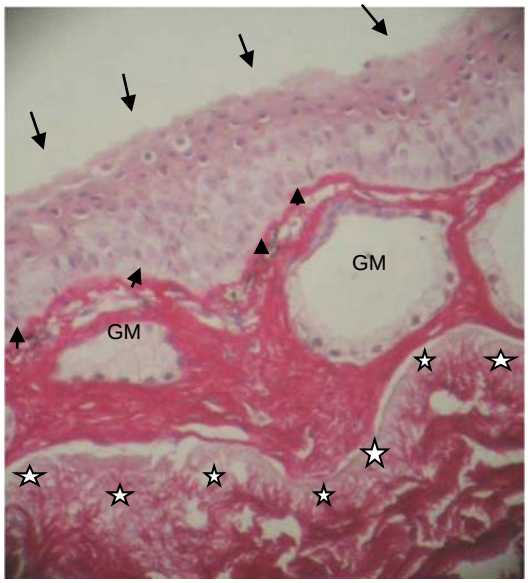

Figure 1. Skin in *Pelophylax ridibundus* specimens exposed to the action of the Dual Gold 960EC herbicide at a temperature of 4-6 °C. Stratified epithelium (black arrow); melanophores (arrowhead); hypertrophied mucous glands (MG); collagenolysis (stars). 100 ×. H-Sirius red coloring.

Around the glands are numerous collagen fibers, intensely colored red with Sirius red. At the base of the glands, a band of collagen fiber lysis can be seen (Figure 1). The deep dermis is made up of irregularly arranged connective fibers.

In conclusion, the sublethal concentration used in the experiment determined histopathological changes in marsh frog skin.

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Section 4

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Extended Abstract

The Temperature Effect on the Retention of Sildenafil under Reversed-Phase Liquid Chromatography †

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Keywords: van't Hoff plots; sildenafil; reversed-phase liquid chromatography; thermodynamics

Generally, the temperature influence on the retention of compounds in liquid chromatography (LC) is described by the linear dependence between the natural logarithm (ln) of the retention factor k and the inverse value of the absolute column temperature (T^{-1}), known as the van't Hoff rule [1]. From this dependence, the variations of the standard enthalpy and the standard entropy can be calculated. In many situations, the linearity of the van't Hoff dependence is not obtained due to secondary equilibrium involving the eluted compound [2] or multiple retention mechanisms [3]. The deviation from linearity can be described by upper mathematical polynoms from which the contribution of enthalpy and entropy variation corresponding to the compound transfer from mobile to stationary phase can be estimated [4].

This study was carried out with a HPLC system having the following configuration: degasser, binary pump, auto sampler, column thermostat, and diode array detector. Two chromatographic columns were used, loaded with octyl or octadecylsilicagel. The mobile phase compositions were generated using two organic solvents (acetonitril or methanol) and aqueous buffers with controlled pH, between 2.5 and 7.5. The temperature interval used for the aim of this study was between 20 °C and 50 °C. The dead time value for calculating the retention factor was measured from the retention time of uracil, under the same elution condition with studied compound (sildenafil).

This study showed that the experimental dependence of ln k on T^{-1} is influenced by the pH of the aqueous component, as well as by the organic modifier used for the mobile phase. From the thermodynamic analysis of the non-linear van't Hoff plots, resulted two different contributions of the enthalpy and entropy to the retention process. In almost all situations, these plots have a maximum on the studied temperature interval, showing that the retention process can be entropy-driven within the interval of 25 °C and the temperature corresponding to the maximum retention, and then the retention process becomes enthalpy-driven.

Deviations from linearity of the van't Hoff dependence can be assigned to the possible structural modifications of sildenafil, under various eluting conditions and temperature. These structures may generate multiple interactions between analyte and the stationary phase, characterized by different values of the standard free enthalpy that are included in the relationship of partition equilibrium constant K on temperature.

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Extended Abstract

Composite Hydrogels Based on Poly (Methacrilyc Acid) Reinforced with Laponite Inorganic Filler †

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Keywords: hydrogels; composite; inorganic filler; swelling; mechanical properties

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Polymeric hydrogels are soft materials that can absorb large amounts of water or biological fluids without dissolving. The three-dimensional network of a hydrogel is made up of hydrophilic polymer chains that are physically or chemically cross-linked. An important drawback of most hydrogels is their low mechanical strength, which can be improved by forming (nano)composites with clay as the filler.

The aim of this study was to synthesize composite hydrogels based on poly(methacrylic acid) and different concentrations of Laponite. These syntheses were conducted via free radical copolymerization in the presence of N,N′-methylenebisacrylamide as a crosslinking agent and ammonium persulfate as the initiator.

The obtained materials were characterized by FT-IR, X-ray diffraction, microscopy analyses (SEM, TEM), rheological measurements, and swelling studies. The rheological measurements proved that both storage and loss moduli increased with Laponite concentrations. The FTIR and XRD analyses confirmed the incorporation of the clay into the poly(methacrylic acid) hydrogel matrix and also the interactions between the inorganic filler and the polymer chain [1]. The swelling degree was influenced by the amount of Laponite incorporated into the polymer matrix. All hydrogels demonstrated porous architectures as observed by microscopy analyses.

Newly synthesized composite hydrogels based on different concentrations of Laponite were prepared and their properties were tested. Due to the fact that hydrogel properties can be modulated by Laponite concentrations, the designed materials are suitable candidates for pH sensitive controlled drug delivery.

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Extended Abstract

Evaluation of Fish Hydrolyzate Interaction with Skin Cells †

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Keywords: peptides; cytotoxicity; cytoskeleton; wound healing

Fish proteins and peptides are well-known for a plethora of biological activities and medicinal value. Fish bones and scales contain mainly type I collagen fibers and hydroxyapatite $Ca_{10}(OH)_2(PO_4)_6$ [1] and represent one of the major source of solid waste generated by the fish processing industry. Recovery of bioactive peptides from these fish by-products brings new perspectives on the wound healing process and is part of developing bioeconomy. In this study, we have evaluated the interaction of fish-derived peptides with fibroblasts and keratinocyte cells, in experimental models in vitro, to show their biomedical potential use for skin tissue regeneration.

Fish hydrolyzate was enzymatically obtained by papain digestion of minced and decalcified bones of *Hypophthalmichthys molitrix* (silver carp). The solution was subjected to centrifugal filtration using membranes with a molecular weight cut-off of 3 kDa, and its protein content was determined by BCA assay. The cytotoxicity of peptides was tested, at different concentrations, in NCTC mouse fibroblasts and HaCaT human keratinocytes cultivated with or without fetal serum, using MTT assay [2]. Their effect on skin cell migration was measured using in vitro scratch assay, after 24 h of cultivation in standard conditions [3]. Cellular and cytoskeleton morphology changes were analyzed by immunofluorescence microscopy after cells were stained with TRITC-phalloidin and anti-tubulin antibodies. Statistical analysis was performed using one-tailed paired Student t-test.

Fish hydrolyzate was not cytotoxic in a wide range of concentrations. At low concentrations, both skin cells cultivated in the presence of fish peptides presented a significantly higher ($p < 0.05$) cell proliferation, compared to untreated cells (control). The images captured overnight, after scratched cell cultures incubation with fish peptides, showed that the cell monolayer was more rapidly formed in treated cell cultures. These observations indicated that fish hydrolyzate stimulated the migration of skin cells, probably due to the presence of Gly-Pro-X and Gly-X-Hyp sequences, frequently encountered in the collagen molecule, and known to be involved in fibroblast activity [4]. No alterations in cell morphology and cytoskeletal structures were observed.

Taken together, our results demonstrated that the enzymatic fish hydrolyzate was efficient in wound healing models in vitro, and had valuable properties which recommend it as a promising solution for tissue regeneration applications.

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Extended Abstract

Voltammetric Analysis of Sulfamethoxazole on Disposable Graphite Electrodes †

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Keywords: disposable pencil graphite electrode; sulfamethoxazole; voltammetry

Sulfamethoxazole (SMX) is a sulfonamide antibiotic used in the treatment of digestive, bronchopulmonary, and urinary tract infections. In pharmaceutical preparations, it is often associated with the antibacterial drug trimethoprim (TMP). Studies have shown that SMX and TMP are among the emerging micropollutants of the aquatic environment leading to high resistance of the bacteria to these compounds [1]. Thus, simple and sensitive methods are required for their quantification in different matrices. The voltammetric measurements are often a better choice even more if cheap, disposable working electrodes, like pencil graphite electrodes (PGE) [2], are used. This work presents the electrochemical behavior of SMX at the PGE and the new developed differential pulse voltammetric method for its determination.

The SMX working solutions were obtained by successive dilutions with the corresponding supporting electrolyte of the daily prepared 10^{-3} M ethanolic stock solution. Voltammetric recordings were carried out on an Autolab PGSTAT 12 electrochemical system equipped with a three electrodes measurement cell (working electrode: PGE) [3] and a PC running GPES 4.9 software.

Using the differential pulse voltammetry (DPV) to study the SMX electrooxidation on the glassy carbon electrode, the Pt electrode and the graphite leads electrode of different hardness (2H, H, HB, 2B and B) it was noticed that the best signal was obtained on type B mines. Electrochemical activation of PGE did not lead to any improvement of the SMX signal. The recording of five repeated cyclic voltammograms has demonstrated that SMX oxidation signal decreased when the scans number increased so it was necessary to use another pencil lead for each voltammetric measurements. The influence of the nature and pH of the supporting electrolyte emphasized that the highest DPV signal of SMX was obtained in Britton Robinson Buffer (BRB) pH 7.96. In the diffusion-controlled oxidation process of SMX on PGE $2e^-$ and $1H^+$ are involved. It was shown that SMX is not accumulated by adsorption on the PGE. Under the optimum working conditions (PGE B, BRB pH 7.96), the DPV oxidation peak of the SMX varied linearly with the analyte concentration in the range 1.0×10^{-5}–1.9×10^{-4} M SMX. The repeatability of the electrode response expressed as percentage relative standard deviation was 5.5 % for a concentration of 4.8×10^{-5} M SMX.

The developed DPV method has applicability in the determination of SMX from pharmaceutical products (tablets) and the PGE is cheap and easy commercially available.

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Extended Abstract

Indoor Shooting Range Ventilation Systems †

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Keywords: shooting range; ventilation; 9 × 19 mm cartridge; toxic fumes

It is understood that bullets are dangerous, assuming that they are fired into a body at high velocity. However, there are other ways in which a bullet can cause harm, such as through the emission of toxic fumes and metals. Performing experimental shooting with 9 × 19 mm caliber weapons systems leads to certain reaction products being generated in quantities that can exceed the exposure limits of the human body. Carbon monoxide (CO) and ammonia (NH_3) are typical components of the fumes that result during shooting. These gases, in addition to smoke particles, can cause symptoms such as nausea, headache, and coughing. Exposure to high concentrations of CO over time can ultimately lead to unconsciousness and death.

Experimental measurements were made for 10 9 × 19 mm caliber cartridges. Under special training conditions, in 1 h, more than 1000 fired cartridges can be produced. In order to keep the indoor air quality at an acceptable level, recirculation of the airflow must be prevented, so the ventilation or air conditioning system's air should be taken from the outside. The minimum fresh airflow is calculated to satisfy the following conditions: the dilution of harmful substances and the maintaining of healthy conditions.

For a given number of fired cartridges, the volumetric mass of the substances with harmful potential obtained is 4.69 g/m^3, as detailed in Figure 1, while the total occupied volume is 3.68 m^3, at standard atmospheric conditions, as shown in Figure 2. In order to dilute these toxic reaction products, the minimum fresh airflow calculated is 891.6704 m^3/h. Also, the minimum fresh airflow needed to maintain safe conditions is 375 m^3/h.

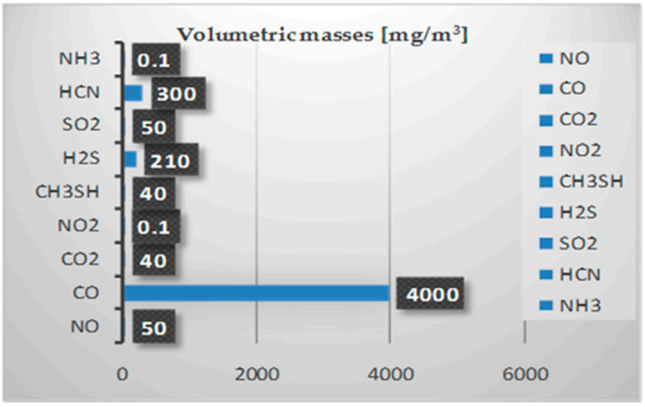

Figure 1. Percentage of substances with harmful potential.

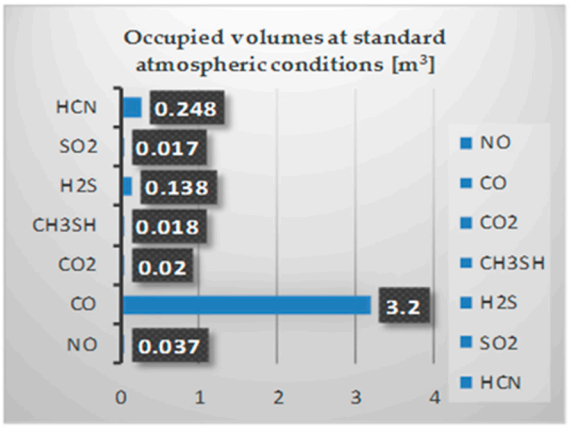

Figure 2. Occupied volumes at standard atmospheric conditions.

In order to prevent health risks due to the emissions of fumes from the use of weapons and ammunition, adequate ventilation and the use of protective measures are mandatory.

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Extended Abstract

Spectrofluorimetric Analyses of Ciprofloxacin and Norfloxacin †

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Keywords: ciprofloxacin; norfloxacin; fluoroquinolones; spectrofluorimetry

The fluoroquinolones (FQ) ciprofloxacin (CIP) and norfloxacin (NOR) are used as broad-spectrum antibacterial agents [1]. CIP is an antibiotic to which most gram-negative bacteria are highly susceptible in vitro and to which many gram-positive bacteria are susceptible or moderately susceptible. Unlike most broad-spectrum antibacterial drugs, ciprofloxacin is effective after oral or intravenous administration [2]. NOR is an antibacterial agent with activity against most gram-negative pathogens, and which is also active against *Pseudomonas aeruginosa* and some gram-positive organisms [3]. There has been an increase in the use of FQs in animal production, which has inevitably generated residues in animal origin foodstuff. These residual drugs cause an in vivo-accumulation, and in the long-term they may determine drug tolerance and have carcinogenesis, teratogenesis, and mutagenesis potential. This work presents a simple, sensitive, and accurate spectrofluorimetric method for CP and NOR assessment, using Al (III) as an enhancer.

The CIP and NOR solutions were obtained by dissolving the needed quantity in water to prepare solutions of 200 ppm, and Al (III) 44×10^{-3} M and Ce (III) 10^{-5} M solutions were used as reagents. Measurements were carried out on a spectrofluorimeter (FP–6500, Jasco, Japan) with a working range of 220–750 nm for excitation and emission wavelength.

After performing a spectrometric study, the optimum wavelength for excitation of CIP and NOR solutions was set at 275 nm, for which both CIP and NOR have a maximum emission at 445 nm. The study of the influence of pH on the fluorescence of the analytes did not produce any improvement of the fluorescence signal. The presence of metal ions can increase the intensity of the fluorescence radiation and improve the shape of the signals in the fluorescence spectrum, as observed in the presence of the Al (III) ion for both CIP and NOR. The Ce (III) ion brings an improvement to the fluorescence signal for CIP, while its presence in a NOR solution does not greatly influence the signal intensity or shape. The method is linear in the range of 0.05–1 ppm, and has a detection limit of 4.48 ppb for CIP and 0.78 ppb for NOR, with a relative standard deviation below 1.01% for CIP, whereas for NOR it is below 0.3%.

The experiment indicates that Al (III) could enhance the fluorescence intensity of CIP and NOR under optimum complexation reaction conditions. The proposed method has the advantages of simplicity, sensitivity, and reproducibility, and can be applied for FQs stability tests.

Acknowledgments: This work was supported by the University of Bucharest; research grant number 1490/2019.

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Abstract

Antioxidant Properties and Cytoprotective Effect Against H_2O_2-Induced Cytotoxicity in Mouse Fibroblasts Cells (L-929) of Horseradish Leaves †

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Keywords: *Armoracia rusticana*; antioxidant activity; cytotoxicity; cytoprotective effect

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Horseradish (*Armoracia rusticana* L.) is a perennial plant from the Brassicaceae family native to Europe and Asia, and globally widespread through cultivation. Horseradish contains phenolic compounds (flavonoids and phenolic acids), vitamins (C and B1), minerals (iron, potassium, calcium and magnesium), and essential oils (sinigrin) [1,2]. Roots, leaves and/or isolated compounds from horseradish possess antioxidant, antimicrobial, chemopreventive, anti-inflammatory, gastroprotective and hypocholesterolaemic activities [3,4]. The aim of this paper was to investigate the antioxidative activity, in vitro citotoxicity, and in vitro cytoprotective effect of *A. rusticana* (leaves) against H_2O_2-induced cytotoxicity in mouse fibroblasts cells (L-929).

Plant material—leaves of *A. rusticana*—were harvested from Dambovita County, Romania, Europe. The antioxidant activity was assessed using the Sanchez-Moreno assay [5]. In vitro cytotoxicity of the plant extract on L-929 murine fibroblast cell line was evaluated through MTS method. The protective effect of *A. rusticana* against oxidative stress on L-929 mouse fibroblast cells was performed by pretreatment with different concentrations of *A. rusticana* (5, 10, 25 μg/mL) for one hour and for 24 h before exposing to H_2O_2 to induce oxidative stress.

The present investigation showed that *A. rusticana* extracts have a moderate cytotoxic activity (IC_{50} = 70.40 ± 0.305 μg/mL) and a significant antioxidant effect. A prolonged pretreatment (24 h) with *A. rusticana* extract was able to protect L-929 murine fibroblast cells against H_2O_2-induced cytotoxicity, while in the case of the short-term pretreatment (one hour) almost no effect was observed.

The results suggest that horseradish leaves exert great potential for the development of dietary supplements.

Acknowledgments: This work was supported by the Ministry of Education and Scientific Research, grant numbers: PN 19-41 041 01/ 2019 and PN 1627-03-02.

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Extended Abstract

Alternative Methods for Antioxidants Determination †

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Keywords: antioxidants; glassy carbon electrode; ellagic acid; voltammetry

Ellagic acid (EA) is a fused four-ring polyphenol found in numerous vegetables, fruits, seeds, and some nuts. Interest in EA has increased during the past few years due to its antioxidant, antiviral, antimutagenic, and anticarcinogenic effects [1]. Furthermore, EA has been marketed as a dietary supplement with a range of claimed benefits against cancer, heart disease, and other medical problems. Extracts from raspberry leaves or seeds, pomegranates, or other sources contain high levels of EA and are available as dietary supplements and juices. EA is known as a stable redox active system only in organic medium, but irreversibly oxidized with coupled chemical reactions showing ill-defined redox peaks in aqueous solutions. This work presents the electrochemical behavior of ellagic acid at the glassy carbon electrode (GCE) in different supporting media.

The EA working solutions were obtained by successive dilutions with the corresponding supporting electrolyte of the daily prepared 10^{-3} M methanolic stock solution. Voltammetric recordings were carried out on an Autolab PGSTAT 12 electrochemical system (Metrohm Autolab B.V., Utrecht, The Netherlands) equipped with a three electrodes measurement cell (working electrode: GCE) and a PC running GPES 4.9 software.

Using cyclic voltammetry (CV), the electrochemical behavior of EA against three different working electrodes was studied: a platinum electrode, a gold electrode, and a GCE. The best signal was obtained with the GCE, when an oxidation peak characteristic of the EA was observed, which begins to separate into two distinct peaks as the scan rate increases. The influence of the nature and pH of the supporting electrolyte emphasized that the highest DPV signal of EA was obtained in acidic medium. The dependence of the potential at which the oxidation peak appears as a function of acid pH was linear, indicating that the reaction from the surface of the indicator electrode is carried out by the exchange of an equal number of electrons and protons. The influence of the scan rate applied to the indicator electrode was studied by cyclic voltammetry in the 25–150 mV/s range. The graphical representations show a linear dependence of the anodic current on the radical from the scan speed, which means that the electrochemical process from the electrode surface is controlled by diffusion.

In order to verify the stability of the electrochemical response of the EA, six consecutive voltammograms were recorded, under different experimental conditions. The difference in intensity between the first scan and the next five is very large, indicating the adsorption of EA on the electrode surface. In this sign, a solution of EA in sodium hydroxide was prepared, and the behavior of the analyte was investigated with respect to an HB pencil graphite electrode (PGE). The results obtained did not differ from those for which the ellagic acid was dissolved in alcohol.

The performed studies on EA electrochemical behavior are promising for the development and application of a voltammetric method for the antioxidant determination of pharmaceutical products.

Acknowledgements: This work was supported by the University of Bucharest, research grand number 1490/2019.

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Abstract

Colored Coating Materials with Spectrally Selective Reflectance for Woodland Camouflage Textile Fabrics †

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Keywords: hybrids; dyes; camouflage; coatings; reflectance; serigraphy

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The camouflage effect aims to reproduce natural or artificial surroundings in terms of color, pattern, texture and gloss [1]. The objective of this work is to obtain pigment materials, with controlled reflectance in the Vis-NIR range, by sequestering some cationic dyes in an achromatic layered silicate, and to use the hybrid pigments in serigraphic pastes for printing camouflage patterns on textile fabrics.

Melacryl dyes (Colorom) were deposited on Kaolinite (Merck) from aqueous solutions, using an ultrasonic processor (Sonics, VCX-750). The colored materials were subsequently used to prepare serigraphic printing pastes by embedding them into a water soluble vinyl acrylic aqueous dispersion self-cross linkable at moderate temperature—Tubvinyl 235 MC (CHT), using an automatic pigment mulling machine (J. Engelsmann AG).

A high coloring power cationic dyes, with increased affinity for achromatic Kaolinite filler, were selected in order to obtain hybrid pigments having fundamental colors. The camouflage colors were obtained by mixing the hybrid pigments in certain ratio, in order to fulfill the shades, which mimic the Vis-NIR reflectance pattern of forest-type surroundings. In order to tune-up the reflectance profile, white and black extender pigments, with optimized NIR reflectance, were added in small proportions to the mixture. The acrylic resin was selected because it provides the optimum value of the ratio between the refractive index of the hybrid pigments and the binder, in order to minimize the emission from the surface due to backscattering. It is worth mentioning that the printing pastes exhibit low absorption throughout the entire spectral range of interest.

Hybrid materials with fundamental colors were successfully obtained. Some colored coating materials, having military recommended spectral characteristics for woodland camouflage pattern, were prepared using trichromy formulation (Figure 1). Textile fabrics, printed with the serigraphic pastes, meet the requirements of the military camouflage standards and specifications.

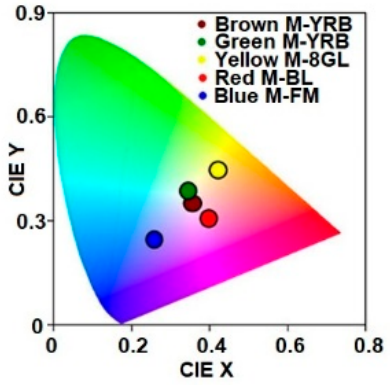

Figure 1. Chromaticity coordinates of colored fabrics.

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Extended Abstract

Flavor Profile for Fusel Oil Pyrazines †

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Keywords: sensory analysis; flavor profile; pyrazines

The aim of the research was to identify the flavor profile and the sensory performance in food matrix applications of new natural flavors extracted from food industry residue (fusel oils). The pyrazine samples were obtained through innovative eco-friendly technology (supported liquid membrane—SML) with one or more organic solvents.

The method used to identify the flavor profile of pyrazines was according to ISO 6564 (Sensory analysis—Methodology-Flavor profile methods). A panel of four experts trained according with ISO 8586 in two stages (several training sessions) using reference substances evaluated the intensity of flavor using a spider diagram, which was based on eight sensory descriptors (coffee, cocoa, chocolate, nutty, sweet, vegetable, potato, roasted meat). In the first stage, they were trained on food flavors with monodimensional profile (cocoa, chocolate, coffee, and nutty) to familiarize themselves with these kind of flavors. In the second stage the training was done using three types of mixtures with commercial pyrazines with multidimensional profile. The food matrix (filling cream) was selected and prepared in such way as to be neutral in terms of smell and taste, and blended with the pyrazines samples. Seven samples of pyrazines and the food matrix were analyzed by conducting a survey with this type of diagram.

For these samples, we had identified two levels of the profile (the main level—with the highest intensity of the descriptors, and the second one—with low intensity of the descriptors). Four samples with a flavor profile above the average intensity of the descriptors, ≥3, were selected to be mixed with the food matrix.

The new natural flavors (from a mixture of pyrazines) obtained through SML technology had developed a sensory profile characterized by two descriptors (cocoa and chocolate). These new natural flavors contributed at the improvement of food products sensory performance.

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Abstract

Synthesis and Physico-Chemical Characterization of the Cu(II), Pd(II) and Ru(III) Complexes with Difloxacin †

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Keywords: quinolones; difloxacin; metal-complexes

The growing interest in metal-quinolone complexes is sustained by a large number of compounds obtained and tested for antibacterial [1], antitumoral [1,2], antifungal [1], and antiparasitic [3] properties. Having these aspects in mind, in this study, the interaction of difloxacin, a second-generation quinolone with veterinary use, with some transition metal ions was investigated.

Four metal complexes of difloxacin were synthesized in different media (weakly acidic: Cu(II) and Ru(III) complexes, weakly basic: Cu(II) complex and neutral: Pd(II) complex) and characterized with physicochemical techniques (elemental analysis, conductivity measurements, IR, UV-Vis spectroscopy) and thermal analysis (TG, DTG, DTA).

Three of the compounds present the characteristic IR absorption bands for the $\nu_{(OCO)}$ symmetric and antisymmetric bands. The difference between the two values is around 200 units, confirming that the carboxylate moiety is bound as monodentate, while the quinolone molecule is acting as a bidentate deprotonated ligand, bounded to the metalion through the pyridone and one carboxylate oxygen [4]. This is not the case of the Cu(II) complex obtained in acidic medium, as it occurs as a salt of the tetrachlorocuprate(II) complex ion. These conclusions are confirmed by the UV-visible spectra and thermal analysis. The intermediate steps corresponding to the quinolone moiety oxidative degradation were also highlighted.

Based on these findings, we propose the chemical formulas for the four synthesized compounds, which will further be subjected to DNA, serum albumin binding, and antimicrobial testing.

Acknowledgments: This research was financially supported by "Carol Davila" University of Medicine and Pharmacy through Contract no. 23PFE/17.10.2018 funded by the Ministry of Research and Innovation within PNCDI III, Program 1—Development of the National RD system, Subprogram 1.2—Institutional Performance—RDI excellence funding projects.

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Extended Abstract

Anti-Inflammatory Activity of Biomaterials Intended for Periodontal Disease Treatment †

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Keywords: collagen; fibronectin; cytotoxicity; cytokine

Periodontal disease is associated with chronic tissue inflammation, which besides bacterial plaque can lead to enzymatic degradation of the extracellular matrix components from the periodontal ligament, cementum, and alveolar bone [1]. Several studies have reported an increased level of pro-inflammatory cytokines, but also apoptosis events that resulted in cell detachment from the extracellular matrix [2]. The aim of this study was to evaluate the anti-inflammatory activity of natural polymeric biomaterials enriched with silver nanoparticles, in view of their use for periodontitis treatment.

Two types of biomaterials were prepared, one as a polymeric composite based on components of the extracellular matrix, collagen, chondroitin sulfate, and fibronectin [3] and one as a hybrid material by adding silver nanoparticles. Ultrastructural observations were performed by SEM with a Hitachi SU 1510 equipment (Tokyo, Japan), operated at 15 kV, in nitrogen atmosphere. To determine the anti-inflammatory activity, THP-1 cells (ATCC) inflamed with bacterial lipopolysaccharide were cultivated in the presence of biomaterials for 24 h and then the culture medium was analyzed for interleukin-1β (IL-1β) and tumor necrosis factor alfa (TNF-α) pro-inflammatory cytokines level using sandwich ELISA kits (R&D Systems Inc., Minneapolis, MN, USA). Statistical analysis was performed using Student *t*-test.

SEM images showed the presence of silver nanoparticles mainly on collagen fibrils and their homogeneously distribution within the polymeric matrix. Unlike the polymeric composite, the hybrid material presented a significant inhibition (60–70%; $p < 0.05$) of pro-inflammatory cytokines secretion (Figure 1). This effect was probably due to silver nanoparticles interference in distinct signaling pathways preventing cell proliferation, as discussed in previous studies [4].

The presence of silver nanoparticles within the hybrid material represented a clear advantage by increasing its anti-inflammatory activity and demonstrating its possible application in periodontitis treatment.

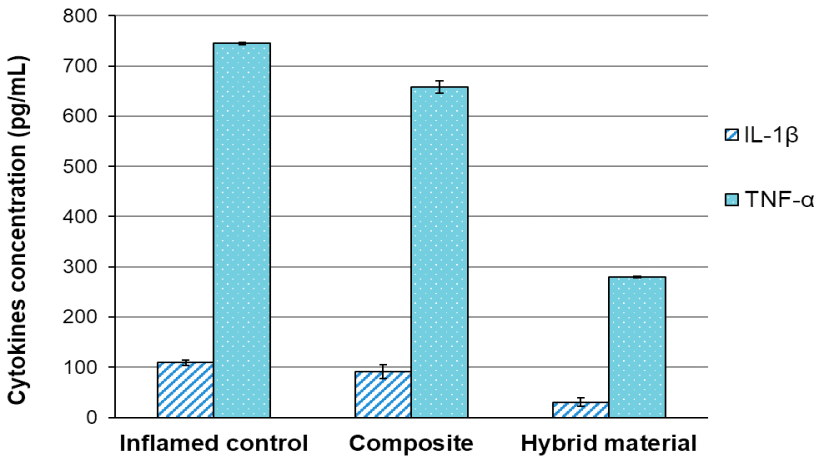

Figure 1. The effect of polymeric biomaterials on secretion of IL-1β and TNF-α in inflamed THP-1 cells, determined by ELISA sandwich assay. * $p < 0.05$.

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Abstract

Characterization of Novel Hybrid Materials Conditioned as Sheets for Skin Repair †

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Keywords: composites; collagen; elastin; silver nanoparticles

The association of natural or synthetic polymers with metal nanoparticles resulted in hybrid materials with improved chemical, physical, and biological properties for the repair of human tissues [1]. Collagen (COL) is a natural polymer and the main protein of skin extracellular matrix, providing high tensile strength to this tissue [2]. Skin proteoglycans decorated with chondroitin sulfate (CS) chains are involved in maintenance of water in the tissue, due to their numerous negatively charged carboxyl and sulfate groups but also in controlling the cell behavior [3]. Elastin (EL) as a protein polymer confers resilience to skin, while soluble EL peptides take part in processes that prevent and regulate skin photoaging [4]. The aim of this study was to evaluate optimal formulations of hybrid materials based on natural polymers, COL, CS, and EL, combined with nanosilver (nAg) for physico-chemical and structural properties, as well as for their interaction with skin cells, in order to provide temporary dressings for skin lesion repair.

Two variants of hybrid materials were prepared by vigorous mixing of COL, CS, k-EL, and nAg, in weight ratios of 10:1:0.5:0.01 (A) and 10:1:1:0.01 (B) and conditioned as thin, elastic membranes by drying in the oven. Density/porosity, swelling degree, and biodegradation were comparatively determined. SEM observations were performed to investigate their microstructure and nAg distribution. In vitro cytotoxicity tests were conducted in L929 mouse fibroblasts using the MTT assay. Cell viability and adhesion of fibroblasts to the hybrid materials were assessed by fluorescence microscopy using Live&Dead kit and phalloidin/DAPI staining.

The porosity and swelling degree were higher for variant A membrane, compared to variant B, even if they contained the same quantity of CS, responsible for water absorption. Membrane incubation in physiological conditions (PBS) for seven days revealed higher stability of variant B, in correlation with its lower swelling degree. However, both membranes exhibited a similar pattern of biodegradation in the presence of collagenase, indicating that an increase of EL amount did not influence the cross-linking of polymeric fibers, and the situs for collagenase attack remained exposed. The hybrid materials showed a dense, microporous structure with tight interaction between polymeric fibrils and a homogeneous distribution of nAg even for swelled samples. Both hybrid materials showed no cytotoxic effect in vitro and stimulated fibroblasts proliferation, especially in case of variant B. Moreover, good adhesion of cells was observed at the surface of hybrid materials after 48 h of cultivation.

All these results demonstrated that the hybrid material with higher concentration of elastin presented good properties to act as an efficient skin wound dressing.

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Abstract

Quality Profile Evaluation of Topical Semi-Solid Systems with Ibuprofen †

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Keywords: hydrogel; carbopol; ibuprofen; kinetics release; flow behavior

The topical administration of non-steroidal anti-inflammatory drugs is described as an alternative route for inflammatory disease treatment and is frequently used because it determines local effects therapeutically, similar to oral administration, but with fewer side effects. The quality control of this type of product is not fully standardized due to technological particularities and the administration route. The aim of this study was to assess the quality profile of topical drug systems such as hydrogels with carbopol and ibuprofen [1,2].

Four hydrogels containing carbopol as gelling polymer and ibuprofen (5% and 10%, respectively) were tested. The hydrogels were evaluated in terms of macroscopic, rheological, and kinetic characteristics. The flow behavior was carried out using a rotational viscometer, at 33 °C and the rheograms, i.e., viscosity versus shear rate, were plotted. The analysis of ibuprofen release kinetics from the hydrogels was performed using two different approaches: Dynamic condition (modified Franz diffusion cell) and static condition (vertical diffusion cell—VDC) [3].

The hydrogels tested at 33 °C presented a non-Newtonian pseudoplastic behavior, the viscosity decreasing with the shear rate increase. The flow profiles were investigated by fitting the Power law model. The release tests in static conditions showed a faster diffusion of ibuprofen, and the release profiles indicated a constant phase after 240 min. On the other hand, the tests performed in a dynamic regime showed that the release of ibuprofen was slower and the constant phase was not reached after 480 min. The square root of time kinetic model fitted the ibuprofen release data, and the diffusion coefficient specific to the Higuchi model was determined [4].

The pseudoplastic behavior is a desirable property for topical systems, both in terms of conditioning and spreadability on the skin, and the formation of a continuous film at the application site. The VDC test is more discriminatory than the other one. For the samples that contain a higher concentration of ibuprofen, a little volume and a static regime of VDC can prevent maintaining sink conditions, and the dynamic method is preferred in this case [5].

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Abstract

The Nanomechanical and Tribological Properties of Polyamide/Hydrotalcite Nanocomposites †

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Keywords: bio-PA nanocomposites; LDH; nanoindentation; nanoscratching

In specific fields of the industry (e.g., aircraft and automotive industry), plastic materials with high performance (improved scratch resistance, fire resistance, thermal stability, and high mechanical properties) are required. In recent years, the interest in nanocomposites based on bio-polymers and nanofillers has grown, as they are a successful alternative to petroleum-based plastics. Both petroleum-based and bio-based polyamides (petro-based PA and bio-PA) are high performance materials that are highly attractive for specific applications. Good effects on improving flame retardancy and thermal stability had been found for polymer matrices containing modified layered double hydroxides (LDH) as nanofiller [1,2]. Usually, for uniform dispersion of nanofiller in the polymer matrix and obtaining homogeneous composites, different dispersion agents are added [3], and a nanoscratching technique can be used in order to measure a wide range of local mechanical properties (hardness, stiffness, reduced modulus, friction coefficient, roughness, etc.) for homogenous and heterogeneous materials [4]. In this study, the behavior in nanoindentation and nanoscratching of bio-PA/LDH nanocomposites, in comparison to petro-based PA/LDH nanocomposites, were studied. The nanomechanical and tribological properties were investigated and compared with dynamic-mechanical and thermal properties of nanocomposites. The dispersion of LDH in the polymer matrix as well as their interactions were explained based on both the results of the mechanical properties and the surface damage mechanism.

Two commercial polyamides (PA10.10 and PA6), layered double hydroxide (LDH), and ethylene bis(stearamide) (EBS) were used. PA nanocomposites with 5 wt. % of LDH and LDH treated with EBS were obtained in dynamical conditions by the melt processing method. The nanoindentation and nanoscratch tests were performed at room temperature on a TI Premier system (Hysitron Inc., Minneapolis, MN, USA) using a three-side pyramidal Berkovich tip. Thermal analyses were performed on the TH-Q 5000IR and DSC Q2000 (TA Instruments, New Castle, DE, USA). Dynamic mechanical analysis was performed using the DMA Q800 (TA Instrument).

The addition of LDH and EBS in both PA 10.10 and PA 6 led to changes of both rigidity and hardness as well as of the elastic behavior and scratch resistance of nanocomposites when compared to the neat polyamides. The results proved that there is a strong interaction between the nanofiller and the polymer matrix when EBS was used. The best results were obtained in the case of the nanocomposite based on PA10.10 and LDH treated with EBS (elastic modulus and hardness were higher by 20% compared with neat PA 10.10). Furthermore, this nanocomposite showed more resistance against deformation caused by normal loads but had smaller elastic recovery compared

with the nanocomposite based on PA and untreated LDH. The friction coefficient and the roughness of PA nanocomposites were higher than for neat PA.

The addition of hydrotalcite into polyamide should provide the nanocomposite materials with improved bulk and surface properties, which in turn can find applications in an industry that requires materials with high performances.

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Abstract

Poly(2-isopropenyl-2-oxazoline) as a Versatile Platform for Multi-Functional Materials †

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Keywords: smart materials; responsive polymers; hydrogels; thermoresponsive; photoresponsive

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Multifunctional materials are designed to meet specific requirements through tailored properties. Nowadays, there is a high demand for "smart" materials with integrated functionalities that make them responsive to multiple stimuli, switchable, and adaptive. [1] "Smart" or stimuli-responsive materials can alter their chemical and/or physical properties upon exposure to external stimuli. The development of specialized stimuli-responsive polymers with potential applications in harvesting the photomechanical energy, healable hard coatings, self-repellent surfaces, detecting, and sensing is witnessing exciting progress. [2] Recently, we developed an unprecedentedly versatile protocol to yield smart materials with promising potential as temperature sensors, [3] ophthalmologic biomaterials, [4] materials for detection and sensing applications, [5] and water purification materials. [6] The method is based on the ring opening addition reaction of poly(2-isopropenyl-2-oxazoline) (PiPOx), which is a hydrophilic and biocompatible polymer, with (di)carboxylic acids yielding polymeric materials with an esteramide structure. The key aspects that differentiate this work from other competitive studies is that the polymer modification reaction (or crosslinking reaction) is "clean" and does not require a catalyst, and that no by-products are formed. Due to these advantages, together with the wide range of available (di)carboxylic acids, we demonstrated that this protocol can be easily adapted to develop polymeric materials that respond to temperature, light, pH, amines, metal ions, and CO_2. Hydrogel materials have been developed via crosslinking with dicarboxylic acids with properties that can easily be tuned from soft, to ultra-tough or elastic, simply by altering the nature of the crosslinker, enabling their potential use as ophthalmologic to water purification materials.

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Abstract

In Vitro Effect of Fungal Chitosan on Tumoral Cells and Microbial Cultures †

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Keywords: polysaccharides; Ganoderma lucidum; cytotoxicity

The ability of marine chitosan to be processed as films or hydrogels makes it a suitable candidate for applications in key areas, such as medicine, environmental protection, agriculture, and cosmetics [1]. Recently, some polysaccharides from *Ganoderma lucidum* have been reported as a potential alternatives to commercial shrimp chitosan for biomedical applications [2,3]. The aim of this study was to evaluate the in vitro interaction of fungal chitosan-rich preparations, extracted by chemical and enzymatic methods from *G. lucidum* with normal, tumoral, and microbial cultures.

Chitosan was chemically extracted (C1) by serial treatment of *G. lucidum* powder with 4M NaOH and 1% HCl. Enzymatically extracted chitosan (C2) was obtained by alkaline treatment in 11M NaOH, at 100 °C and incubation with α-amylase (Protemyl) at 85 °C, for 3 h. The chitosan extracted from shrimps (CS) was purchased from Sigma-Aldrich and used as a control. The anti-proliferative activity of chitosan was determined in Hep-2 carcinoma cells and cytotoxicity in normal fibroblasts from NCTC clone L929 cell line using methylthiazolyldiphenyl-tetrazolium bromide (MTT) assay [4]. Several concentrations of extracts were added in the culture medium and cultivated for 48 h. Cell morphology observations were performed in treated cell cultures after Giemsa staining. The antimicrobial activity of chitosan extracts was investigated on two pathogenic bacterial species, *Staphylococcus aureus* (ATCC 25923) and *Pseudomonas aeruginosa* (ATCC 27853) using disc diffusion method and incubation at 37 °C, for 24 h.

The in vitro test results showed that C1 and C2 fungal chitosan extracts, as well as the CS control sample, did not affect the cell viability of normal NCTC cells in the range of concentrations 50–1000 μg/mL. Incubation of samples with Hep-2 carcinoma cells indicated a significant anti-proliferative activity in the range of concentrations 500–1000 μg/mL, similar to CS control sample. Cell morphology observations showed a normal phenotype of fibroblast cells cultured in the presence of both chitosan extracts, while concentrations of over 500 μg/mL led to morphological changes of Hep-2 tumoral cells. All tested samples interfered with bacterial growth. Thus, the images of bacterial cultures showed the appearance of inhibition zones around chitosan extracts. The measured diameter was higher for C1 extract than that for C2 extract.

Fungal chitosan extracts exhibited anti-proliferative effects on human carcinoma cells and efficiently inhibited microbial growth, suggesting significant biomedical potential.

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Extended Abstract

Preparation and Characterization of Vegetable Oil-Based Microemulsions †

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Keywords: microemulsion; vegetable oil; biocompatibility

Microemulsions are thermodynamically stable and transparent systems composed of an aqueous phase, oil, a surfactant, and usually also contain a co-surfactant [1]. They have the capacity to incorporate large quantities of hydrophilic and lipophilic active principles, protecting them from degradative reactions and ensuring delivery of the cosmetic actives [2]. Due to these characteristics, microemulsions are adequate for the delivery of topical cosmetic actives. In order to create microemulsions with dermatocosmetic applications, grape seed oil was used as the oily phase, Tween 80 and plurol diisostearique CG as the surfactant blend, and ethanol as a co-surfactant for some of the samples. All components are safe for skin and are used as cosmetic ingredients. The obtained systems (Figure 1) were physically characterized based on electrical conductivity, dynamic light scattering, and rheometric measurements.

Figure 1. Appearance of the W IV microemulsions.

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Abstract

Novel Formulations of PEG–Silica Phase-Changing Materials (PCMs) with Applications in Passive Storage of Thermal Energy †

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Keywords: thermal energy storage; phase-changing materials; PEG-silica hybrids; latent heat storage; polycrystalline polymers

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The aim of the present study is to design new PEG–silica hybrids (PEG_x–Si) as phase changing materials that can be integrated into construction elements for green buildings with positive impacts on different aspects such as saving of primary energy (expensive energy), reduction of maintenance costs (economic aspect), and increasing the thermal comfort of the inhabitants (environmental aspects) [1]. In order to prevent PEG's flow or solubilization, it needs to be stabilized or incorporated in different matrices while retaining its thermal energy storage capacity [2]. Our approach to overcome these problems consists in the covalent bonding of a fraction of PEG chains to an in situ generated silica network, forming the so-called PEG–silica hybrid systems. (Figure 1).

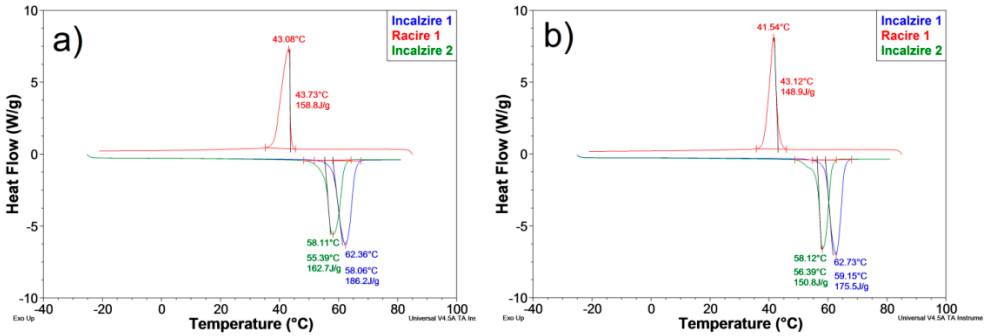

Figure 1. DSC curves of mixtures of PEG_{4000}–Si with (**a**) PEG_{4000} and (**b**) PEG_{6000} at a 1:1 ratio (grav.).

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Extended Abstract

Improved Method for Determination of Chemical and Radiochemical Purity †

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Keywords: radiopharmaceutical; chemical purity; 2-[^{18}F]fluoro-2-deoxy-D-glucose products; validation; radio-HPLC

Radiopharmaceuticals are radioactive compounds that have in their structure a radioisotope attached to drugs, which accumulate in certain organs or tissues. The radioisotope undergoes decay processes that result in specific amounts of radiation, which are used in nuclear medicine to diagnose and treat different types of diseases. The radiopharmaceutical product 2-[^{18}F]fluoro-2-deoxy-D-glucose ([^{18}F]FDG) is a fluorinated glucose analog, which is used for positron emission tomography (PET) for diagnostic purposes, which are based on the evaluation of cellular glucose metabolism and cell viability [1]. [^{18}F]FDG is obtained by a nucleophilic substitution (SN II type) [2]. The aim of this study was to identify the most suitable method for the determination of radiochemical and chemical purity of [^{18}F]FDG. A fast analytical approach for the determination of chemical and radio-analytical impurities in radiopharmaceutical [^{18}F]FDG was developed using radio-high performance liquid chromatography (radio-HPLC).

Following on the radiopharmaceutical synthesis of [^{18}F]FDG, the chemical impurities resulted are: 2-fluoro-2-deoxy-D-glucose (FDG), 2-chloro-2-deoxy-D-glucose (ClDG), and 2-fluoro-2-deoxy-D-mannose (FDM). The equipment used to accomplish the purpose has been proposed as a high-performance liquid chromatograph—Agilent 1260 Bio-inert, which is equipped with both the RayTest Gaby Star gamma radiation detector and the DECADE II electrochemical detector. The separation was obtained using a strong anion exchange column (CarboPac PA100, 4 × 250 mm).

The HPLC method was developed for chromatographic separation of standards 2-fluoro-2-deoxy-D-glucose, 2-chloro-2-deoxy-D-glucose, and 2-fluoro-2-deoxy-D-mannose, considering the shorter retention time and better operation. Separation on CarboPac 100 was performed at flow rates in the range of 0.5–1.1 mL/min to the CarboPac PA100 column; the best resolution was obtained using 0.5 mL/min from a rate at 40 °C. The chromatographic method for determining the chemical and radiochemical purity was validated according to ICH (The International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use) standards.

Excellent repeatability and internal precision were obtained. The linearity of the method was proved using six concentrated levels. The method was found to be precise, accurate, and specific for FDG determination.

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Extended Abstract

Synthesis and Characterization of New Homo- and Heteronuclear Schiff Base Complexes †

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Keywords: Schiff base ligands; Copper(II) complexes; coordination polymers

Schiff bases are the most extensively used versatile ligands, capable of coordinating several chemical elements and stabilizing them in numerous oxidation states. Coordination complexes of Cu(II) with Schiff base ligands have been extensively studied due to their properties, structural aspects, and potential biological activity [1]. Three new copper Schiff base complexes have been synthesized: a 1-D copper coordination polymer, $[Cu_2(L)_2(\mu\text{-}ClO_4)]_n$, **1**, a mononuclear copper complex, $[Cu(L)]ClO_4$, **2**, and a 1-D copper-tin coordination polymer, $[Cu_2(L)(\mu_4\text{-tma})Ph_3SnCl]_n$, **3**, where L = 4-Chloro-6(N-2-picolyl-1′-iminomethyl)phenol and tma = benzene-1,3,5-tricarboxylate. The newly obtained compounds were synthesized and then characterized by elemental analysis, IR and UV-Vis spectral studies. Their crystal structures were determined by single-crystal X-ray diffraction.

Compound **1** is a coordination polymer bridged with a bidentate perchlorate ligand and it was obtained from $Cu(ClO_4)_2{\cdot}6H_2O$ and the condensation product of 5-chlorosalicylaldehyde and 2-picolylamine. The copper atom is hexacoordinated: Four of the coordination sites are occupied by the three donor atoms of the Schiff base ligand and one oxygen atom from a water molecule that have a square-planar arrangemet and the apical sites are occupied by two perchlorato ligands. Complex **2** was obtained from the first one, overtime. The experimental research has shown that after a few days, in the absence of any interfering factors, the polymer crystals change their shape turning into a mononuclear copper complex where the geometry around the copper(II) ion is square pyramidal. Compound **3** was also prepared by the reaction of 5-chlorosalicylaldehyde and 2-picolylamine in the presence of a copper salt—$Cu(ClO_4)_2{\cdot}6H_2O$, Ph_3SnCl and deprotonated trimesic acid. From the stereochemical point of view (Figure 1), two copper atoms are triply bridged by one of the trimesic acid carboxylate group and by the phenolic oxygen atoms of two tridentate Schiff base ligands. Each copper(II) atom is five-coordinated with a square pyramidal geometry. Tin(IV) atoms are pentacoordinated having a trigonal bipyramid geometry.

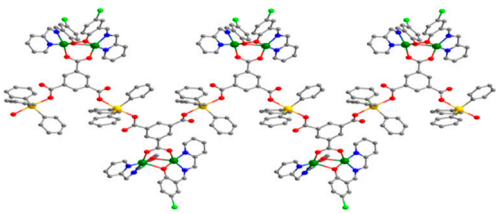

Figure 1. Structure of compound **3**.

In conclusion, three new coordination compounds containing Schiff base ligands have been synthesized and characterized.

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Abstract

1-D Coordination Polymers of Organotin(IV) Nodes with Alternating Spacers †

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Keywords: organotin nodes; alternating spacers; coordination polymers

Coordination compounds of organotin(IV) with diverse dimensionalities are obtained due to the ability of the tin atoms to have different coordination numbers, such as 4, 5, 6, or 7 [1].

New 1-D organotin(IV) polymers were obtained starting from triphenyltin chloride (Ph_3SnCl) and, concurrently, two different bidentate organic ligands: one having N donor atoms, such as 1,2-bis(4-pyridyl)ethane (bpa) or 4,4′ azopyridine (azopy), and the other one having O donor atoms, such as for example terephthalate (tpa), 2-aminoterephtalate (atpa), or naphthalene dicarboxylate (ndc). Elemental analysis, spectroscopic techniques, such as FTIR and UV–Vis, as well as single crystal and powder X-ray diffraction were used to characterized the obtained compounds.

Five new polynuclear coordination compounds with the general formula $\{(Ph_3Sn)(L^1)(Ph_3Sn)(L^2)\}_n$, where L^1 = bpa and L^2 = tpa (compound **1**), L^1 = bpa and L^2 = atpa (compound **2**), L^1 = bpa and L^2 = ndc (compound **3**), L^1 = azopy and L^2 = tpa (compound **4**) and L^1 = azopy and L^2 = ndc (compound **5**, Figure 1) have been synthesized and characterized. The resulting complexes were 1-D coordination polymers in which the triphenyltin(IV) nodes were linked by alternating dicarboxylate and organic diamines ligands. The tin(IV) atoms exhibit a trigonal bipyramidal geometry, with the three phenyl groups in equatorial positions, while O and N atoms from the spacers are in apical positions.

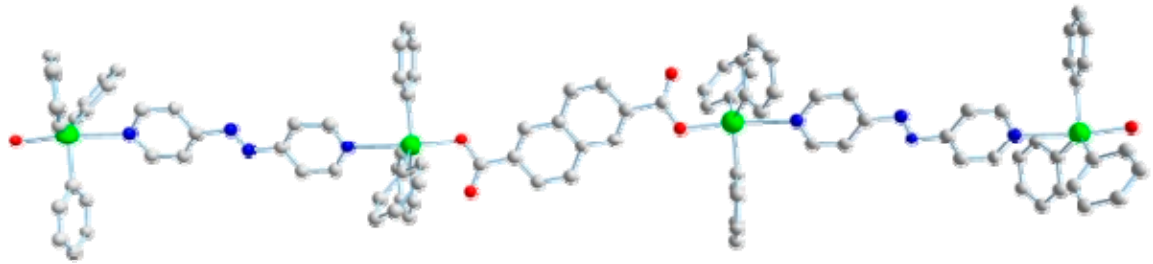

Figure 1. Molecular structure of compound **5**. Hydrogen atoms were omitted for clarity.

The resulting compounds showed an interesting and quite rare feature in the chemistry of organotin coordination polymers, namely that the organotin(IV) nodes are connected through alternating ligands ofcarboxylato anions and organic diamines.

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Abstract

Preparation of Transparent Sol-Gel Modified Silica Hydrophobic Coatings on Plastic Substrates †

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Keywords: silica materials; transparent thin film; plastic substrate; wettability; anti-reflective coatings

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Transparent hydrophobic or super-hydrophobic thin films prepared on plastic substrates have attracted attention in recent years because they can be suited to optical applications such as lenses, mobile phones, touch panels, and waveguides [1].

The aim of this work was to realize transparent coatings based on modified silica materials by the acid-catalyzed sol-gel process at room temperature, and then depositing them onto plastic substrates. Silane precursors having different hydrophobic functional groups (methyl, vinyl, octyl, hexadecyl), as silica sources were employed in order to investigate the potential effect of the alkyl groups in the properties of the obtained thin films.

Different alkoxysilanes (methyltriethoxysilane (MTES), vinyltrimethoxysilane (VTMES), octyltriethoxysilane (OTES), hexadecyltrimethoxysilane (HDTMES) were used as modifier agents. Infrared absorption spectra of the sol-gel silica films were obtained using a FTIR-ATR spectrophotometer. The transmittance and diffuse reflectance of the prepared coatings were measured by a UV-visible spectrometer. The static contact angle between water and coating surface was measured by Contact Angle Tensiometer. The surface topography was investigated through AFM analysis.

FTIR spectra of obtained materials shows the absorption bands at ~1020 cm^{-1} correspond to the stretching vibrations of Si-O-Si bonds. The UV-visible spectra of all prepared coatings reveal that these coatings were highly transparent (Figure 1). These sol-gel single-layered, antireflection coatings showed a reduction in the reflectance compared with un-coated plastic surface. The wettability of thin modified silica layers on the plastic substrate varies as a function of the hydrophobic functional groups belonging to the silane precursors.

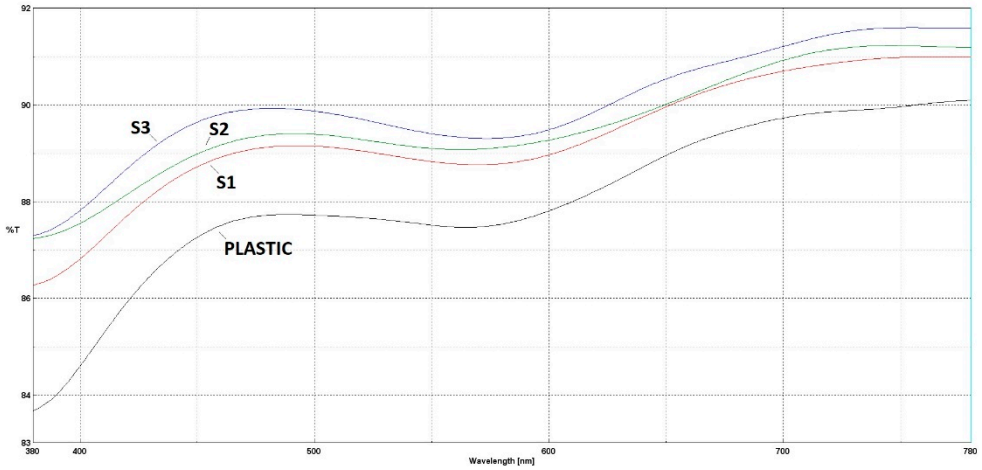

Figure 1. Transmittance spectra of coatings covered with sol-gel silica materials modified with silane precursors: S1 (MTES+OTES), S2 (MTES+VTMES), S3 (MTES+HDTMES).

Transparent coatings with anti-reflective and hydrophobic properties were prepared by acid-catalyzed sol-gel process, using silane precursors with long alkyl chains. Plastic substrates coated with the antireflective coating films may be used in solar photovoltaic applications.

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Abstract

Mineralogical Composition Assessment of Soils from Covurlui and Braila Plains by ATR-FTIR Technique †

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Keywords: mineralogy; soil; clay minerals; ATR-FTIR

The main purpose of this study is to determine the composition of the mineralogical and organic fraction of the soils from the High Plain of Covurlui and in the Plain of Braila—two relief units located in the south of Moldavia, East Romania. The present study focused on identifying the main clay and non-clay minerals with an important role in the absorption and migration of nutrients (micro- and macro-elements) on the physiologically useful depth of the soil, but also on the content of organic matter, determining the interdependence of these in the development of the cation exchange processes at the pedosphere level [1].

The samples were taken from different locations within the two mentioned relief units, from the first 30 cm of the soil. The materials used consisted of topographic maps and a portable GPS for the location of sampling points, spatulas and labeled plastic bags, and a register of field data recording. Prior to their analysis, the samples were subjected to a preparation phase which consisted of the removal of tin bodies and vegetable debris, fine grinding in porcelain mortar, homogenization and storage in plastic vials. The samples were analyzed by the Total Attenuated Reflectance–Fourier Transform Infrared Spectrometry (ATR-FTIR) technique, using a Bruker Tensor 27 FTIR spectrometer coupled with a diamond ATR device [2]. At the same time, the samples were subjected to a physical–chemical analysis to quantify the proportions of the granulometric fractions and the concentration of organic matter. Soil spectra were recorded in absorbance mode, in the 4000–400 cm^{-1} range. Soil granulometry was determined by the gravimetric method (STAS 7184/10-79), calcite by the volumetric method (SR EN ISO 10693/2014), and organic matter content by the volumetric method (STAS 7184/21-82).

ATR-FTIR analysis showed that the soils contain minerals from the clay group (montmorillonite and kaolinite) but also non-clay minerals (quartz and calcite), which were identified by the absorption bands specific to the vibrations of the chemical groups characteristic of these minerals. The proportion of the granulometric fractions shows that the analyzed soils are predominantly sandy.

Regarding the presence of organic matter in the soil, the obtained spectra highlight a reduced content, underlined by the low intensities of the characteristic peaks, which is well correlated with the quantitative analytical results of this component of the soil.

The ATR-FTIR method is a widely used technique to research the mineralogical structure of the soil. Based on the resulting spectra, we obtained relevant data regarding the presence of some types of minerals involved, in different proportions, in the regime of chemical elements in the soil and

qualitative information about the presence of organic matter. The data were very well correlated with the quantitative chemical results.

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Abstract

Determination of Benzalkonium Chloride from Biocide Products: Selectivity Study †

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Keywords: benzalkonium chloride; biocides; selectivity

Biocidal products are substances or mixtures of several substances, used to combat harmful organisms for human or animal health. Substances with antibacterial effects include quaternary ammonium salts, such as benzalkonium chloride (BAC), didecyl chloride (DDAC), etc. Benzalkonium chloride (BAC) is a compound of the class of quaternary ammonium compounds (QAC) used as a cationic surfactant in personal hygiene, cosmetic and skin disinfection products [1]. BAC is a mixture of alkylbenzyldimethylammonium chlorides [$C_6H_5CH_2N(CH_3)_2RCl$], in which R = C_{12}, C_{14}, C_{16}, C_{18} are the main compounds, and the antibacterial effects being given by the alkyl chain length and the quaternary ammonium groups [1,2].

In this study we compare two methods of analysis for quantitative determination: chemical titration [3] and liquid chromatography (HPLC-UV) [4]. Chemical titration is an iodometric method in a strongly acidic medium, in which the 0.05M potassium iodate solution is used as titrant (titration with extracted end point) [3]. HPLC determinations were performed using an Agilent 1100 Series HPLC, equipped with a binary pump, a degasser, an autosampler and a spectrophotometric detector in UV-Vis, and Agilent Chemstation software was used for data acquisition and analysis. Chromatographic parameters were injection volume, 10 µL; analysis time, 25 min; a Zorbax Eclipse XDB-C18 column (5 µm, 4.6 mm × 150 mm); and flow rate, 1.5 mL/min, isocratic conditions 20:80 A:B (v/v), where A = 0.4 M/L NaCl solution and B = methanol [4]. BAC monitoring was performed at a wavelength of 210 nm with the help of a UV-Vis spectrophotometric detector. The identification was performed by comparing the retention time of the analyzed compound with the retention time of the standard solution. Confirmation of the presence of BAC alkylic homologues, prior to quantitative determination, was performed using the mass spectrometry detection technique with a time-of-flight detector (TOF LC/MS).

As a measure of selectivity, for calculating the degree of recovery, the standard method of addition was applied. As a measure of selectivity, the degree of recovery determined by the standard addition method was used. For the titrimetric method we studied the influence of the presence of possible interferences different from those of the QAC class, such as ethyl and isopropyl alcohols, glutaraldehyde, non-ionic surfactants, stabilizers, etc. Regarding the HPLC-UV method, we were particularly interested in the selectivity with respect to other quaternary ammonium salts, such as didecyldimethylammonium chloride (DDAC) and cationic surfactants.

The data obtained demonstrate the selectivity of the titrimetric method in relation to the following compounds: ethyl and isopropyl alcohols, glutaraldehyde, non-ionic surfactants, stabilizers, etc. The HPLC-UV method is additionally selective in relation to other quaternary ammonium compounds, such as DDAC and cationic surfactants. The titrimetric method proves to be usable for biocidal products on the market that contain only a single quaternary ammonium salt in the presence of the other compounds studied, while the chromatographic method is specific only for the benzalkonium chloride contained by the biocidal products in the co-presence of other quaternary ammonium salts and other classes of compounds.

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Extended Abstract

Influence of Soil Fertilization with Plant Waste on the Phytochemical Composition of Some Medicinal Plants †

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Keywords: medicinal plants; plant waste; soil fertilization

Agricultural activities generate a large amount of crop residue that can create environmental problems, such as occupying vast areas and often being a source of pathogenic microorganisms. However, this plant waste can be a potential source of organic carbon and other major macronutrients (nitrogen, phosphorus, and potassium (NPK)) that are essential for plant growth. Given this background and the fact that Hofigal is a major producer of dietary supplements and medicinal plants and produces an important amount of plant waste from plant processing, its researchers aimed to study the influence of soil fertilization with plant waste on the phytochemical composition and growth of some medicinal plants.

For this purpose, we selected three medicinal plants (French marigold (*Tagetes patula* L.), marigold (*Calendula officinalis* L.), and lavender (*Lavandula angustifolia* Mil.)), which were cultivated from organic certified seeds. The experiment was carried out in a 300 m^2, with 100 m^2 for each plant divided into two sections of 50 m^2 each: one fertilized with plant waste (Sample) and the other one unfertilized (Control). Prior to conducting the study, the plant waste was converted into compost over a three-year period. The soil quality was tested for major macronutrients (NPK) and pH levels for both the Control and the Sample.

The difference in growth between plants cultivated on fertilized soil versus the ones on unfertilized soil was visually observed. Regarding the phytochemical composition of the three studied plants (in the Control and Sample), they were harvested during the flowering period and analyzed for total polyphenols, total tannins, and antioxidant activity. Volatile oils from dry French marigold and marigold flowers and fresh lavender flowers were also determined. The phytochemical composition was higher for all analyzed compounds, as shown in Figure 1.

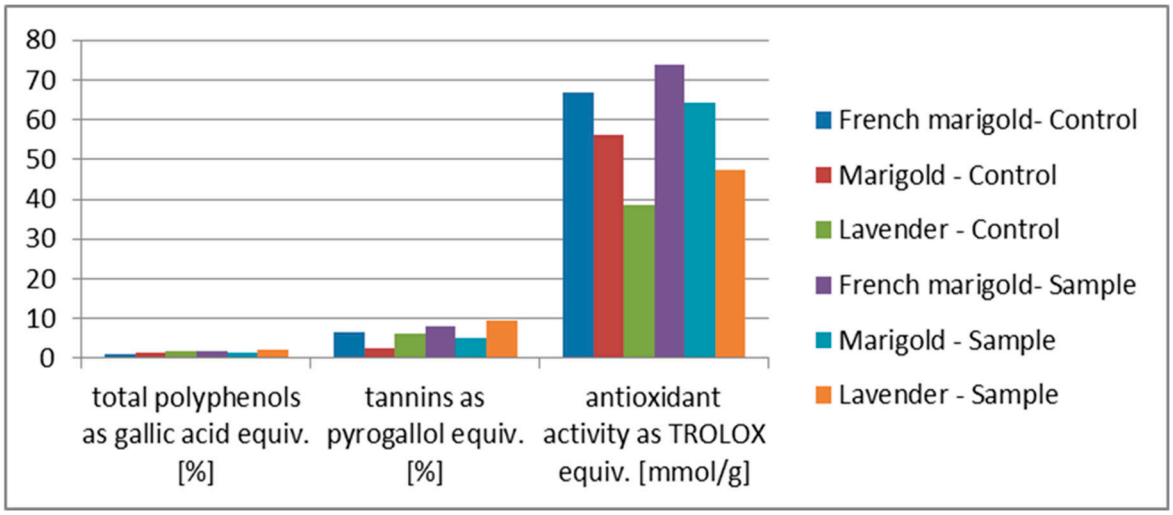

Figure 1. Chemical analysis of sample and control plants.

During the experiments, it was observed that the studied plants were healthier as they grew in the fertilized soil, and their productivity also increased. The quantity of French marigold flowers increased from approximatively 460 g to 940 g, marigold increased from 280 g to 570 g, and lavender increased from 640 g to 1530 g.

A soil analysis revealed that the pH value decreased from 7.8 in the unfertilized soil to 7.1 in the fertilized soil, which was beneficial for the growth of the selected species. Regarding the major macronutrients, the nitrogen, phosphorus, and potassium contents were higher in the Sample group. The phytochemical composition was higher for all analyzed compounds.

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Abstract

Synthesis and Characterization of a New Cr(III) Complex with 5-Hydroxyflavone as a Potential Antidiabetic Agent †

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Keywords: Cr(III), 5-hydroxyflavone; adipogenesis

Diabetes mellitus (DM) is a disease characterized by chronic hyperglycemia caused by absolute or relative insulin deficiency and/or insulin resistance, which in turn affects glucose, protein, and lipid metabolism, and ultimately causes characteristic secondary complications [1]. The adipose tissue provides a link between diabetes and obesity [2]. The accumulation of adipose tissue, as in obesity, and its deficiency, as in acquired or inherited lipodystrophy, are both associated with insulin resistance [3]. The aim of this study was to synthesize a new compound as a potential antidiabetic agent. In this regard, the antiadipogenic activity of the complex of Cr(III) with 5-hydroxyflavone was evaluated in vitro on human adipose tissue-derived stem cells (hASCs) engaged in adipogenesis.

The Cr(III) complex was synthesized by refluxing an ethanolic solution containing 5-hydroxyflavone and $CrCl_3$ in a molar ratio metal to ligand of 1:3. The red solid product obtained was characterized by elemental and thermal analyses and several spectroscopic techniques (Electrospray Ionization-Mass Spectrometry, Infrared, Ultraviolet-Visible, fluorescence spectroscopy). The antiadipogenic potential of the chromium (III) complex with 5-hydroxyflavone on hASCs was evaluated over 3 weeks after its administration in an adipogenic environment. The expression of perilipin was evaluated both quantitatively (flow cytometry) and qualitatively (fluorescence microscopy).

The physicochemical analyses revealed the formation of mononuclear complexes with 1:3 metal to ligand stoichiometry. Histograms obtained by flow cytometry showed that the expression of perilipin decreases significantly in the presence of the chromium (III) complex with 5-hydroxyflavone.

The newly synthesized complex of Cr(III) with 5-hydroxyflavone displayed *in vitro* antiadipogenic activity, a premise for further in vivo studies using a murine model of diabetes.

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Abstract

Application of PASS Algorithm for the Discovery of New Trpa1 Antagonists †

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TRPA1 is a calcium ion channel found on the plasma membrane of many animal cells and it is involved in the cellular response to endogenous inflammatory mediators as well as a plethora of volatile irritants [1,2]. It istherefore a promising therapeutic target for the discovery of new treatments that relate to pain, irritationand sensory hypersensitivity [3–5]. PASS (Prediction of Activity Spectra for Substances) is a software used for predicting the biological activity profile of given molecules based on their chemical structure. The current study seeks to validate the use of PASS for the discovery of new therapeutic agents that act as TRPA1 antagonists.

The molecular structures of inhibitors with known IC50 values were searched and downloaded from the ChEMBL database. With the use of PASS, we calculated "Pa" (the probability of a compound being active) and "Pi" (the probability of a compound being inactive). We evaluated the sensitivity of the method based on these values.

A number of 371 small molecules retrieved from ChEMBL database and their predicted activity spectra were analyzed. We identified the optimal threshold for finding new TRPA1 antagonists. The method was used to confirm new inhibitory structures based on previous repurposing studies.

The PASS software can be used for further studies regarding the discovery of new TRPA1 inhibitors.

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