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1950-2020



**Edition dedicated to the 70th anniversary
of research in chemistry and chemical
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FOREWORD

Founded in 1950, ICECHIM has been carrying out research activities of high academic standing in the fields of chemistry and chemical engineering uninterruptedly for seven decades.

Dedicated to the 70th anniversary of research in chemistry and chemical engineering at ICECHIM, the XVIth edition of the International Symposium “PRIORITIES OF CHEMISTRY FOR A SUSTAINABLE DEVELOPMENT” – PRIOCHEM 2020 (28-30 October 2020) gathered more than 250 researchers from ten countries: Bulgaria, Belgium, Finland, Poland, Russia, France, Portugal, South Africa, Spain and Romania.

In the three days of the symposium, were presented five plenary (invited) lectures, 17 oral communications and 90 posters. Seven workshops were organized within PRIOCHEM 2020 symposium.

We would like to thank to all the participants and the scientific, technic and organizing committees' members, which made possible the successful organization of the scientific event:

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INVITED LECTURES



REINFORCEMENT STRATEGIES OF SILICA AEROGELS FOR THERMAL INSULATION APPLICATIONS

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Keywords: aerogel; silica; mechanical reinforcement; organic modification; silylation; fibers.

Introduction: Silica aerogels are usually known by their distinctive feature of thermal superinsulation. The fine pearl-necklace 3D structure of linked nano-sized secondary silica spheres provides an extensive mesoporous network (> 90% porosity), 10 times lighter than water and with ability to avoid the gas phase heat transfer component of thermal conductivity due to the Knudsen effect [1-3]. Still, this structure is inherently brittle, as expected for a ceramic material, imposing severe constraints to bear load applications and handling of these materials. There are several ways to overcome this ‘weakness’ and reinforcement of the underlying silica structure has been a matter of study that has kept the attention of the scientific community of the field. In this presentation, a review of the main strategies to improve the mechanical properties of silica aerogels is presented, giving however more emphasis to the ones tested by the authors’ group which provide superior thermal insulation performance.

Materials and methods: Structural reinforcement of silica aerogels with organically-modified silica precursors and the introduction of fiber networks will be the main strategies implemented for improving the mechanical properties of these materials [4,5]. In order to reduce capillary forces and, thus, the shrinkage during evaporative drying of aerogels, an extra silylation step is accomplished to the hydrophobization of the network (substitution of hydroxyl groups of silica by methyl groups). Moreover, this surface state prolongs the service life of these hybrid/composite aerogels, since they exhibit degradation when exposed to moisture.

Results: Achievements of AerogelDustFree and AeroXTreme projects in terms of novel reinforced and thermal insulating silica-based aerogels are presented, as well as their structural and thermomechanical properties. Illustrating examples of these superinsulating aerogels are shown in Fig. 1.

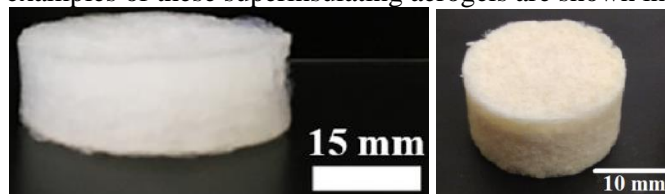


Figure 1. Aerogels from AerogelDustFree (left) and AeroXTreme (right) projects.

Acknowledgements: Work developed under the projects: 1) AeroXTreme (CENTRO-01-0145-FEDER-029533) - High-performance silica aerogel nanocomposites for insulation under extreme temperature Space environments, co-funded by Foundation for Science and Technology (Portugal) and the European Regional Development Fund (ERDF), through the Regional Operational Program of the Center of Portugal (Centro2020); 2) AerogelDustFree - Aerogel for Space applications ISO8 without dust release”, Contract No 17815, developed by the consortium Active Aerogels/University of Coimbra, funded by ERDF through the Operational Program for Competitiveness and Internationalization & Centro2020.

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CLASS II HYBRID PROTECTIVE COATINGS THROUGH THE SIMULTANEOUS GROWTH OF SILOXANE NETWORK AND ORGANIC POLYMERIZATION

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Organic-inorganic hybrid coatings have been prepared from 3-glycidoxypropyltrimethoxysilane (GPTMS) and tetraethoxysilane (TEOS) with triethylenetetramine (TETA) through the simultaneous growth of the siloxane network and organic polymerization. Hybrid samples were prepared with stoichiometric ratios of epoxy:amine from 2:1 through 1:1 to 1:3. From ^{29}Si HRMAS NMR spectroscopy, it was shown that TETA catalysed the hydrolysis reaction but it increased even more drastically the rate of the self-condensation reactions. GPTMS displays a higher reactivity towards self-condensation reactions compared to TEOS. An excess of active hydrogens in the amino groups of TETA results in faster kinetic reactions and shorter gelation times but at the same time, it results in a less complete inorganic network in the final dried film. This resulted in a rapid deterioration of the protective properties of the coatings in 3.5 % NaCl solution. ^{13}C solid state NMR indicated that none of the samples studied contain a high amount of TETA dangling chains, even when they are prepared with an excess of amine. Interestingly, the films based on epoxy rich off-stoichiometric formulation and those based on stoichiometric formulation resulted in similar barrier properties but a higher resistance to interfacial delamination was observed for the epoxy rich off-stoichiometric films. This is explained by noting that the fast build-up of the siloxane network at high TETA content decreases the amount of silanol groups available to react with hydroxyl surface groups and, at the same time, results in rapid gelation and insufficient wetting. On the other hand, the geometrical constraints imposed by the quick reaction between TETA and epoxy groups can also hamper the ability of the film to create interfacial bonds with the metal.

BIOBASED POLYURETHANES

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Keywords: *Polyurethane; biobased; macromolecular architecture; biomass.*

Nowadays, the use of renewable biobased carbon feedstock is highly taken into consideration because it offers the intrinsic value of a reduced carbon footprint with an improved life cycle analysis (LCA), in agreement with a sustainable development. Besides and compared to conventional fossil-based materials, innovative macromolecular architectures with improved or additional properties can be obtained.

In this presentation, we report two decades of active researches [1-11] on the synthesis and characterization of several innovative and biobased polyurethanes (PUR, PIR, TPU [1] and NIPU [4,11]), with controlled macromolecular architectures to elaborate membranes and foams. These materials are synthesized from different biobased building blocks: (i) aliphatic structures from PHA, or modified glycerides (dimer fatty acids,) sugar-based molecules ... and (ii) aromatic structures from lignins, tannins and furans.

In our lab, a large range of materials with nice properties and durable applications are developed from these different architectures, for a greener and durable future. The end of life of these materials is also considered by e.g., bio-recycling [10].

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IMMOBILIZATION OF METAL SELECTIVE LIGANDS UPON POLYMER NANOFIBRES: SUCCESSES AND CHALLENGES

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Modifying nanofibers with specific ligands for metal chelation or adsorption purpose is no doubt a great idea. Several nanofibers have been modified via different mechanisms for various applications. For example, polyacrylonitrile (PAN) in the form of nanofibres has been modified for adsorption and separation of metals ions. Ndayambaje et al. [1] was able to chemically modify the surface of polyacrylonitrile nanofibers with 2-2'-pyridylimidazole ligand to generate PAN-pim nanofibers for adsorption of Ni(II). Pereao [2] developed a nanofiber-based adsorbent containing glycolic acid functional groups for the recovery of rare earth elements (REEs). The surface modification of nanofiber-based adsorbents have been reported in literature [3, 4]. In surface modification, surface chemical compositions and characteristics are altered either for general purposes or for specific purposes [5]. There are two main approaches for the surface modification of nanofiber materials. The first focuses on direct modification (chemical, radiation and plasma treatment) of the surface of the material while the second intends to immobilize (grafting; attachment) the active ligand onto the surfaces of the material. An understanding of the selectivity of the immobilized ligand-metal ion interaction is important, as well as the coupling of the ligand to the nanofibre. In addition to these two approaches, blending, which is done by mixing two or more materials, is found to be the easiest technique; but getting the desired active functional groups to the surface of a material is not adequately achieved.

Cross-linked nanofibers with functional groups capable of binding metal ions offer potential advantages such as ease of operation, regeneration and reuse and environmental compatibility. Crosslinking is used for improving the chemical and/or mechanical properties of nanofibers for the removal of metals from aqueous solutions [6]. Stripping and recovery of the metal ions from the ligand is crucial to nanofiber-based adsorption processes; regeneration and reuse of the nanofibers are also important to the economics of the application. The fate of the nanofiber adsorbent after the modification process should be considered so that the resolution of one problem does not lead to a new problem since control of the surface properties of an adsorbent are essential for its adsorption efficiency and selectivity. Care should be taken that the surfaces of the modified nanofibers exhibit similar morphologies when compared to the pristine nanofiber mats by showing little signs of fusion, degradation or cracks. The fibrous structure of the nanofiber membrane should not be distorted or over swelled. Many modification processes may be too harsh to maintain delicate nanofiber integrity. The nanofibers should be handled properly to ensure that the porous and large surface areas are not compromised during modifications and applications [5].

The nanofiber support should be physically and chemically stable, with ample inter-fiber porosity to allow access of reagents for the surface functionalisation reaction and subsequently, for the metal ion's interaction with the ligand. The stability of the attached ligand upon the nanofiber should also be confirmed before use to ensure that the ligand is not leached during application or regeneration by washing in acid or alkaline solution [5]. Thus, the nanofiber adsorbent can then be reused successfully over several cycles, especially during the regeneration of the adsorbent. Many research studies failed to report nanofiber stability, reuse and regeneration. Nanofibres with functional ligands are complex and expensive to make and therefore they will not be commercially viable unless they are highly durable, stable, and highly selective for extraction of metals that have commercial value. The nanofiber adsorbents may not be very useful for low value, or toxic metal recovery unless there is a specific demand for high purity metal [6].

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CARBON NANOPARTICLES DETECTED BY TEM AND RAMAN SPECTROSCOPY

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Keywords: *carbon materials; Raman spectroscopy; TEM.*

Introduction: New carbon materials with high mechanical strength were produced using precursors obtained after thermo-oxidation treatment of polymer precursors with mineral acids. The composition and properties of the modified pitches allow foam formation without using pressure and stabilization step.

The chemical composition of the initial mixture significantly affects the physicochemical properties of the obtained carbon materials. Increasing oxygen content leads to formation of nanoporous carbons with large surface area and oxygen-containing functional groups of a basic nature.

The investigation of the relation between the properties of the precursor and the structure of the carbon composites indicates, that the precursor composition affects the synthesis procedure, and consequently, the final characteristics of the product.

Materials and methods: The object of this investigation is synthesis of porous carbon materials from different polymer waste materials. The carbon composites were synthesized by thermo-oxidation treatment with mineral acids at 200° C and subsequent carbonization at 600° C, was applied to produce porous carbon materials. Some samples were subjected to graphitization at 1500° C. For other samples hydrolysis at 800° C was used as additional procedure to increase the porosity. The structure and properties of obtained carbon materials were studied by SEM, XRD, TEM-EDS, Raman spectroscopy, BET, etc.

Structure, phase and surface composition of obtained materials are examined by TEM at accelerating voltage of 200 kV. The preparation procedure of the specimens is consisted of dispersing them in ethanol by ultrasonic treatment for 6 min. The suspensions are dripped on standard holey carbon/Cu grids.

Results: By XRD, HRTEM and SAED it was established that obtained carbons contain mainly graphitic structure. The interplanar distances of the lattice fringes of about of 0.701 nm and 0.216 nm correspond to (002) and (100) planes of the graphite phase. Some nanostructures were detected by Raman spectroscopy and TEM

Conclusions: The results show that obtained carbon materials are characterized by high surface area and high mechanical strength, which imply their possible application as adsorbents, constructive materials, etc.

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ORAL PRESENTATIONS



ELECTROCHEMICAL SENSOR BASED ON MOLECULARLY IMPRINTED POLYMERS FOR LIPOPOLISACCHARIDES DETECTION

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Keywords: *lipopolisaccharides; molecularly imprinted polymers; sensor; detection.*

Introduction:

The detection of pathogenic microorganisms remains a major scientific challenge and a very important global problem. The health of the population can be affected by infection with various pathogens, which in some cases even result in death, due to high resistance to antibiotics [1, 2]. This resistance is attributed to the outer membrane, in which the main component is LPS. Given the environments that favours the development of bacteria, like food, wastewater and drinking water, a careful monitoring is required. Existing detection methods are not very fast and, in some cases, are not indicating conclusive results. Considering all of these issues, it is mandatory to develop new and low cost sensors that possess high selectivity and reusability, which can be used “on-site” [3-5].

As a result, the aim of this study was to develop sensors based on molecularly imprinted polymer (MIP) films, obtained *via* sol-gel techniques, for the electrochemical detection of lipopolisaccharides (LPS, from *Pseudomonas Aeruginosa*). The films were deposited on screen printed electrodes by drop casting.

Materials and methods:

Monomers (3-(2-trimethoxysilyl)-propyl methacrylate, tetraethyl orthosilicate), LPS from *Pseudomonas Aeruginosa*. Methods of characterization: FT-IR, TGA, BET, UV-VIS, XRD, SEM, TEM and Cyclic Voltammetry.

Results:

Stable MIP films, with a good compatibility with the electrode and with selectivity for the LPS molecule from *Pseudomonas Aeruginosa* (comparing to LPS from *E. coli*).

Conclusions:

The sensor was successfully obtained and characterized by different methods. The overall characteristics of the films make the final product suitable for detecting LPS from aqueous media. Perspectives: Application of sensors for detecting Gram-negative bacteria.

Acknowledgements: *The authors thank to UEFISCDI for the funding of projects TE123/2018 and 255PED/2020 through the Romanian National Programme PN III.*

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NEW β -KETOPHOSPHONATES FOR THE SYNTHESIS OF PROSTAGLANDIN ANALOGUES. 1. PHOSPHONATES WITH A BICYCLO[3.3.0]OCTENE SCAFFOLD SPACED BY A METHYLENE GROUP FROM THE β -KETONE

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Keywords: mono and bis β -ketophosphonates, bicyclo[3.3.0]octene, prostaglandin analogues.

Introduction: The modifications of the ω -side chain have led to the most interesting biological activities of the prostaglandin analogues [1-2] and the researches in this direction were most extensive. In the total stereo-controlled Corey synthesis of natural prostaglandin and prostaglandin analogues, the ω -side chain is introduced by an *E*-selective Horner-Emmons-Wadsworth (HEW) olefination of an aldehyde with a β -ketophosphonate in the presence of a base. For obtaining new prostaglandin analogues, we planned to introduce a *bicyclo[3.3.0]octane scaffold* in the ω -side chain, this fragment being found in the molecule of carbacyclins and their analogues, in the molecule of many natural products, like hirsutic acid, isocomene or antitumor compounds like coriolin, pentalenolactone, quadrone. **Materials and methods:** The starting compounds **1** were obtained as previously [3] and the key step for obtaining β -ketophosphonates was the reaction of an ester with lithium salt of dimethyl methanephosphonate, usual used in the prostaglandin synthesis. **Results:** Starting from the diol **1**, protected with good leaving groups (mesyl and tosyl), we performed a sequence of reactions with good yields: the carbon chain lengthening by reaction with KCN, the hydrolysis of the nitrile groups to carboxyl, the esterification of carboxyl to ester and finally the phosphonate synthesis, which gave one bis- β -ketophosphonate **7** and two mono β -ketophosphonates, **8** and **11** (Scheme 1). **Conclusions:** The synthesis of β -ketophosphonates, linked by a methylene group to a bicyclo[3.3.0]octene fragment, was performed by the reaction of dimethyl methanephosphonate with the ester group (as previously we used for obtaining prostaglandin intermediates for hydrogenation and prostaglandin analogues obtained in microproduction) of two intermediates with this scaffold in good yields (74% **7**, 92% **11**, 16.6% **8** as secondary compound).

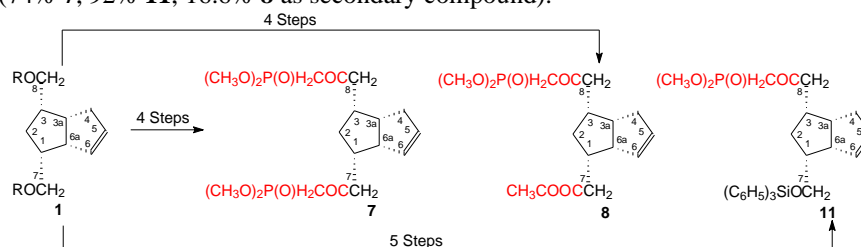
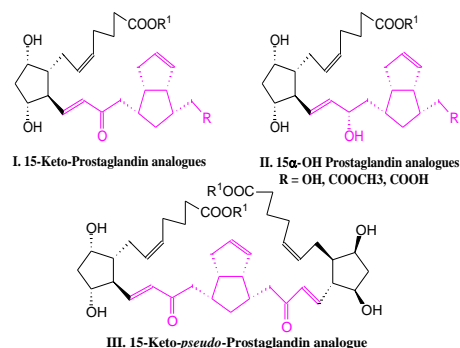


Figure 1. Synthesis of β -ketophosphonates **7**, **8** and **11** for obtaining new prostaglandin analogues of type **I** and **II**

The new β -ketophosphonates are key intermediates for obtaining new prostaglandin analogues with a bicyclo[3.3.0]octene fragment in the ω -side chain **I** and **II**.

The use of bis β -ketophosphonate **7** in the usual stereoselective *Z*-Horner-Emmons-Wadsworths olefination conditions should gave the *pseudo*-prostaglandin compound **III**:



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MECHANICAL AND THERMAL PROPERTIES OF BLENDS BASED ON POLYHYDROXYALKANOATES

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Keywords: bioblends; polyhydroxyalkanoates; copolyesters; thermal analyses

Introduction: Polyhydroxybutyrate (PHB) is a biodegradable and biocompatible thermoplastic polymer with good properties, similar to that of polypropylene, but with a higher price. In addition, it is very brittle and difficult to process by melting, which limits its usage [1-3]. To overcome these drawbacks, PHB is usually blended or copolymerized with other polymers [2,3]. In this study PHB was blended with medium-chain-length polyhydroxyalkanoates (PHAs), which are elastomeric materials. For this purpose, two copolymers with different ratios of monomers, namely PHO and PHN were added in 20 wt% in PHB using a melt processing technique.

Materials and methods: Neat PHB was purchased from Goodfellow, PHO, with a high fraction of C8, and PHN, with a high fraction of C9, were obtained by microbial biosynthesis. The PHB/20PHO and PHB/20PHN blends were obtained via melt mixing in a Brabender Labstation at 160°C, for 8 minutes. The thermal characteristics of pristine PHB and blends were investigated via TGA and DSC, and thermomechanical ones via DMA.

Results: An increase of crystallinity was noticed in all the blends compared to plain PHB due to the nucleating effect of PHN and, especially PHO (Fig. 1). A slight increase of the thermal stability was also observed in the blends due to the elastomeric nature of PHAs and improved processability. Importantly, the addition of elastomeric copolyesters in a concentration of up to 20% does not reduce the modulus of elasticity of PHB.

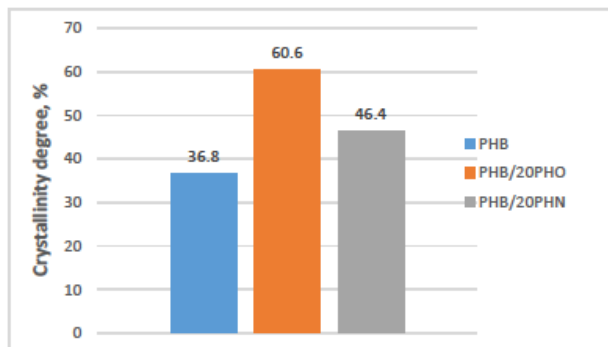


Fig. 1. Crystallinity degree of PHB and its blends

Conclusions: This study revealed the importance of modifying highly brittle PHB with elastomeric PHAs in order to improve both flexibility and melt processability. In addition, the effect of PHAs with different compositions was highlighted in this study.

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SYNTHESIS AND „*IN SILICO*” EVALUATION OF THE BIOLOGICAL ACTIVITY OF THE NEW DUAL INHIBITORS OF GYRASE DNA AND TOPOISOMERASE IV

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Keywords: Molecular docking, Quinolones, Dual inhibitors.

Introduction: Quinolones are effective against a broad range of bacterial species and provide potent treatment options for a few infections [1,2]. Quinolones act in a highly unusual mode, and kill bacteria by converting essential enzymes, DNA gyrase or topoisomerase IV, into potent cellular toxins that generate high levels of double-stranded chromosomal breaks. In addition to their effects on the bacterial enzymes, some quinolones display high activity against a variety of eukaryotic type II topoisomerases, including human [3]. The understanding the ability of quinolones to preferentially target the different prokaryotic and eukaryotic type II topoisomerases remains a major challenge for the researchers.

Materials and methods: The DFT/B3LYP/6-311 G* level of basis set has been used for the computation of molecular structures. The score and hydrogen bonds formed with the amino acids from binding site of receptor protein are used to predict the binding modes, the binding affinities and the orientation of the docked quinolones. The quinolone compounds were synthesised and characterized by physical-chemical methods and by biological activity.

Results: Some quinolone compounds have been designed and synthesized. For these compounds there have been performed calculations of characteristics and molecular properties and molecular docking studies to identify and visualize the most likely interaction ligand (quinolone) with the receptor targets, which were imported from the Protein Data Bank (PDB ID: 4P8O, 3M4I, 1ZXN, 2ZD1). The study has been performed relating to some quinolone compounds known in medical therapeutics: ciprofloxacin, vosaroxin, elvitegravir. The result of molecular docking study (docking score), (Figure 1) shows that the nature of the substituents on the quinolone nucleus influences the binding affinity and binding mode of a quinolone to the receptor protein.

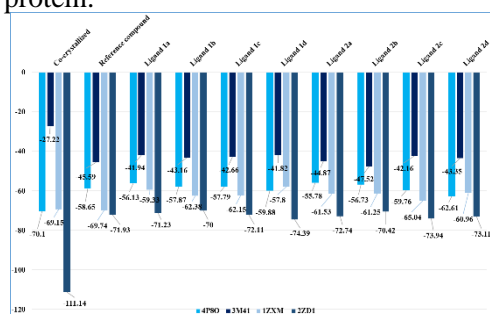


Fig. 1 Docking score of quinolone compounds

Conclusions: The prediction of the binding affinity of a new compound to an identified target is a significant parameter in the development of a new drug and would allow restricted the synthesis to the most promising compounds.

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SUPERSATURATING SYSTEMS OBTAINED USING MESOPOROUS SILICA WITH SOLUBILITY AND DISSOLUTION RATE ENHANCEMENT

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Keywords: mesoporous silica; kinetics model; solubility enhancement; dissolution rate; supersaturating systems.

Introduction: A large fraction of biological active compounds suffer from poor aqueous solubility, which in turn limits their adsorption into the organism. The strategies for improving bioavailability through solubility enhancement focus on: a) increasing dissolution rate through particle size reduction; b) increasing solubility by using a less thermodynamically stable solid form, such as an amorphous phase and c) decreasing the precipitation rate through crystallization by the addition of surfactants and other additives. [1] Mesoporous silica nanomaterials (MSN) are a promising matrix for dissolution rate (a) and solubility (b) enhancement due to their large surface area, ordered and monodisperse 2-50 nm pores and non-toxic properties. [2] The large surface area and small pore size usually leads to the adsorption of biologically active compounds as an amorphous phase. [3] Supersaturating drug delivery systems obtained using MSN should therefore exhibit higher biological active molecule concentrations than the solubility limit. The objective of this work is to investigate the influence of MSN textural properties on the dissolution rate and solubility enhancement of a model molecule with low aqueous solubility, as well as on the kinetics parameters affecting the release of the cargo molecule.

Materials and methods: Four MSN of SBA-15 and mesocellular foam (MCF) type were obtained through sol-gel synthesis in the presence of Pluronic P123 as the structure directing agent. These materials together with commercial MCM-41 with a pore diameter of 2.8 nm were used to encapsulate the model molecule through incipient wetness impregnation. The samples were characterized by nitrogen porosimetry, calorimetry, thermogravimetric analyses and IR spectroscopy. Release profiles were obtained at 37 °C in phosphate buffer solution using *in-situ* UV-Vis spectroscopy. Two total concentrations of active compound were used for each sample, corresponding to 0.35 *S* and 2.0 *S*, where *S* represents the equilibrium solubility. Kinetics models were constructed using surface adsorption, diffusion and crystallization processes.

Conclusions: Encapsulation into SBA-15 and MCF mesoporous silica increases the dissolution rate with respect to the pure compound by 4 – 10 times at low concentration (0.35*S*) and between 2 and 25 times at high concentration (2*S*). Furthermore, the solubility of the compound is increased by 25 % after 24 h when it is encapsulated into the mesoporous silica matrices. Mesoporous silica materials are therefore suitable matrices for supersaturating systems with increased dissolution rate and solubility.

Acknowledgements: This work was supported by the Romanian Executive Agency for Higher Education, Research, Development and Innovation Funding through the PCCDI no. 85/2018 project.

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LAYER-BY-LAYER PREPARATION OF ORMOSIL NANOMATERIAL FOR AMPHIPHOBIC SURFACES

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Keywords: functional coatings, amphiphobic, layer-by-layer

Introduction: Surfaces with special wetting properties are still in the attention of researchers, especially due to the numerous industrial applications, for example corrosion protection materials, anti-caking, anti-soiling, separations, etc. [1]. Many methods have been developed for creating coating materials for surface modification, in order to obtain superhydrophobic or superhydrophilic properties. Obtaining surfaces that efficiently repel both polar (water) and non-polar liquids, respectively with amphiphobic properties is another great challenge. In the present work a simple multi-step method to produce amphiphobic coatings on cellulosic substrate is proposed, combining the layer-by-layer deposition of nanoparticles and polymeric films, with final step of fluorination of the coatings.

Materials and methods: Zinc oxide and silica nanoparticles were studied as nanopowders to produce the suitable roughness of the coating materials. ZnO and SiO₂ nanoparticles have been prepared by simple hydrothermal route. Tuning the reaction conditions in both cases, nanoparticles with various size of nanocrystallites and different shape have been obtained. As model solid substrates commercial available paper and cotton fabric were studied. The surface of the paper and textile samples were activated by deposition of polymeric films from natural polyelectrolyte Chitosan. Further steps involved the deposition of NPs layers, followed by the deposition of a fluorosilane derivative, as main reagent to ensure hydrophobization of the surface. The obtained films were characterized by using FTIR, SEM and colorimetric measurements.

Results: Hybrid coatings material were obtained with various degree of roughness and optical properties. The samples of paper and cotton fabrics exhibited high liquid repellence to water, oily phases with lower surface tension, showing a contact angles of 150° and 135° respectively. The coatings based on SiO₂ NPs show increased transparency and produced minimum visual changes to the original surface.

Conclusions: On both substrates investigated filmogenic material were deposited, produced by layer-by-layer technique, using polyelectrolytes and various types of nanoparticles. The micro and nanoscale 3D morphology and external coating with very low surface energy results in good amphiphobic properties, either on paper or cotton materials.

Acknowledgements: This work was supported by grants of the Romanian National Authority for Scientific Research and Innovation, CCCDI - UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0743(PC5) and project number PN-III-P1-1.2-PCCDI-2017-0428 (PC2), within PNCDI III.

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PORPHYRINS IN COMPETITION WITH THEIR NANOMATERIALS CONTAINING PtNPs AND AuNPs. SYNERGISM IN BENEFIT OF SENSING APPLICATIONS

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Due to their amazing optoelectronic properties, porphyrins have intrinsic sensing properties that might be highly improved when they are associated to a proper partner, such as: PtNPs or AuNPs.

A novel optical sensor destined for uric acid detection was developed based on a nanomaterial realized from tetra-(4-amino-phenyl)-porphyrin complexed with PtNPs. PtNPs was obtained by double reduction method, using first time trisodium citrate and second time NaBH₄, in order to tailor its shape and size. The porphyrin-PtNPs hybrid nanomaterial optically detects uric acid with high confidence, selectivity and sensitivity in the range of 5×10^{-6} - 1.6×10^{-5} M that is in the targeted domain of medical relevance tests in biological samples.

Another sensor, capable to optically detect trace amounts of triiodide ion in the range of 10^{-9} - 4×10^{-8} M, was based on a nanomaterial organized in 1D supramolecular architecture with large voids, realized from Pt-metalloporphyrin, namely: Pt(II) 5,10,15,20-tetra(4-methoxy-phenyl)-porphyrin, complexed with plasmonic nanoparticles of AuNPs.

Taken into consideration that the excess of uric acid is leading to kidney disease, cardiovascular, hypertension, and a risk factor for 2-type diabetes and that iodine deficiency, besides other disorders can result in infant congenital hypothyroidism and causes mental retardation, their precise determinations are of tremendous importance in analytical chemistry. The effect of interfering ions was investigated and the two materials are not blocked by common ions, lipids or amino acids and not even by salicylate anion highly present in biological samples.

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INVESTIGATION OF EMBEDDING BLACK CHOKEBERRY EXTRACT IN MESOPOROUS SILICA SUPPORTS ON ITS BENEFICIAL EFFECTS

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Keywords: black chokeberry; mesoporous silica, antioxidant activity, antimicrobial, cell viability.

Introduction: Black chokeberry extracts are effective antioxidants and antimicrobials, proving also antitumor potential [1]. These beneficial properties of extract phytochemicals could be preserved on long-term through the embedding of extract in chosen matrices. Mesoporous silica nanoparticles present high porosity and capacity to accommodate natural compounds, as well as good mechanical and thermal stability leading to the extract phytocomponents protection from environmental factors. The purpose of this study was to evaluate how the embedding of the black chokeberry extract into mesoporous MCM-41-type silica influenced the beneficial properties of *A. melanocarpa*.

Materials and methods: The chemical profile of *Aronia* ethanolic extract was determined by RP-HPLC-PDA, as well as spectrophotometric determination of polyphenols main groups (polyphenols, flavonoids and anthocyanins). The antioxidant activity of embedded extracts was compared to that of free extract and supports in the same amount as in the materials containing embedded extracts [2] and the embedded polyphenolic extract were characterized using FT-IR spectroscopy, N₂ adsorption-desorption isotherms and thermal analyses. The antimicrobial activity was tested against ten selected standard bacterial strains. The cell viability of both free and embedded *A. melanocarpa* ethanolic extract was assessed on a cancer cell (A375 human melanoma) and healthy keratinocytes (HaCaT cell line) by MTT assay.

Results: The ethanolic extract of *A. melanocarpa* showed high amount of polyphenols being correlated with a good radical scavenger activity (RSA). A slight improvement of RSA was noticed for the embedded extracts after up to six months of storage at 4 °C [3]. The cellular viability assessment on cancer cell line at tested concentrations (up to 250 µg/mL) showed an increased effect of embedded extract and a lower toxicity for the normal keratinocytes cell line (HaCaT) in comparison with the free extract. Also, for concentrations up to 100 µg/mL, no toxicity was observed for the embedding extracts on HaCaT cells. Moreover, an improved antimigratory potential was observed for Ar@Zn-MCM-41 (1.6 %) or Ar@MCM-41E (6.8%) in comparison with the free extract (48.2%) and Control (76.4%) after 24 h.

Conclusions: The loading of the *A. melanocarpa* extract into silica-type supports led to preservation of its radical scavenger capacity and antimicrobial activity on Gram-positive bacteria, while the extract embedded in Zn-MCM-41 showed an improved antimicrobial capacity than the free extract due to the presence of ZnO nanoparticles on silica pore walls that led to synergistic effect. Also, a slightly better time and dose dependent antiproliferative effect on A375 human melanoma cells was observed for the embedded extracts.

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EXPERIMENTAL – DEMONSTRATIVE PILOT INSTALLATION BIOGAS – MICROALGAE

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Keywords: Biogas; Microalgae; Anaerobic digestion; Wastewater treatment.

Introduction: The installation presented is the main result of complex project 32PCCDI/2018, with the propose of 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.

Materials and methods:

The experimental - demonstrative pilot installation biogas - microalgae is comprised of the following elements (material: polystyrene armed with glass fiber): Anaerobic digestion installation: Mobile vessel for substrate homogenization (500 L); Digester (5m³); Digestate collection vessel (200 L); Liquid digestate collection vessel (200 L); Installation for microalgae cultivation: Nutrient preparation vessel (500 L); Vessel for CO₂ absorption in nutrient medium (500 L); Microalgae growth raceway pond (10m³); Microalgae harvesting installation: Microalgae suspension harvesting vessel (sedimentation /storage) (500 L); Filtered water collection vessel (500 L).

Results: The digester (Figure 1A) is equipped with a recirculation loop, that ensures a better homogeneity and availability of the substrate for the process bacteria, in order to reduce the process time and maximize methane yield. The retention time in the digester was reduced considerably compared to the conventional process, without recirculation of the substrate, obtaining biogas with over 40% methane (compared to <10% without recirculation), and after 30 days, 50% methane in the biogas (compared to 15% without recirculation). Microalgae growth reduced the nutrients from the liquid digestate, over 90% N and over 80% P.

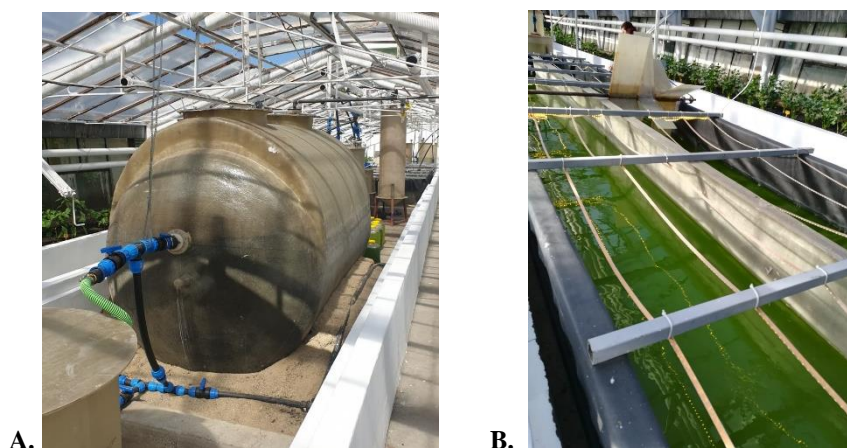


Figure 1. Main constituents of the Experimental – Demonstrative Pilot Installation BIOGAS – MICROALGAE:
A. 5m³ anaerobic digester; B. 10m³ open raceway pond for microalgae cultivation on wastewater;

Conclusions: Besides the efficient production of biogas with high yield in methane, we also achieved an efficient reduction of the 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.

Acknowledgements: 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.

MESOPOROUS SBA-15 BASED MATERIALS FOR CATALYTIC HYDROPROCESSING REACTION OF MICROALGAL BIOMASS

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Keywords: mesoporous, hydrothermal, ceria, zirconia, microalgae, hydroprocessing

Introduction: Mesoporous silica materials have attracted increasing attention to be considered as an important class of nanostructured support materials in heterogeneous catalysis. Their large surface area, well-defined porous architecture and ability to incorporate metal atoms within the mesopores lead them to be a promising support material for designing a variety of different catalysts. In particular, SBA-15 mesoporous silica has its broad applicability in catalysis because of its comparatively thicker walls leading to higher thermal and mechanical stability. In the current investigation were presented the results for the hydroprocessing of microalgae *Chlorella* on a static reactor system, using mesoporous SBA-15 based catalysts. Comprehensive analysis is carried –out on the bio-crude. The GC-MS analysis is used to revealed the compositions of bio-crude oil.

Materials and methods: Ce-SBA-15, Zr-SBA-15, and Zr-Ce-SBA15 catalyst supports were prepared by direct hydrothermal synthesis method using amphiphilic Pluronic P123 triblock copolymer ^[1]. The products were obtained and designed as Ce-SBA15-HM (molar ratio of Ce/Si=0.1), Zr-SBA15-HM (molar ratio of Zr/Si=0.1), and Zr-Ce-SBA15-HM (molar ratio of Zr/Si=0.05 and Ce/Si=0.05). For the second procedure, the post synthesis method, cerium and zirconium were incorporated into SBA-15 support by wet co-impregnation method. These catalysts are named as Ce-SBA15-PM, Zr-SBA15-PM and Ce-Zr-SBA15PM. The prepared catalysts were characterized by TGA, BET, FTIR, IR and XRD analysis. Hydroprocessing reactions of microalgal biomass were carried out at 350°C and the pressure of H₂ was 40 bar. The heating rate of the reactor was 5°C/min, once the operating temperature was reached, the temperature was held for 2.5h.

Results: From XRD analysis we obtained relevant data about the crystalline phases formed during synthesis. Wide angle XRD of the catalysts suggested that Zr species are well dispersed on the mesoporous structure. The N₂ adsorption-desorption isotherms showed typical type IV isotherm with type H1 hysteresis cycle, indicating a hexagonal array typical of SBA-15 mesoporous structure. The modification of SBA-15 by adding promoters like Ce and Zr via direct-synthesis method keeps almost unaltered its mesoporous structure. However, when Ce and Zr are incorporated into the sample by post-synthesis method, the N₂ adsorbed volume isotherms decreases and the hysteresis loop is briefly altered.

Conclusions: In this study ceria, zirconia, ceria-zirconia based mesoporous catalysts were coupled to enhance the performance and physicochemical properties of the catalysts. The characterization results of the catalysts have revealed the presence of mesopores in the catalysts. Microalgae suspension was successfully processed in a static catalytic hydroprocessing reactor, at temperature 350°C. Our results show that algae feedstock can be converted into high quality bio- products (bio-crude, bio-oil).

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OPTIMIZATION OF YEAST PROTEIN EXTRACTION THROUGH A COMBINED ENZYMATIC AND HIGH-PRESSURE HOMOGENIZATION METHOD

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Keywords: yeast extract, protein, optimization, Response surface methodology.

Introduction: Yeasts have a very high content of protein, therefore they could be used as an easy source of protein. Spent brewer's yeast is a good substrate to use, as it is produced in large quantities from the brewing industry and it offers a great way of utilizing a subproduct to create value-added products, such as plant biostimulants.[1]

Protein hydrolysates have been used as plant biostimulants for a long time and they have been proved to be efficient in mitigating the side-effects of harsh climatic conditions such as drought and cold. [2]

The aim of this study is to present an optimization method for the extraction of yeast proteins, through enzymatic treatment coupled with high pressure homogenization.

Materials and methods: The protein extraction from yeast was carried out following several steps. The yeast was pre-treated with a β -glucanase at different concentrations, for one hour at 50°C and afterwards lysed through a homogenizer (GEA Lab Homogenizer PandaPLUS) at different pressure levels and different number of passes. The experiments were planned out through response surface methodology, based on a plan of two levels and four variable factors, which were temperature, pressure, number of passes and β -glucanase concentration.

Results: The data analysis shows that some of the parameters have higher significance than others. Pressure and β -glucanase concentration were highly significant ($p < 0.05$) while yeast concentration was only marginally significant when it comes to establishing a model. The interaction between two factors was also taken into consideration and the data shows that the interaction between yeast concentration-enzyme concentration, yeast concentration-pressure were not significant. However, the interaction between the enzyme concentration and pressure was marginally significant. The R^2 coefficient for the fitted model was 0.86 and the corrected R^2 value was 0.77.

Conclusions: The data analysis provided a set of optimal values for the predefined parameters in order to create a better process with a higher yield of proteins from yeast which could be used for other applications.

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EXTRACTION OF PROTEINS FROM MICROALGAE USING LYTIC ENZYMES PRODUCED BY *TRICHODERMA* STRAINS

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Keywords: *enzymes; Trichoderma; proteins; extraction; microalgae;*

Introduction: Filamentous fungi are well known as sources of industrial enzymes with high capacity for extracellular protein production [1]. The aim of this study was to use lytic enzymes produced by *Trichoderma* strains grown on whey for the extraction of proteins from microalgae. By this approach the use of lateral flows to produce high value bioactive compounds is achieved, which can be further formulated and used as nutritional supplements or plant biostimulants.

Materials and methods: *Trichoderma* isolates were grown on whey, a by-product of the food industry. *T. asperellum* and *T. atroviride* were incubated for 2 weeks in minimal medium (MM) supplemented with 20% whey, using PDB (Potato Dextrose Broth) at same concentration as control. Protease and cellulase activities were assayed using casein and Folin-Ciocalteu reagent, and, respectively carboxymethylcellulose (CMC), microcrystalline cellulose (MCC) and DNS (3,5-dinitrosalicylic acid) reagent [2]. Sterile filtrates of *Trichoderma* isolates grown on whey and PDB were used for the enzymatic extraction of proteins from microalgae at different temperatures. The molecular weights of the proteins were determined by SDS-PAGE.

Results: The protease (caseinase) activity of the *T. asperellum* strain (T36) was significantly increased due to the incubation in whey medium. Sterilization of whey by filtration induced the highest activity, while autoclaving appears to decrease the induction of caseinase activity. For the cellulase activity, the whey induced an increase in the enzymatic activity of *T. asperellum* (T36) compared to control. High cellulase and protease activity was observed only for autoclaved whey in the case of *T. atroviride*. The extracellular enzymes secreted by *Trichoderma* strains amplified the cell lysis of microalgae. The SDS-PAGE profile (Fig. 1) of extracted proteins at 25°C showed a wide distribution of molecular weights, with several intense bands between 5-30 kDa.

Conclusions: In this study we developed a biotechnological method for using co-products resulting from dairy industry for inducing lytic enzymes in *Trichoderma* cultures capable of amplifying the protein extraction from microalgae cells. The biomass resulting from *Trichoderma* growing on whey can be used as plant biostimulants.

Acknowledgements: The work on this paper was supported by the Government of Romania, Ministry of Research and Innovation, MCI Core Programme in the frame of project PN 19.23.01.01 Smart-Bi, Project10PCCDI / 2018 Closing the loop into bioeconomy value-chains by manufacturing innovative bioproducts – PRO-SPER, funded by UEFISCDI, and Project PFE 31/2018.

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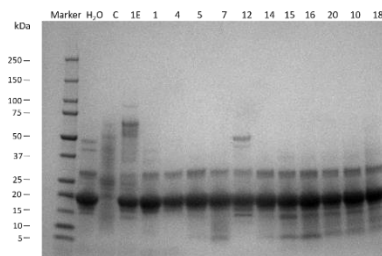


Figure 1. SDS-PAGE of extracted proteins

PREPARATION AND CHARACTERIZATION OF DEEP EUTECTIC SOLVENTS THAT CAN BE USED IN CO₂ ABSORPTION PROCESSES

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Keywords: green solvent, deep eutectic solvent, characterization, CO₂ absorption

Introduction: CO₂ emissions are well known for bringing a lot of environmental issues, at a global scale. One of the most used technology for CO₂ capture is the post-combustion method, which consists in separating the CO₂ from the combustion gases, using a solvent, usually amine. In this study, we propose alternative solvents: DESs[1] (deep eutectic solvents) – based on choline chloride and amine, and switchable hydrophilicity DESs – based on fatty acids and diluted amines solutions.

Materials and methods: *I. ChCl-Amine:* Choline chloride (ChCl) was used as hydrogen bond donor HBD and amines (monoethanolamine MEA, diethanolamine DEA, triethanolamine TEA) as hydrogen bond acceptor HBA[2][3], in different molar ratios: 1:5, 1:6, 1:8 and 1:10. All the components were precisely weighed and mixed at 300 RPM, 60°C, until a clear solution was obtained. *II. Switchable hydrophilicity DESs:* The hydrophobic part is represented by hydrophobic DES[4], made up of octanoic acid OA and successively, other three acids: dodecanoic DA, myristic MA, stearic acid SA, in a 3:1 molar ratio. The hydrophilic phase consists of 10% amine solution[5] MEA, DEA, and TEA. The two phases were blended at 1:13 v/v oil-water, and then analyzed.

Results: The obtained solvents were in liquid state at room temperature, except DES OA-SA. After adding the amine solutions, the DESs OA-SA-amine were also liquid. All DESs were characterized using pH, density, viscosity, electrical conductivity, refraction index, surface tension, FTIR, NMR. The prepared DESs are used for solubility tests to determine CO₂ absorption capacity. The hybrid DESs-amine have a higher absorption capacity than ChCl-based DESs and conventional MEA 30%, up to double CO₂ absorption capacity. Comparing the three amines type, MEA gives the best results, even in hybrid DESs.

Conclusions: DESs represent a new greener solution for CO₂ absorption. Their advantages consist of cost-effective solvent price, easy preparation, easy reuse and regeneration. Based on the previous observations that amines and DESs can absorb CO₂ we developed combinations between them that improve the CO₂ absorption capacity and that could be tailored for controlled release for various applications.

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SILICON-DOPED GRAPHENE NANOFLLAKES: CONTROLLABLE DOPING AND APPLICATION AS METAL-FREE CATALYST AND ELECTRODE MATERIAL

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Keywords: silicon doping, graphene nanoflakes; metal-free catalysts; lithium-ion batteries

Introduction: Doping of graphene-based nanomaterials is one of the most effective approaches for the modification of their physicochemical properties, defectiveness, and surface structure. Nitrogen is usually used as a dopant due to the simplicity of the synthesis technique and high stability of the produced materials, while boron, sulphur and phosphorous are less popular dopants. Silicon doping is rather exotic because the formation of Si–C bonds is difficult, and mostly SiO₂ is produced. At the same time, doping of graphene-based materials with silicon distorts carbon layers and generate unique out-of-plane defects.

Materials and methods: Si-GNFs were synthesized by pyrolysis of the hexane+tetramethylsilane mixtures over the MgO template using tubular quartz reactor. To prepare the electrodes, 80 wt % active materials, 10 wt % super-P and 10 wt % polyacrylic acid binder were mixed homogeneously in N-methylpyrrolidinone solvent to form a uniform slurry. The slurry was coated on the copper foils and then dried at 100 °C under vacuum for 16h. Galvanostatic charge/discharge measurements were carried out at a potential range of 0.01-3.0 V using LAND CT2001A battery tester.

Results: The present study is devoted to the development of a simple and controllable technique for the synthesis of Si-doped graphene nanoflakes (Si-GNFs) with the small domain size (20–50 nm) and 3–10 monolayers thickness (Fig.1) with different silicon content and high Si–C and C–Si–O_x bond concentrations up to several at. %. The produced materials were tested as metal-free catalysts in the dehydrogenation and dehydration of aliphatic alcohols and as electrode materials of Li-ion batteries. It was found that the defectiveness of Si-GNFs affected their catalytic and electrochemical properties. Si-GNFs electrodes showed a specific capacitance up to 650 mAh/g at 0.5 A/g after 300 cycles and a capacity retention of ~65% at 5A/g after 3000 cycles.

Conclusions: Developed technique allows synthesis of new type of graphene materials: Si-doped graphene nanoflakes with controllable doping level, localization, and defectiveness. Tuning the silicon concentration one can change the catalytic properties and capacity of the materials.

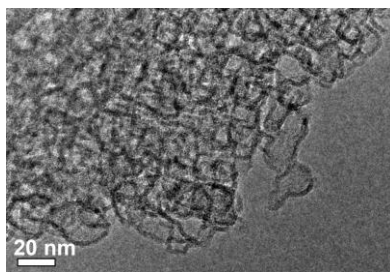


Figure 1. TEM image of Si-doped GNFs

Acknowledgements: This work was supported by Russian Federation President grant #MK-2144.2020.3.

Ti–Ni AND Ti–Co MIXED OXIDES SUPPORTED ON Y ZEOLITE WITH DIFFERENT POROSITY AS PHOTOCATALYSTS IN DEGRADATION OF AMOXICILLIN

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Keywords: Y zeolite, hierarchical Y zeolite, Ni/Co modified TiO₂, photocatalytic degradation

Introduction: Zeolites are very useful supports for synthesis of catalysts. Many of these materials with photocatalytic properties contain active species with TiO₂ homogeneously dispersed [1] and often a co-dopant in order to enhance their efficiency. Among different transition metal ions, Ni and Co have been used in photocatalytic degradation of organic pollutants. The present work reports the synthesis of Y zeolite with microporous and hierarchical structure containing Ti–Ni and Ti–Co mixed oxides as photocatalysts for degradation of amoxicillin from water. The effects of supports, TiO₂ loading and type of the second immobilized metal (Ni or Co) on formation of reactive species, photocatalytic performances and mechanism were studied.

Materials and methods: In the first step, there were obtained zeolite supports (Y zeolite- named Y and hierarchical Y zeolite-named hY). In the second step, these supports were impregnated with active species (Ti, Co and Ni). Firstly, different Ti amounts (5%, 10% TiO₂) were supported, followed by loading of Ni/Co species (5% NiO, CoO). The obtained samples were named YT5N, hYT5N, YT10N, YT5C, hYT5C, YT10C and were characterized by XRD, N₂ sorption, UV-Vis absorption, Raman spectroscopy and H₂-TPR. Photocatalytic activity was evaluated in degradation of amoxicillin (AMX) as a model test. The photocatalytic mechanism was investigated using ethanol, p-benzoquinone and KI as •OH, •O₂[–] radicals and hole (h⁺) scavenger. Formation of •OH radical on the samples surface under irradiation was investigated by fluorescence technique.

Results: The X-ray diffraction evidenced that the crystallinity of the zeolite Y was not altered after impregnation with Ti and Co/Ni species. Also, the XRD results evidence the presence of TiO₂ as anatase on zeolite materials. The intensity of the anatase characteristic peak increased with TiO₂ loading. N₂ adsorption-desorption results showed type IV isotherms for hY samples and a combination of type IV and I isotherms for Y samples. UV–Vis diffuse reflectance spectra presented characteristic peaks of TiO₂, NiO and CoO species. The absorption edge of photocatalysts shift to visible region with increasing of Ti loading and especially with Co and Ni addition. TPR profiles indicated the presence of bulk NiO and some Ni sites incorporated into the zeolite framework in all the samples modified with Ni. Furthermore, Ni ions located inside the channels of zeolite were evidenced only for the samples with hierarchical zeolite support. The photocatalytic evaluation evidenced the effect of support, TiO₂ loading (5% was the optimal concentration), Ni or Co and irradiation wavelength. Better degradation efficiencies were obtained for Ni containing photocatalyst.

Conclusions: New active photocatalysts were obtained by dispersion of TiO₂ and Ni /Co oxides on zeolite. The support properties, TiO₂ amount and immobilization of Co or Ni species influenced their dispersion and metal-titania interaction, leading to formation of different reactive species responsible for the photocatalytic degradation of amoxicillin. In fact, degradation efficiency is a result of active radicals and depends on their number and time of the photocatalytic process.

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BIO-BASED POLYESTER/CELLULOSE FILMS FOR ENGINEERING APPLICATIONS

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Keywords: Poly(lactic acid); Poly(hydroxybutyrate); Nanocellulose; Nanocomposites.

Introduction: A large part of the materials intended for engineering applications are still based on non-renewable resources thus contributing to the accumulation of plastic wastes [1]. The replacement of petroleum-based polymers with bio-based ones is a must of the current period. Poly(lactic acid) (PLA) is the most used biopolymer due to its many advantages arising from its high mechanical properties and transparency along with the availability on the market, and easy processing [2]. Poly(3-hydroxybutyrate) (PHB) is one of the most promising biopolyesters obtained from bacterial fermentation and is seen as a substitute of petroleum-based polymers in biomedical and engineering applications [3]. Nanocellulose represents a renewable and innovative filler, that incorporated or combined with other biopolymers may give rise to a multitude of performing and sustainable multifunctional materials [1, 3]. This work aimed to obtaining PLA/PHB composite films reinforced with different concentration (0 - 4 wt%) of nanocellulose extracted from cheap sources.

Materials and methods: Nanocellulose extracted from agricultural waste (NC), polylactic acid (PLA 4032 D), in the form of pellets, containing 1.4% D isomer and with an average molecular weight of 220 kDa (NatureWorks LLC, USA) and PHB powder from Biomer (Germany) were used in this study. The polymer composites were obtained by melt – mixing method using a fully automated Brabender plastograph and pressed into films with 0.28 mm (± 0.001 mm) thickness.

Results: Incorporation of NC in the PLA/PHB matrix influenced the Young's modulus (Y), which was improved in relation to the control sample regardless NC concentration. The thermal stability of the resulted composites was not diminished by the addition of NC. Moreover, an increase of the onset temperature with 9°C was attained in the composite samples containing the highest NC amount. DMTA results showed an enhancement of the storage modulus for all PLA/PHB/NC composites, especially at room temperature, revealing the reinforcing effect of this type of fibers.

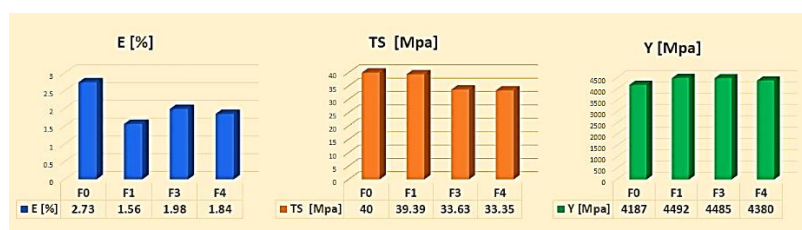


Fig. 1 Mechanical properties of PLA/PHB matrix and PLA/PHB/NC composites

Conclusions: Polyesters - nanocellulose composite films intended for engineering applications were obtained using only bio-based materials. TGA analysis highlighted the positive effect of NC fillers in improving the thermal stability of the PLA/PHB matrix. Both static tensile test and dynamical mechanical analysis pointed out an improved stiffness upon the incorporation of NC. Thus, the obtained composites can be considered as potential candidates for safe toys.

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PREPARATION OF TRANSPARENT AND ANTIREFLECTIVE SILICA THIN COATINGS ON PLASTIC SUBSTRATES BY SOL-GEL PROCESS

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Keywords: sol-gel, thin films, plastic substrate, wettability

Introduction: Due to their range of applications, from anti-icing to self-cleaning, low-adhesion, antibacterial, anti-reflection, anti-contamination and anti-fogging, multifunctional silica thin films are becoming very attractive in recent years.¹ Their application is widespread, including lenses for glasses, photovoltaic solar panels and mobile phones.² The objective of this work was to synthesize the sol-gel modified silica materials using silane precursors with various functional groups, and depositing them onto plastic substrates in order to realize transparent and antireflective coatings.

Materials and methods: Different alkoxysilanes (tetraethoxysilane (TEOS), dimethylethoxyvinylsilane (DMVES), octyltriethoxysilane (OTES), hexadecyltrimethoxysilane (HDTMES)) were used as silica source and as modifier agents. Hybrid silica systems were synthesized by the acid-catalyzed sol-gel process at room temperature. The resulted films were dried at a temperature of 25 °C and irradiated by UV lamp (365 nm) for 10 minutes. The final samples were characterized both as powders (obtained after solvent evaporation) and as films deposited on plastic. The physico-chemical and structural properties of prepared sol-gel silica materials were characterized by FT-IR and UV-VIS spectroscopy, contact angle measurements and TGA analysis.

Results: The functional groups present in the silica hybrid films were identified by FT-IR spectroscopy. Resulted coatings showed a reduction in the reflectance compared with un-coated plastic substrate (Figure 1). The reflectance of thin films was about 10% at 550 nm. In order to establish the wettability of the coatings, the sol-gel silica hybrid films were subjected to water contact angle analysis. Thermogravimetric analysis was used to test the thermal stability of the sol-gel silica hybrid materials produced from the sol-gel phase.

Conclusions: Transparent and antireflective silica thin films were prepared by acid-catalyzed sol-gel process, using silane precursors with different functional groups (vinyl, octyl, hexadecyl) and these obtained materials can generate coatings with potential use in various fields.

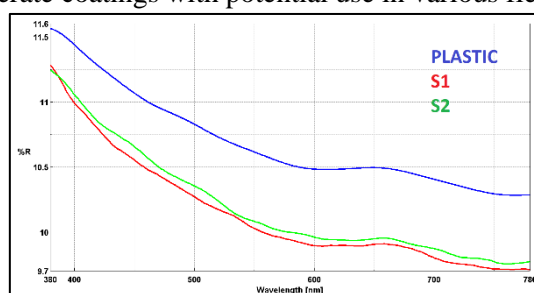


Fig 1. Diffuse reflectance spectra of thin films (S1-TEOS+DMVES+OTES; S2-TEOS+DMVES+HDTMES)

Acknowledgements: The work on this paper was supported by the INCDP ICECHIM Bucharest 2019-2022 Core Program PN. 19.23–Chem-Ergent, Project No.19.23.03.04

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POSTER PRESENTATIONS



STABILISATION OF PHOTSENSITIVE CURCUMIN BY MICROENCAPSULATION

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Keywords: *curcumin, encapsulation, photocatalyst, TiO₂*

Introduction: The natural dyes extracted from plants are efficient sensitizers for TiO₂ particles involved in photocatalytic processes. Curcumin, extracted from turmeric powder, presents an intense sensitizing effect, leading to very good efficiencies of TiO₂ in the degradation processes of contaminants [1,2]. One of the important issues that have to be solved is the photochemical degradation of sensitizer, which results in loss of the catalysts efficiency over time. Experimental data regarding the photochemical stabilization by encapsulation of curcumin used as sensitizer in photocatalytic processes are presented.

Materials and methods: For the extraction of curcumin, both conventional and microwave assisted methods were used. The extraction was optimized by analysing the influence of the main parameters. The encapsulation via silanization [3, 4] was performed using tetraethoxysilane (TEOS) and 3-aminopropyl-triethoxysilane (APTES) or lysine, which can successfully interact with the carbonyl groups of curcumin. The photodegradability of the stabilized curcumin was studied, which showed an increase with 40% of light stability after its encapsulation in silica matrix.

Results: The studies regarding the optimal parameters showed that the extraction of curcumin is more efficient when increasing the temperature: the absorption maximum was double for ethanol reflux extraction than for maceration. For the microwave assisted extraction (MAE), the optimal parameters are: 60°C, 15min, and 900rpm. Analysing the required extraction time and the corresponding energy consumption, MAE proves to be a more efficient extraction method.

Curcumin encapsulation leads to the formation of nanometric spherical capsules with porous morphology. The process is influenced by the electrostatic interaction between TEOS and the amino group of the surfactant, as well as by the working conditions. According to the quantity of curcumin encapsulated in a gram of silica, it can be stated that a very good dispersion of the dye is achieved.

Conclusions: Natural dyes represent a viable alternative for TiO₂ sensitizing in photocatalytic processes. Encapsulation can be an efficient strategy regarding the increase of natural dyes stability during photodegradability processes.

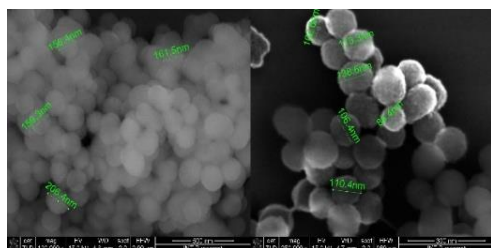


Figure 1. SEM analysis of encapsulated curcumin

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STRUCTURE AND PROPERTIES OF ELECTROCHEMICAL COMPOSITE METAL COATINGS CONSISTING OF CARBON NANOWALLS AND COPPER

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Keywords: carbon nanowalls; copper deposition; corrosion-resistant; composite metal coatings.

Introduction: This research details the electrodeposition of **copper** onto **carbon nanowalls** film, on a **steel** substrate. In the past decade, electrodeposition was one of the most widely used methods for the metallic matrix production industry, used to obtain anti-corrosion coatings. In this research was analysed the structure and physical-chemical properties, as well as quality control methods and testing methods, of a composite metal electrodeposition consisting of a first layer of carbon nanowalls, followed by a secondary layer of copper, on steel substrate. The main objectives were to increase the **corrosion-resistant properties**, the uniformity of grains on the surface of the substrate and also, solving some problems that may appear on the surface (such as: exfoliation, spots, unevenness, adhesion problems). The novelty regarding this work appears by using a matrix consisting of multi-walled carbon structures followed by a metallic element deposition. So far, only carbon nanotubes have been used for this purpose.

Materials and methods: The test where realized on stainless-steel samples (K455, weight percentage as follows: C 0,60%, Si 0,69%, Mn 0,34%, Cr 1,19%; V 0,18%, W 2%, P 0,015%, S 0,012%; Fe balance, (2 mm thick) available from BOHLER. All copper electrodepositions processes were performed from an alkaline solution containing CuCN 60 g / L; KCN 30 g / L on K455 steel samples. Experiments were realized using an Autolab 302 N potentiostat-galvanostat. An electrochemical cell formed by a 3-electrode system was carried out (as a working electrode prepared K455 steel sample was used, as reference electrode Ag / AgCl, 3M KCl and copper electrode as auxiliary electrode).

Results: The uniformly distributed multi-walled carbon structures on the metallic matrix decreases the grain size of the metallic coating and helps to have a homogeneous metallic layer. This homogeneous layer, also acts as a protection against corrosion. Obtained samples were characterized by scanning electron microscopy (SEM). Corrosion stability was evaluated by recording Electrochemical Impedance Spectroscopy (EIS) spectra, Tafel plots and cyclic voltammetry curves.

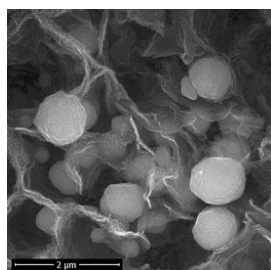


Figure 1. SEM images of Cu deposited on K455

Conclusions: Copper incorporation into carbon nanowalls was successful realized even though the surface is hydrophobic, obtaining a layer with improved properties for steel substrate.

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RDF WASTE CONVERSION TO CARBON ADSORBENT

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Keywords: *RDF fuel, waste materials, adsorbent*

Introduction: RDF is a mixture of materials, characterized by a higher combustibility (e.g. paper, plastic) as compared with the components in the total waste stream. RDF is successfully used as a fuel additive in coal-fired boilers (calorific value between 12,000 and 16,000 J / g) in thermal power plants or as a stand-alone fuel for specially designed facilities.

A big problem with thermal power plants is the high content of hazardous organic substances in pyrolysis gases. This requires their purification as this are commonly used filters containing a carbon adsorbent.

The aim of the research is to develop a method for processing RDF fuel, which leads to production of liquid and gaseous combustible products and solid product with carbon adsorbent properties are obtained.

Materials and methods: RDF from waste tarpaulin made of polyvinyl chloride was subjected to thermo-chemical treatment with sulfuric acid at 200° C, followed by carbonization at 600° C and subsequent hydro-pyrolysis.

Results: The final product is nanoporous material with a high surface area of 700 m²/g.

The initial material was examined by TG and DSC analysis. The resulting carbon adsorbent was characterized by elemental analysis, BET, etc.

Conclusions: The obtained results show that the material has a potential application for adsorption of contaminants.

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DIFFERENT APPROACHES IN DESIGNING SENSITIVE TOOLS BASED ON NANOCOMPOSITE MATERIALS FOR BIOLOGICAL ANALYTES DETECTION

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Keywords: carbon nanoribbons, nanotubes, metallic nanoparticles, electrochemical impedance spectroscopy

Introduction: Sensitive, stable and robust electrochemical sensors have been designed through modification of the working electrodes with different complex matrices based on carbon nanomaterials and metallic nanoparticles. Therefore, screen-printed electrodes were modified with complex matrices of hybrid nanomaterials using physical deposition or entrapment in polymeric film. The designed sensors allowed a fast and sensitive detection of some important biological analytes involved in the degradation process of several food products [1], as well as in the electrocatalytic activity towards oxidation of some phenolic compounds found to be environmental pollutants [2].

Materials and methods: The electrochemical sensitive platforms have been designed by modification of the carbon screen-printed electrodes with hybrid nanocomposite matrix, through entrapment into a polymeric film of 2,6-dihydroxynaphthalene and 2-(4-aminophenyl)-ethylamine. By functionalization of carbon nanomaterials with metallic nanoparticles were obtained multifunctional materials with uniform structure and improved electrocatalytic behavior, allowing the acceleration of the electron transfer to the electrode surface and further sensitive detection of analyte of interest. The functionalized sensors were characterized by electrochemical studies, the kinetics of the electron transfer were investigated by electrochemical impedance spectroscopy, while the morphology of the surface by SEM, TEM and FTIR spectroscopy.

Results: The FTIR spectroscopy studies showed that easily dispersion of carbon nanomaterials and metallic nanoparticles into the polymeric matrix leads to the formation of a stable film. The electron transfer resistance recorded for unmodified and modified sensors revealed that the presence of carbon nanomaterials together with platinum nanoparticles considerable decrease the resistance to electron transfer. This decrease shows that the nanocomposite materials poses high conductivity, accelerating the electron transfer and demonstrating the synergy of the materials used and the increase in the electrocatalytic capacity of the sensor surface. Further, amperometric detection of hydrogen peroxide has been performed at an applied working potential of +0.15 V vs Ag/AgCl, in a concentration range of 0.01 to 5 mM.

Conclusions: The modification of sensors with hybrid nanomaterials provides an electroconductive network and a large active surface of the sensors, thus accelerating the transfer of electrons, allowing a sensitive detection of some biological analytes without need of a bioreceptor.

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IN VITRO BIOCOMPATIBILITY STUDIES OF CHEMOTHERAPEUTIC DRUG DELIVERY SYSTEMS BASED ON POLYMER-CLAY NANOCOMPOSITES

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Keywords: nanocomposites, Salecan, doxorubicin.

Introduction: Encapsulation of nanoclays into polymers to obtain a complex network could represent a promising way to improve the capacity of retaining and releasing therapeutic drugs [1,2]. In the present study, *in vitro* biocompatibility of nanocomposites systems containing different concentrations of Salecan and loaded with doxorubicin (DOX) was investigated. The drug loading efficiency of the nanocomposites systems and their effect on cellular viability and proliferation on normal and tumoral cell lines was tested *in vitro*.

Materials and methods: Nanocomposites systems were prepared as previously described [3] and DOX loading efficiency and release was calculated. Cytotoxic effect was evaluated by MTS reduction assay at 30 min and 3 hrs on normal MDBK (Madin-Darby Bovine Kidney), human colon adenocarcinoma HT-29, and Colo 205 human colon adenocarcinoma cells. Cell proliferation and internalization were investigated by immunofluorescence microscopy.

Results: DOX loading efficiency was found to increase with Salecan concentration and its release from the nanocomposites systems pH dependent. A good viability of normal and HT-29 cells exposed to all nanocomposites systems was observed. In the case of Colo 205 cells, the system containing the highest amount of Salecan led to a drop in the cell viability of ~ 40%. The results correlated with the fluorescence microscopy observations revealing DOX internalization and its nuclear localization.

Conclusions: Hydrogel nanocomposites with Salecan and clay could be good candidates as vehicles for a chemotherapeutic agent.

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IN VITRO CYTOTOXICITY OF POLYMERIC NANOPARTICLES COATED WITH LIPID LAYER LOADED WITH CARDIOVASCULAR DRUGS

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Keywords: nanoparticles, amlodipin, valsartan, in vitro cytotoxicity

Introduction: Nanomedicine is a rapidly growing field that uses nanotechnology to solve clinical problems, mainly diseases with high risk of mortality (eg. cardiovascular, cancer diseases). A new class of nanoparticles, polymeric nanoparticles coated with lipid layers, aimed at combining the advantages of both polymeric nanoparticles and lipid vesicles, has received attention in recent years [1]. Since cytotoxicity is one of the most important indicators for biological evaluation in vitro studies, the main aim of this study was to investigate the cytotoxicity of polymeric nanoparticles coated with lipid layer loaded with a mixture of two cardiovascular APIs (active pharmaceutical ingredients) on human epithelial cell line [2, 3].

Materials and methods: Polymeric nanoparticles coated with lipid layer were prepared via nanoprecipitation method using poly(lactide-co-glycolide) (PLGA), Pluronic F127 and phosphatidylcholine. The APIs loaded in nanoparticles were valsartan and amlodipine besylate, used mainly in the cardiovascular diseases therapy. The nanoparticles were characterised by entrapment efficiency, size and polydispersity index using spectrophotometric and dynamic light spectrophotometry (DLS). Also, the nanoparticles were investigated in terms of cytotoxicity in comparison with sample without lipid material - phosphatidylcholine. The cytotoxicity of these nanoparticles was evaluated through the tetrazolium-based colorimetric assay (MTT) on human epithelial cells. The MTT assay involves NAD(P)H-dependent cellular oxidoreductase enzyme that converts the yellow tetrazolium MTT into insoluble compound (formazan), which was dissolved with dimethyl sulfoxide (DMSO) to give a purple colour with characteristic absorption at 540 nm [4]. Intensity of purple colour is directly proportional to the cell number and thus indicating the cell viability.

Results: DLS analysis of nanoparticles indicated sizes lower than 300 nm with good dispersity (PDI<0.3). Nanoparticles showed higher encapsulation for amlodipin and valsartan as well. Both samples - with and without lipid material - showed no significant cytotoxicity on human epithelial cell line.

Conclusion: Polymeric nanoparticles coated with lipid layer represent an important potential drug delivery system for future cardiovascular applications.

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THE PRELIMINARY RESULTS OF PULLULAN NANOPARTICLES LOADED WITH 5-FLUOROURACIL

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Keywords: pullulan, nanoparticles, 5-fluorouracil, cancer

Introduction: Cancer is the second leading cause of death worldwide and one of the most challenging diseases to cure being a health problem in spite of the rising number of nanoscaled technologies. Although the development of both diagnostic and therapeutic tools is increasing, nonselective distribution of drugs, enhanced drug toxicity, and undesirable side effects to normal tissues aggravate the challenges for chemotherapy [1]. In order to overcome these disadvantages, carrier-mediated drug delivery offers a number of design opportunities for engineering the delivery of a particular drug, with enhanced therapeutic effect. Nowadays, many studies in cancer therapy are focused on drug delivery systems based on biopolymeric nanoparticles [2-3]. In this study, we aimed to obtain and evaluate pullulan acetate-based nanoparticles loaded with an anticancer agent, 5-fluorouracil (5-FU).

Materials and methods: Pullulan was produced through fermentation process by *Aureobasidium pullulans* strain and was further chemically modified with dimethylformamide, pyridine and acetic anhydride obtaining pullulan acetate. The 5-FU-loaded pullulan acetate nanoparticles were successfully obtained by various methods. Nanoparticles were characterised in terms of entrapment efficiency, size and polydispersity index.

Results: The 5-FU-loaded pullulan acetate nanoparticles showed satisfactory size and polydispersity index. Also, the results revealed a good entrapment efficiency of 5-FU.

Conclusion: The present study implied that pullulan and their derivatives have a high potential for the production of nanoparticles with application in anticancer agent delivery.

Acknowledgements: his work was supported by Ministry of Research and Innovation CNCS-UEFISCDI, program NUCLEU PN 1941-04 01.

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NANOPOROUS CARBON FROM RDF WASTE FOR DYE REMOVAL

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Keywords: *adsorption; carbon; RDF; water purification; phenol*

Introduction: Phenol is one of the most common organic water pollutants, stable towards biodegradation. Phenol and substituted phenols are toxic organic pollutants, usually present in industrial waste waters, especially these from oil refineries, coal conversion plants, pharmaceuticals, etc. Refuse-derived fuel (RDF) is a fuel produced from various types of waste such as municipal solid waste and industrial waste. RDF consists of combustible components, like polymers, paper and other waste materials. RDF can be also produced from used tyres or biomass waste. The combusted biomass fraction of RDF is used by stationary combustion operators to reduce their overall reported CO₂ emissions.

Materials and methods: Nanoporous carbons is prepared from RDF waste tarpaulin by pyrolysis at 600 °C and subsequent hydro-pyrolysis at 800 °C. The synthesized carbon was characterized by N₂ physisorption at -196 °C, determination of oxygen-containing surface groups, IR spectroscopy, etc.

Nanoporous carbon from RDF is characterized by high surface area of 650 m²/g and significant content of micro- and mesopores. The results suggest that obtained nanoporous carbon material is suitable for application as effective adsorbent of organic and inorganic pollutants.

Aqueous solutions with different initial known concentrations were used, as model water bromothymol blue solutions in the range from 10 mg/l to 50 mg/l. Adsorption isotherms were determined by using stoppered flasks, containing 0.1 g of carbon in 50cm³ of solution. They are agitated by a mechanical shaker for predetermined time intervals at room temperature to reach equilibrium conditions. The concentrations are determined spectrophotometrically, at maximum adsorption wavelength of 544 nm, using spectrophotometer Pfaro 300 UV spectrometer.

The Langmuir equation is applied to calculate the maximal adsorption capacity.

Results: Nanoporous carbon with high surface area and well developed micro- and mesoporosity is obtained using solid waste from RDF as precursor. The obtained carbon show moderate adsorption capacity towards phenol in aqueous solution.

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FUNCTIONALIZATION OF PET AND WPET NANOFIBRES GRAFTED WITH OPRPY FOR THE RECOVERY OF Cu^{2+} IONS FROM AQUEOUS SOLUTION

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Keywords: Waste polyethylene terephthalate; Polyethylene terephthalate; Nanofibres; Ligands; Adsorption.

The plastic and metal pollution accumulating in the marine environment have given many researchers motivation to investigate and provide solutions to this problem. The most abundant plastic waste found in the marine environment is polyethylene terephthalate (PET) based plastic waste. Because PET based plastics are the most used polymers and globally polluting the marine environment, recycling these polymers is required so as to reduce the accumulated PET based waste in the marine environment. Plastic waste which is PET based can be recycled using electrospinning techniques. Nanofibres made of PET or waste PET (WPET) are rarely active adsorbents, however, chemical reactions can be carried out with the nanofibres to make them active for any desired purpose. The PET and WPET nanofibres were functionalized through grafting reactions respectively. Grafting is one of the immobilization methods under amination, which is defined as introducing primary amines onto the surface of the PET or WPET nanofibres. The grafting method involves the reaction of the pendant amine compounds with the chelating ligand 2-(3-octyl-1H-pyrazol-5-yl) pyridine (oPrPy) as applied in this study. The ATR-FTIR patterns of PET-oPrPy and WPET-oPrPy nanofibres showed NH_2 and N-H peaks at 3258 cm^{-1} and methyl C-H and methylene in the range of 2952 to 2853 cm^{-1} that was assigned to oPrPy verifying the attachment of the oPrPy on the PET and WPET nanofibres surface. The degree of surface modification on PET or WPET nanofibres was examined through the adsorption of Cu^{2+} ions from an aqueous solution. Batch adsorption experiments were carried out using the functionalized materials and showed that the PET-oPrPy and WPET-oPrPy nanofibres were active adsorbents for recovery of Cu^{2+} ions. PET-oPrPy and WPET-oPrPy nanofibres achieved adsorption equilibrium within the initial 90 min and 60 min of contact time respectively with 9.70 mg/g and 16.43 mg/g Cu^{2+} adsorption capacity. The WPET-oPrPy nanofibres was best fitted in isotherms with this order Langmuir > Freundlich > Redlich-Peterson with correlation coefficient $R^2 = 1$ and ERRSQ approaching zero. While WPET-oPrPy nanofibres was best fitted in isotherms with this order Langmuir > Freundlich > Redlich-Peterson with correlation coefficient $R^2 > 0.99$ and ERRSQ approaching zero.

SYNTHESIS, SPECTRAL CHARACTERIZATION, AND ANTI-TUMOR ACTIVITY OF SOME PYRAZOLE DERIVATIVES

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Keywords: organic synthesis, pyrazoles, NMR spectroscopy, cytotoxicity

Introduction: Cancer is a terrible disease that is spread around the world. Chemotherapy remains a significant way of treating cancerous diseases. Although some impressive progress has been made in cancer therapy, drug resistance and toxicity, the development of new anticancer chemotherapeutic agents is being sought [1, 2].

Materials and methods: Commercial reagents have been used in the synthesis of intermediate pyrazolic compounds. All synthesized pyrazolic compounds were characterized by IR, ¹H-NMR ¹³C-NMR, UV-Vis, MS, elemental analysis, and tested *in vitro* for their anti-tumor activity.

Results: In this study a series of pyrazole derivatives were synthesized in two steps with good yields: In the first step, pyrazoles reacted with a aqueous 30% formaldehyde solution to give the 1-(hydroxymethyl)pyrazole derivatives [3]. In the second step, the 1-hydroxymethyl-pyrazoles reacted with, aromatic amines giving pyrazole Mannich bases [4, 5]. The structures of all compounds were confirmed by ¹H, ¹³C-NMR, FTIR, UV-VIS spectra and elemental analysis. All compounds were tested *in vitro* for their anti-tumor activity.

Conclusions: It was found that the presence of halogen atom into the pharmacophore structure exhibited the most significant anti-tumor activity.

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REMOVAL OF NAPHTHALENE BY CARBON FOAM

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Keywords: Carbon foam; furfural; industrial coal tar pitch, naphthalene.

In this study naphthalene was chosen as a representative model compound of polycyclic aromatic hydrocarbons applying carbon foam as adsorptive material.

Introduction: The unique properties, which depend on the precursor properties and synthesis conditions, make carbon foams high performance engineering materials, and determine their many potential applications [1-3]: shipbuilding – space modules, deck structures; aerospace – aerospace modules, rocket nozzles and motors, radar adsorbing and antennae systems; energy and electronics – fuel cells, battery electrodes, nuclear shields, rods for nuclear reactors; shields and body lightweight armour; bone surgery material, prosthetics, tooth implants [1-3].

PAH constitute an important class of highly toxic and long persistent environmental pollutants. For recognition of their toxicity and high mobility in the environment, the World Health Organization has recommended a limit for PAH in drinking water, and the European Environmental Agency (EEA) has included these compounds in its list of priority pollutants to be monitored in industrial effluents.

Materials and methods: Coal tar pitch was heated up to 120 °C till melting conditions. Furfural was heated to the same temperature and added to the pitch with continuous stirring. The obtained mixture was treated at 120–200 °C (during the reaction the temperature rises up to 200 °C) with concentrated H₂SO₄ (98 wt%) or HNO₃ (68 wt%) - drops of acid were added to the mixtures with continuous stirring until solidification. The obtained solid product was heated at 1000 °C in a covered silica crucible with a heating rate of 15 °C min⁻¹ under nitrogen atmosphere.

Adsorption measurements of naphthalene from aqueous solutions on carbon adsorbents were performed at room temperature. Initial and equilibrium concentrations of the aqueous solutions were measured using a UV spectrometer at a wavelength of 275.5 nm.

Results: Carbon foam is characterized by X-ray analysis, Scanning Electron Microscopy, TG and DSC analysis, Elemental analysis, BET. The proposed new, less energy consuming synthesis method, allows to avoid the use of pressure and stabilization step, which enables the production of material with very good physico-chemical properties.

Conclusions: Carbon foam with a developed porous structure with predominant macroporous content is obtained. Naphthalene uptake on carbon foam is 100 mg g⁻¹.

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SYNTHESIS OF SOME HETEROCYCLIC COMPOUNDS WITH NONLINEAR OPTICAL PROPERTIES

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Keywords: organic synthesis, heterocycles, nonlinear optical properties, hyperpolarizability (β).

Introduction: Organic compounds have been mentioned recent decades, as an alternative to their inorganic counterparts, due to their strong nonlinear optical (NLO) properties, with many applications [1]. Field effect transistors, organic light-emitting diodes (OLEDs), photovoltaic devices and white light sources for indoor and outdoor lighting are some of the applications of organic materials [2,3]. In addition to the classic organic push-pull molecules with high values of dipole moment and polarizability, there are a number of other compounds, such as fullerenes, perylenes, polymers or dyes that possess very notable nonlinear optical properties [4,5].

Materials and methods: Organic commercial and synthetic materials were used for the synthesis of the heterocyclic compounds. All compounds were characterized with physicochemical techniques (elemental analysis, ¹H, ¹³C, FTIR and UV-Vis spectroscopy). The SHG capability of samples was measured by using an experimental set-up.

Results: Three series of heterocyclic compounds (octahydroacridines [6-9], thioamides [2] and azo-pyrazolone [5] with classical push-pull structures) were synthesized and characterized. The SHG (second harmonic generation) value was determined for each compound. The molecular polarizability (α), first order hyperpolarizabilities (β_{tot}), dipole (μ_{tot}) and quadrupole (Q) moments, were calculated using DFT (density functional theory) method.

Conclusions: It was found that the NLO efficiency was best in the case of one compound with low HOMO-LUMO energy gap (HOMO = high occupied molecular orbital; LUMO = low unoccupied molecular orbital) and high total hyperpolarizability.

Acknowledgements: List funding sources in compliance to funder's requirements.

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SYNTHESIS, SPECTRAL CHARACTERIZATION ANTIMICROBIAL ACTIVITY AND DFT STUDIES OF SOME TETRAHYDROPYRIMIDINONES

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Keywords: organic synthesis, tetrahydropyrimidines, NMR spectroscopy, density functional theory (DFT).

Introduction: Dihydropyrimidine and tetrahydropyrimidine derivatives are pivotal heterocycles in medicinal chemistry. The reaction most often involved in the synthesis of these compounds is the multicomponent synthesis of Biginelli, which has been improved over the years [1].

Materials and methods: Organic commercial and synthetic materials were used for the synthesis of the heterocyclic compounds. All compounds were characterized with physicochemical techniques (elemental analysis, ¹H, ¹³C, FTIR and UV-Vis spectroscopy).

Results: In this study a series of tetrahydropyrimidinones were synthesized in two steps: 1. Biginelli synthesis [2]; 2. alkylation of intermediates from step 1. The structures of all compounds were confirmed by ¹H, ¹³C-NMR, FTIR, UV-VIS spectra and elemental analysis. A DFT analysis of molecular structure and frontier molecular orbitals HOMO-LUMO was performed using the GAMESS 2012 software [3-6]. All compounds were evaluated by qualitative and quantitative methods against a panel of selected bacterial and fungal strains.

Conclusions: It was found that the presence of nucleophilic group and symmetry of the molecule are advantages for a high antimicrobial activity.

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SILICA NANOPARTICLES LOADED WITH CURCUMIN – ENCAPSULATION EFFICIENCY

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Keywords: curcumin, silica nanoparticles, surfactant, antioxidant, dialysis

Introduction: Curcumin is a natural compound, being a well-known ingredient in different foods. There are also multiple therapeutic benefits favorable to the dietary intake of curcumin, most of these benefits being due to its antioxidant and anti-inflammatory effects [1, 2]. Despite its benefits, one of the major problems associated with ingesting curcumin is its poor bioavailability, which is mainly due to poor absorption, rapid metabolism and rapid elimination. Several methods have been tested to overcome these drawbacks, one of them being encapsulation. In this study, DMSO-solubilised curcumin was *in situ* encapsulated in silica nanoparticles, as transport vectors.

Materials and methods: Silica nanoparticles were produced by sol-gel process, starting from tetraethyl orthosilicate (TEOS) and vinyltriethoxysilane (VTES). The *in situ* growing of silica nanoparticles was carried out in the presence of three different surfactants polyethylene glycol *tert*-octylphenyl ether (Triton X), polysorbate 80 (Tween 80) and dioctyl sodium sulfosuccinate (AOT). Purification by dialysis was also performed on the obtained nanoparticles, to eliminate the DMSO and the excess of surfactant.

Results: UV-Vis, DLS and TEM analyses were performed on the obtained transport vectors in order to study their structure, size and morphological aspect. Figure 1 shows the overlap of the UV-Vis spectra of samples B1-B3, the observed maxima being at the value of 425 nm [3]. According to TEM analysis (Figure 2), the particle size ranges between 20 and 40 nanometers. The particles shape is spherical, but traces of surfactant can still be observed, indicating that this component has not been completely removed by dialysis.

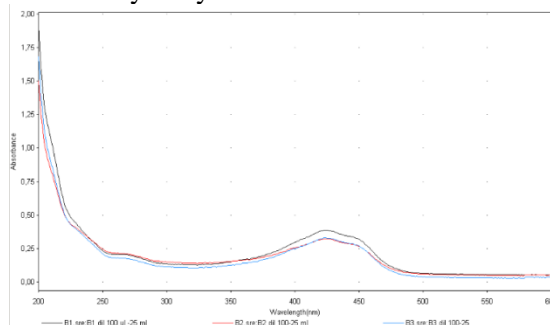


Figure 1. UV-Vis spectra of samples B1-B3

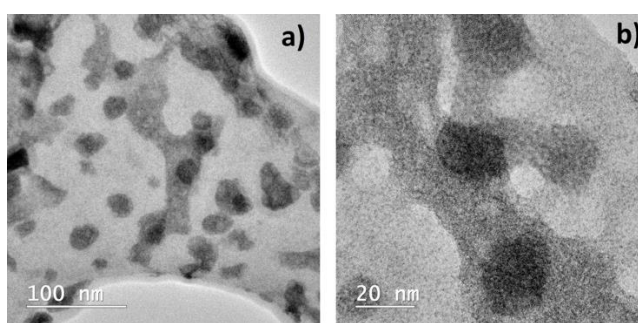


Figure 2. TEM images of particles a) B2 and b) B3

Conclusions: *In situ* encapsulation of curcumin in silica nanoparticles was successfully achieved using three different types of surfactants. The obtained transport vectors are expected to increase the bioavailability of curcumin in the human body.

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SYNTHESIS AND MORPHOLOGICAL INVESTIGATION OF FLOWER-LIKE ZnO NANOSTRUCTURES

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Keywords: *flower like, ZnO nanoparticles*

Introduction: In recent years, ZnO nanostructures have attracted great interest due to their significant potential applications. The important role of morphology related properties of nanostructures has stimulated tremendous efforts in the design and synthesis of ZnO nanoparticles with special morphology [1]. They are widely used in several industrial areas such as UV light-emitting devices, ethanol gas sensors, photo-catalysts, anticorrosive coatings, pharmaceutical, and cosmetic industries. ZnO is a bio-safe material, with distinctive abilities such as structure-dependent electrical and thermal transport properties, that might vary according to the particle size, shape, morphology, orientation and ratio [2].

Materials and methods: Flower-like ZnO nanostructures were synthesized through simple and environmentally-benign hydrothermal and solvothermal processes at 70 °C. The size and shape of resulted ZnO nanoparticles have been characterized by Dynamic Light Scattering (DLS) analysis and Transmission Electron Microscopy (TEM).

Results:

Variation of shape and size with the two different preparation methods was investigated in this study. It was observed that the flower-like structures are connected with each other through contacts between the rods [3]. Figure 1 is the TEM image of a single flower-like ZnO microstructure which indicates that the entire structure is built from ZnO nanorods and they are radiated through the centre to form flower-like structures.

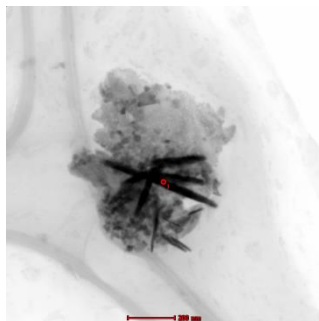


Figure 1. TEM image of flower-like ZnO nanoparticles

Conclusions: Flower like ZnO nanoparticles have been prepared by both hydrothermal and solvothermal processes. Their size and morphology have been studied using DLS and SEM analyses.

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NANOFIBERS WITH ANTIBACTERIAL PROPERTIES BASED ON THERMOPLASTIC ELASTOMERS AND ISOFURAL

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Keywords: nanofibers, isofural, thermoplastic elastomers, antibacterial, electrospinning

Introduction: The study aim was the synthesis and characterization by thermal and structural properties of nanofibers, obtained by electrospinning using styrene-butadiene block-copolymers (SBS) and styrene-isoprene block-copolymers (SIS), as well as their composites with isofural.

Materials and methods: In the first step, styrene-butadiene block-copolymers (SBS) and styrene-isoprene block-copolymers (SBS) 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 with antibacterial properties were obtained, using the synthesized thermoplastic elastomers and isofural in tetrahydrofuran solution.

The polymeric composites with antibacterial properties obtained from thermoplastic elastomers and isofural were used for the manufacture of nanofibers by electrospinning (Figure 1, 2).

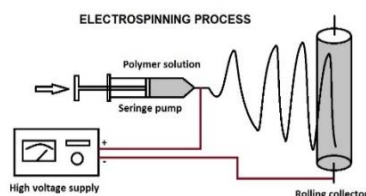


Figure 1 Schematic representation of electrospinning process



Figure 2 Electrospinning equipment

Results: The polymer nanofibers manufactured by electrospinning were characterized by ATR-FTIR analysis, Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA).

Conclusions: The results indicated that the nanofibers obtained from composites of thermoplastic elastomers and isofural have a corresponding thermal stability. The thermal decomposition starting after 330°C using SBS and 300°C using SIS.

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SYNTHESIS AND CHARACTERIZATION OF SUPERHYDROPHOBIC FILMS WITH RASPBERRY –LIKE SILICA NANOPARTICLES AS FUNCTIONAL COATINGS

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Keywords: functional coatings, superhydrophobic, raspberry-like silica nanoparticles

Introduction: Superhydrophobic materials of innovative products were intensively studied during the last decades and many methods for their fabrication have been developed [1]. The basic concept to obtain ultra and superhydrophobic properties is the simultaneous presence of a low energy material and suitable roughness on the surface. Biomimetic strategy to achieve superhydrophobic properties that mimic lotus leaf consists in special hierarchical morphology replication. The paper presents a facile synthesis of filmogenic material, based on silica nanoparticles with unusual morphology (raspberry – like) and the changes in wettability of various solid substrates treated with the proposed coating.

Materials and methods: Functional nanoaterials have been prepared by embedding silica nanoparticles with raspberry-like morphology in polysiloxane matix. Silica nanoparticles have been synthesized using a simple sol-gel method, at room temperature, using methyl triethoxysilane (TMES) as silane precursor. Raspberry –like silica particles have been obtained by the self-assembling process of oppositely charged SiO₂ nanoparticles, functionalized with various organo-modified silane reagents. SiO₂ nanoparticles were characterized from the point of view of size, surface potential and shape using dynamic light scattering, scanning electron microscopy (SEM) and transmission electron microscopy TEM. Filmogenic nanomaterial was investigated in terms of composition using FTIR, morphology using SEM and wettability by using contact angle measurements, respectively.

Results: The coatings deposited on model paper and textile exhibits static contact angle for water of 155° and 158° with contact angle hysteresis less than 8°.

Double hierarchical morphology of nanomaterial deposited was evidenced by SEM images, that confirm the AFM results of high roughness of coated films.

Conclusions: The presence of silica nanoparticles with raspberry-like morphology in the coating material leads to a structure of the final film that closely resemble to the hierarchical aspect of natural superhydrophobic surfaces. A simple, cost effective way to produce functional nanomaterials for superhydrophobic modification of surfaces was obtained.

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CONDUCTIVE TEXTILE COATED WITH POLYANILINE

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Keywords: SEM, PANI, PES textile

Introduction: New trends in the development of conductive coated textile materials include applications as supercapacitors [1], solar cells, sensors [2], electrochromic devices [2] etc. Electronic textiles and smart wearable devices are undergoing a rapid development and actively entering user market [2-5]. Sensors and sensing systems detecting pressure, temperature, strain, as well as disease biomarkers and cellular metabolites, including glucose, lactate, and ascorbic acid have been successfully integrated into textile fabrics [2]. In this paper we aimed to obtain textiles with electrically conductive properties improved by coating polyester textile with polyaniline. Due to structure of polyaniline as a conjugate polymer containing aromatic rings and amino groups bonded by C = C double bonds, C-C bonds and N-C bonds high conductive properties were established.

Materials and methods: Preparation of conductive fabrics require following reagents: aniline 99% (Sigma-Aldrich), HCl 37% (Sigma-Aldrich), ammonium persulphate (Sigma-Aldrich), polyester fabric (from Romanian market). Coated textiles were characterized structural by Infrared Spectroscopy with ATR device and morphological by Scanning Electron Microscopy (SEM). The surface resistivity of the fabrics was measured according to standard SR EN 1149-1:2006 employing the 2 electrodes method, using a PROSTAT 800 meter.

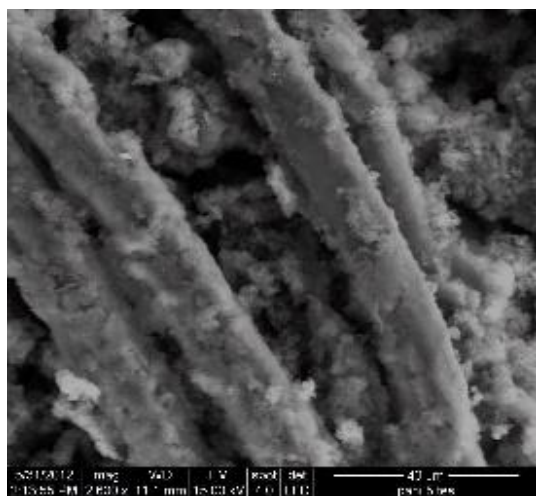


Fig.1. SEM image of polyester textile coated with polyaniline

Results:

The coated textile material present green dark color; permeability in air of 1076.6 l/m²/s; surface resistivity has a value lower than 10⁵Ω. Figure 1 shows the morphology of the polyester textile coated with polyaniline by „in situ” polymerization using HCl. FTIR spectrum shown characteristic bands of polyaniline as reported in other papers [3-5].

Conclusions: Experiments show uniform coating and good electrical properties for studied textile coated with polyaniline. The conductivity increased by six times in coated vs uncoated polyester textile.

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INNOVATIVE HYBRID HYDROGEL BASED INKS WITH APPLICATION IN TISSUE ENGINEERING

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Introduction: In recent years, identifying suitable soft materials that can be effectively printed to manufacture customized 3D parts has presented a larger challenge [1, 2]. Hydrogels proved to be suitable candidates for 3D printing due their excellent biocompatibility and physiological degradation, high swelling and crosslinking capacity. Biopolymer-clay based hydrogels are highly attractive as biomaterials in the field of regenerative medicine, owing to their low cytotoxicity, hydrophilicity and enhanced mechanical properties [1, 3]. Therefore, present study aims to investigate the capacity of a natural polymer to generate composite hydrogels in the presence of clay. These composites hydrogels will be further used as biomaterial-based inks in order to fabricate 3D scaffolds by additive manufacturing technique.

Materials and methods: The hydrogel systems were prepared at room temperature using various clay types. Several techniques were used to investigate the structural and morphological properties of the composite inks/materials as: FT-IR, swelling studies, microCT, XRD, contact angle and microscopy analyses. The biological features of the composite materials were analysed, too.

Results: The use of different types of inorganic agents in the synthesis of composite hydrogels/printing inks influenced the morphological and structural properties of the resulted materials/3D constructs but also the printing parameters.

Conclusions: The novel synthesized biopolymer-based hydrogels have proven to be suitable inks for the additive manufacturing of predefined 3D constructions that may further serve as a customized support for the administration of nutrients or drugs to the target damaged tissue.

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STRUCTURAL PARAMETERS INFLUENCING THE SHAPE MEMORY OF NEW POLYMERIC MATERIALS DESIGNED FOR 4D PRINTING

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Keywords: *shape memory, polymeric materials*

Introduction: Smart polymeric materials with shape memory are those materials which exist, on a macro scale, in temporary and permanent forms. The transition between these forms is made under the action of external stimuli that generates changes in shape and / or volume and / or color and / or physical properties etc. [1-2]. The shape memory materials are designed for application in medicine, auto industry, aerospace engineering etc. and also for academic studies [3]. The paper presents the first results in the attempt to design smart polymeric materials with shape memory for 4 D printing based on PLA.

Materials and methods: New PLA-based compounds were achieved, in a classical melt compounding Brabender – roller procedure by modification of PLA with a second polymer, synthesized using renewable monomer, for both polymers being considered grades with various chemical structures. A program for memory's setting and highlighting the shape memory property went after that. The memory setting was done using a DMA instrument Q800 V20.24 Build 43, Module DMA Controlled Force, Inst Serial 0800-1017, Geometry Rectangular (Length, Width, Thickness), Geom Factor 0.9378 1/mm 0.0784 1/mm 0.0735 1/mm², Size 12.7569/ 6.8700 /1.9800 mm, Samp Params 0.4400. The highlighting of the shape memory property was made by using a thermal route and measuring the dimensional parameters specific to the applied procedure.

Results: The behavior at the memory's setting stage depends on the structure of the macromolecules of the two polymers that have been melt compounded (figure 1). The measurement of the length of each sample with set memory before and after the thermal procedure, applied after the memory setting, varies depending on the chemical structure of the melt compounded polymers.

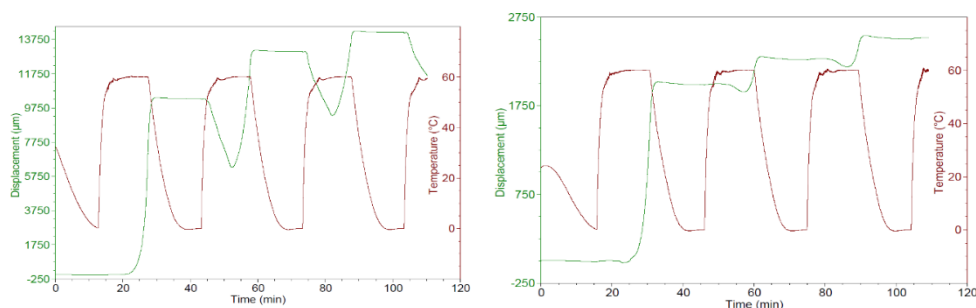


Figure1. Behavior at the memory's setting stage of two new compounds

Conclusions: The studies on the designing smart materials with the shape memory for 3D printing will continue with the deepening of the correlations between the chemical and morphological characteristics of the compound polymers and the behavior of the new compounds at the two procedures for memory's setting and recovering stages.

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ESTIMATING THE 3D PRINTING DEFECTS BY MICRO-COMPUTED TOMOGRAPHY

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Keywords: 3D printing; micro-computed tomography; defects; PLA-based compounds

Introduction: Micro-computed tomography (μ -CT) is an X-ray technique with (sub)micron resolution, typically using an X-ray tube with cone-beam geometry as a source and a rotating sample holder. While conventional CT maintained a strong position in life science and low-resolution high-energy CT became widespread in industrial quality control, micro-CT has enjoyed a boost in interest from the materials science research community in the past decade [1]. The purpose of this paper is to present the usage of micro-computed tomography as method to estimate the defects of the 3D printed items.

Materials and methods: A PLA-based compound was shaped as filaments (fig.1a) with optimal diameter and ovality (fig.1b) for 3D printing (fig.1c). The identification of the defects of the 3D printed item was performed by micro-computed tomography. To capture the global image of the 3D printed sample, a Bruker 2211 nano-computer tomography (nano-CT) equipment was used. The scanning parameters were: voltage: 60 kV, current intensity: 150 μ A, exposure: 475 ms, resolution: 3 μ m, rotation step: 0.2 degrees, rotation 180 degrees. The scanning process did not involve the use of a filter. The resolution of an X-ray was 4904x3280 pixels.

Results: The obtained results showed that the defects are placed mainly at the interface between the superimposed layers and in the contact areas with the surface on which the deposit is made.

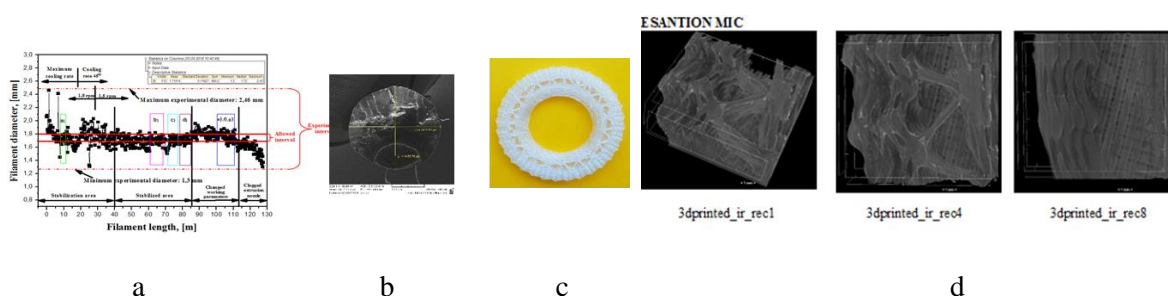


Fig.1 Variation of filament diameter obtained from selected material (a), filament's ovality (b), 3D printed item and morphology of the 3D printed item visualized by μ -CT (d)

Conclusions: The versatile and non-destructive micro-CT is a characterization method widespread in industrial quality control. It can be used also for identifying of the defects of the 3D printed items. The obtained results showed that the defects are placed mainly at the interface between the overlaid material and in the contact areas with the surface on which the deposit is made.

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ELECTROCHEMICAL STUDY OF FERULIC ACID AT A PENCIL GRAPHITE ELECTRODE

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Keywords: ferulic acid, voltammetry, pencil graphite electrode, disposable.

Introduction: Ferulic acid (FA), a hydroxycinnamic acid naturally found in fruits, vegetables and alcoholic beverages has antioxidant, antiaging, antiviral and antibacterial activity being used in medicine, food and pharmaceutical industry [1]. Therefore, there is a huge need for the rapid sensitive and selective determination of FA in various complex matrices. FA electroactivity is due to the phenolic group contained in its molecule. Thus, electroanalytical methods using proper electrodes [2] are often the best choice for FA investigation and quantification. A sensitive, cheap, eco- and user-friendly electrode is the pencil graphite electrode (PGE), which is commercially available and has also good electrochemical characteristics [3]. The present work describes the electrochemical behavior of FA at PGE and, based on this, a method for its voltammetric quantification.

Materials and methods: Working solutions were obtained from the daily prepared 10^{-2} M FA ethanolic stock solution by successive dilutions with the supporting electrolyte. A 3 electrodes cell (working electrode: PGE [4]) and a Autolab PGSTAT 12 system connected to a PC running GPES 4.9 software were used for cyclic (CV) and differential pulse voltammetric (DPV) measurements.

Results: DPV recorded for FA in acetate buffer pH 4.00 at different working electrodes (Pt, glassy carbon and PGE with graphite leads of different hardness) showed an oxidation signal at ~ 0.50 V, the highest sensitivity ($0.386 \text{ A} \times \text{L/mol} \times \text{cm}^2$) being obtained at the non-electroactivated H type PGE. FA CVs recorded at different pH values presented in the first scan a well-defined oxidation peak and a reduction signal. In the second and third scans the reduction peak remained almost unchanged but in the anodic scan a supplementary oxidation signal appeared at less positive potentials in comparison to the main one. All signals were pH dependent and their $E_p = f(\text{pH})$ equations emphasized that the processes involved an equal number of electrons and protons. The highest CV and DPV oxidation signals were recorded in Britton Robinson Buffer pH 3.00, this electrolyte being used for further investigations. The different relations between the peak currents obtained by CV at various scan rates indicated that FA main oxidation signal is governed by a controlled diffusion process, whereas the reduction signal is generated by an adsorption controlled one. Instrumental parameters (modulation amplitude and time, step potential, interval time) were optimized for FA DPV quantification.

Conclusions: CVs studies emphasized that FA presents a complex voltammetric behavior at PGE. The main oxidation signal can be exploited for its quantitative determination by DPV.

Acknowledgements: This work was supported by University of Bucharest, research grand number 20045/2018.

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VOLTAMMETRIC BEHAVIOUR OF HESPERIDIN AT A COMPOSITE GRAPHITE ELECTRODE

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Keywords: flavonoid, hesperidin, voltammetry, composite graphite electrode, disposable.

Introduction: Flavonoids are natural antioxidants with important roles in plants growth and human health. They are polyphenols with a benzene- γ -pyrone structure, the hydroxyl groups grafted on the conjugated benzene rings being responsible for their antioxidant and electrochemical activity. Thus, electrochemical studies on the electrode reactions of these compounds can give a significant insight in their action mechanism as antioxidants [1]. Hesperidin (HESP) is a flavone glycoside found predominantly in the peel of citrus fruits. Literature reports voltammetric determination of HESP on mercury or different carbon-based electrodes [2] but none of the studies refers to the cost-effective and easy-to-use pencil graphite electrode (PGE) (Fig.1). This work presents for the first time HESP voltammetric behaviour at PGE.



Figure 1. The composite pencil graphite electrode (PGE)

Materials and methods: 10^{-3} M HESP stock solution was daily prepared by dissolving the proper amount of HESP in 2 mL 0.2 M NaOH and subsequent dilution with bidistilled water to 10 mL. The working solutions were obtained by successive dilutions of the stock solution with the corresponding supporting electrolyte.

PC running GPES 4.9 software and the Autolab PGSTAT 12 system equipped with a 3 electrodes cell (working electrode: PGE) were used for voltammetric recordings.

Results: The voltammetric response of HESP was investigated by differential pulse voltammetry (DPV) at different working electrodes (Pt, glassy carbon and PGE with different types of pencil leads). Graphite leads are composite materials consisting of graphite powder (~60%), clay (~30%) and a binder (resin or a high polymer) [3]. The hardness of the composite graphite leads (2H, H, HB, 2B and B) decreases when the graphite content is higher. The harder H type graphite composite material exhibited the highest sensitivity ($0.743 \text{ A}\times\text{L}/\text{mol}\times\text{cm}^2$) for HESP voltammetric determination. PGE potentiostatic/potentiodynamic electrochemical activation in different media did not enhance the HESP DPV signal. Both oxidation signals of HESP were shifted towards lower potential values when the solution pH was increased indicating that an equal number of electrons and protons are involved, the highest DPV signals being recorded in Britton Robinson Buffer pH 1.81. HSP cyclic voltammograms present in the first scan a controlled diffusion oxidation peak at about 0.78 V and signal at about 0.48 V due to a diffusion-adsorption controlled reduction of HESP oxidation product.

Conclusions: The highest and best shaped voltammetric response of HESP was observed at type H composite leads having lower graphite content. HESP oxidation is pH dependent and diffusion controlled involving an equal number of electrons and protons.

Acknowledgements: This work was supported by University of Bucharest, research grand number 20045/2018.

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INJECTION MOLDING AND COMPRESSION MOLDING OF POLYAMIDE 10.10

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Keywords: Bio-based polyamide, Injection molding, Compression molding.

Introduction: In today's industry, molding is a common process used to manufacture a product or a component with the use of heat and pressure. Polyamide 10.10 (PA1010) is a semi crystalline polymer with emerging applications in the industry due to its promising mechanical properties and relatively low melting temperature [1-3]. However, there are not many studies regarding the behavior and properties of PA1010 through different molding processes other than injection molding. The objective of this study is to compare and correlate the structural, thermal and nanomechanical properties of PA1010 samples subjected to different molding processes in order to establish the structure-processing-properties interdependence.

Materials and methods: A commercial polyamide (PA10.10) was used and processed in dynamic conditions by melt processing in order to obtain samples (PA1010-I and PA1010-C) through injection molding and compression molding. Structural analysis was done with a Shimadzu 6000X-ray diffractometer while thermal analysis was performed with DMAQ800, TGAQ5000 and DSC Q2000 and the nanomechanical properties (reduced modulus, Er, hardness, H, roughness and coefficient of friction) were obtained using a TI Premier system (Hysitron Inc., USA).

Results: XRD analysis revealed a main contribution for the macromolecular structure's orientation from the α and γ phases. PA1010-C has a more oriented structure compared to PA1010-I due to the processing method. Thermal analysis shows small differences between the two materials with PA1010-C having a higher thermal stability. Nanomechanical analysis showed that PA1010-C properties increased over 40% for Er and H compared to PA1010-I but as a result presents a lower degree of elastic recovery. Nanoscratching shows very low values of roughness and coefficient of friction for PA1010-C compared to PA1010-I meaning that the surface properties are depending on the processing method heavily and correlate well with the XRD analysis.

Conclusions: Due to its applications, PA1010 may be used in several industries based on the processing method. The properties of polyamide 10.10 rely on the processing method in close correlation with the structural behavior and respectively with the nanomechanical properties.

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ANTIMICROBIAL ACTIVITY OF AN *ACHILLEA MILLEFOLIUM* L. EXTRACT

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Introduction: Yarrow (*Achillea millefolium* L.) is one of the best-known and most widespread species, listed among the most commonly used plant species in both folk and conventional medicine for over 3000 years [1], primarily for wounds, digestive problems, respiratory infections, and skin conditions, and secondarily, among other uses, for liver disease and as a mild sedative [2].

Pharmacological effects are due to the presence of several chemical constituents, essential oils, sesquiterpenes, phenolic compounds etc.[3]. In particular, it was suggested that the presence of various secondary metabolites such as phenols and flavonoids is responsible for antibacterial activity of yarrow [4].

Different extracts (hexane, petroleum ether and methanol) of *A. millefolium* aerial parts were found to be active towards *Staphylococcus aureus*, *Escherichia coli*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Salmonella enteritidis*, *Aspergillus niger* and *Candida albicans* [5]. Methanol extract is also active against *Helicobacter pylori* at a MIC of 50 µg/mL [6].

This study reveals the antimicrobial potential (towards Gram-positive and Gram-negative bacteria, a fungus and a yeast) of a hydroalcoholic extract of *A. millefolium* growing in Romania.

Materials and methods:*Plant material*

The vegetal material consisting of *Achillea millefolium* L. flowers (Millefolii flores) was obtained from culture, dried and ground as a fine powder (sieve VII).

Preparation of extracts

The method consisted of two repeated extraction of the active substances from 100 g dried plant, with 30% ethylic alcohol v/v (vegetal material / solvent ratio = 1/10 m/v) at boiling temperature of the solvent for 2 hours per extraction with continuous mechanical stirring, followed by cooling and filtration of the extracts. The reunited hydroalcoholic solutions were concentrated for alcohol removal, let to settle at 4-6°C for 6 days and further centrifugated. At the end, 15% alcohol was added to the solution up to 5/1 v/g (solution/ dried herb).

Chemical analysis

Flavones were quantified by a colorimetric method based on their property to form intensely yellow complex with Al_3^+ , (rutin was used as reference substance) and polyphenolcarboxylic acids by a colorimetric method based on the property of phenols to form nitrocompounds or nitro oxime with nitrous acid which give red stain when dissolve in alkaline solutions due to their weak acid character (caffeic acid was used as reference substance) [7]. Saponins were also quantified by a spectrophotometric method, using Merck saponin as reference substance.

Test organisms and antimicrobial assay

The organisms used comprised of Gram-negative (*Escherichia coli* ATCC 25922, *Proteus vulgaris*, NTCTC HK, *Yersinia enterocolitica* IP76, *Klebsiella pneumoniae*, *Salmonella typhimurium* TA100), Gram-positive (*Staphylococcus aureus* ATCC 25923, *Streptococcus salivarius* IP 55126) bacteria, a fungus (*Candida albicans* ATCC10231) and a yeast (*Aspergillus niger* ATCC 16404). The antimicrobial activities of the extracts were determined by the cylinder-plate diffusion method according to Romanian Pharmacopoeia X/2000 edition.

Results and discussion: We conducted a screening of antimicrobial potential of a yarrow hydroalcoholic extract containing 0,24% g/g flavonoids expressed as rutin, 0,0625 % g/g polyphenolcarboxylic acids expressed as caffeic acid, 0,5% triterpenic saponins (determined spectrophotometrically).

Achillea millefolium extract exhibited weak antimicrobial activity towards *Yersinia enterocolitica* and *Streptococcus salivarius* (mean inhibition zone of 10-11mm) and strong activity towards *Staphylococcus aureus* (mean inhibition zone of 21mm). No antifungal effect was detected.

Similar results were found previously; ethanol extract of aerial parts of *A. millefolium* was screened for antimicrobial activity against *E. coli*, *B. cereus*, *P. aeruginosa*, *S. enteritidis* and *C. albicans* and it was found that the highest MIC value of 62.50 mg/mL was observed against *B. cereus* and *S. enteritidis*, while no activity was observed in other three tested strains (Kokoska et al., 2002).

On the other hand, different results regarding antifungal effect were showed by Fierascu et al., They found that the *Achillea millefolium* L. hydroalcoholic extract strongly affected the growth of some fungi (70.19% for *Aspergillus niger* and 47.40% for *Penicillium hirsutum*, compared with negative control) (Fierascu et al., 2015).

Conclusion: *Achillea millefolium* L. hydroalcoholic extract exhibits strong antibacterial effect against *Staphylococcus aureus* and it could be used as active ingredient in various formulations (cosmetic, nutritive, etc.).

Acknowledgements

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CHEMICAL COMPOSITION AND ANTIOXIDANT ACTIVITY OF SOME LAMIACEAE SPICES

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Keywords: basil, oregano, tyme, total phenolic content, essential oil

Introduction: Spices are widely used for culinary purposes as well as for therapeutic effects. Medicinal plants of the *Lamiaceae* family have been used for centuries, throughout the world. Aerial parts of thyme (*Thymi herba*), basil (*Basilici herba*) and oregano (*Origanum herba*) have a complex chemical composition represented by essential oil, phenolcarboxylic acids, flavones and triterpenic compounds [1, 2]. The above mentioned herbal products are intensively studied due to their anti-inflammatory, antibacterian, antioxidant, gastroprotective, hypolipidemic, hypoglycemic and antitumor effects [3-5]. **The aim** of our work was the phytochemical screening and evaluation of antioxidant activity of oregano, basil and tyme aerial parts, acquired from indigenous manufactures.

Materials and methods: Spices were purchased from a local supermarket (Bucharest) in October 2019. For phytochemical screening, qualitative (specific chemical reactions, thin layer chromatography - TLC) and quantitative assays have been used. TLC analysis has been used for evaluation of analysed spices essential oils composition. Total phenolic (expressed as tannic acid equivalents), flavones (expressed as rutin equivalents), phenolcarboxylic acids (expressed as caffeic acid equivalents) and essential oil contents were determined by means of spectrophotometric and volumetric methods. The antioxidant capacity was evaluated by means of ferric reducing power assay. The antioxidant activity was expressed as EC₅₀ (μg/mL).

Results: Qualitative analysis revealed the presence of phenolcarboxylic acids, polysaccharides, flavones, coumarines, tannins and proanthocyanidins for all analysed spices. TLC analysis showed the presence of linalool (for oregano aerial parts) and eugenol (for basil and oregano aerial parts). Regarding the quantitative assays, the essential oil content varied between 2-3.5%. Oregano aerial parts showed the highest content of phenolcarboxylic acids (0.68 g%) while basil had the highest total phenolic content (3.05 g%). The flavones content decreased as follows: oregano > basil > tyme. The highest antioxidant capacity was found for oregano aerial parts (EC₅₀ = 0.61 μg/mL) followed by basil (EC₅₀ = 0.85 μg/mL).

Conclusions: Analysed *Lamiaceae* spices are a source of bioactive compounds with antioxidant activity and can be used as an adjuvant for diseases in which oxidative stress represents a key factor.

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POLYPHENOLIC CONTENT, ANTIOXIDANT AND ANTIMICROBIAL ACTIVITY OF HYDROSOLS FROM SOME AROMATIC LAMIACEAE PLANTS

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Keywords: steam distillation, by-products, polyphenols, antioxidant activity, antimicrobial activity.

Introduction: Hydrosols, also named hydrolates or aromatic waters, are considered distillation by-products obtained during essential oil extraction from herbs or spices, which are usually discarded. However, they contain certain amounts of bioactive molecules, such as water-soluble components of the essential oils and other polar plant components with valuable biological activities [1,2]. This study aimed to evaluate the polyphenolic content, as well as the antioxidant and antimicrobial activity of three aromatic plant hydrosols obtained from *Lavandula officinalis*, *Rosmarinus officinalis* and *Salvia officinalis*, belonging to Lamiaceae family, in order to develop new products for pathogenic microorganisms control management.

Materials and methods: Aerial parts of lavender, rosemary and sage were subjected to steam distillation in an essential oil extraction equipment, for 3 h. The resulting essential oils and the corresponding hydrosols were separately collected and stored in the dark, at 4 °C. The hydrosols were analysed in terms of total phenolic and flavonoid content by Folin-Ciocalteu assay and aluminium chloride colorimetric method, respectively [3]. The antioxidant activity of the hydrosols was evaluated using Trolox equivalent antioxidant capacity (TEAC) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical assays [3]. The hydrosols were also tested for their antimicrobial activity against the Gram-positive *Staphylococcus aureus* strain and Gram-negative *Pseudomonas aeruginosa* strain by agar disc diffusion assay.

Results: Sage hydrosol had the highest content of polyphenols, followed by rosemary and lavender hydrosols. Significant level of flavonoids was found in sage hydrosol, while rosemary and lavender samples contained similar amounts of flavonoids, but lower than that of sage hydrosol. Rosemary and sage hydrosols exhibited the strongest antioxidant activity, as assessed by TEAC and DPPH assays. Antimicrobial tests showed that rosemary hydrosol exerted antimicrobial activity against *S. aureus*. Sage and lavender hydrosols were less effective against *S. aureus* growth. The three hydrosols did not show any inhibiting activity against *P. aeruginosa*.

Conclusions: Among the tested plant hydrosols, those obtained from sage and rosemary contained significant amounts of bioactive molecules, in terms of polyphenols, exhibiting at the same time good antioxidant activity. Rosemary hydrosol also showed antimicrobial activity against G-positive bacteria. All these results indicated rosemary hydrosol as a useful by-product that could be recycled to develop novel products for prevention of plant diseases caused by microbiological spoilage.

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PROTECTIVE ACTIVITY OF FISH PEPTIDES FRACTION IN OPTIMIZED MODEL OF UV-B IRRADIATED MOUSE FIBROBLASTS

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Keywords: fish by-product; peptides; skin photoprotection; cytotoxicity; cytokines.

Introduction: UV-B exposure induces cell structure and function deterioration through accumulated mutations due to excessive production of reactive oxygen species, which result in alteration of cell cycle progression and dysregulation of matrix metalloproteinases (MMPs) [1]. Destruction of skin connective tissue was reported after prolonged exposure to UV radiation that triggers cytokines and growth factor receptors activation, leading to MMPs overexpression [2]. In this study, we have evaluated the biologic activity of fish bone-derived peptides (FBDP) in an optimized model of UV-B irradiated fibroblasts by cell viability tests and cell morphology observations. Moreover, their influence on pro-inflammatory cytokine secretion in THP-1 cells was investigated.

Materials and methods: FBDP were extracted from *Hypophthalmichthys molitrix* skeleton by papain digestion, isolated by centrifugal ultrafiltration and fractionated by size-exclusion chromatography. They were separated according to their molecular weight using tricine gel electrophoresis and to their hydrophobicity by cation-exchange chromatography. Several exposure times and doses were tested to optimize the experimental model of UV-B irradiated mouse fibroblasts from NCTC clone L929 cell line. Pretreatment and co-treatment with cytocompatible concentrations of FBDP were assessed by MTT and LDH cell viability tests [3] and cell morphology observations. Specific secretion of IL-1 β in FBDP-treated THP-1 macrophages was analysed in harvested conditioned media using ELISA kit.

Results: A heterogeneous mixture of both hydrophilic and hydrophobic (oligo)peptides with an average molecular weight of 7.1 kDa was obtained. *In vitro* tests showed that the viability of irradiated cells decreased in a time-dependent manner, while FBDP-treated fibroblasts showed higher viability by ~10, 5 and 3% at 25, 60 and 90 s of irradiation, respectively (fig. 1). In the other respect, FBDP-treated macrophages presented an inhibition of IL-1 β secretion, compared to that quantified in inflamed cells.

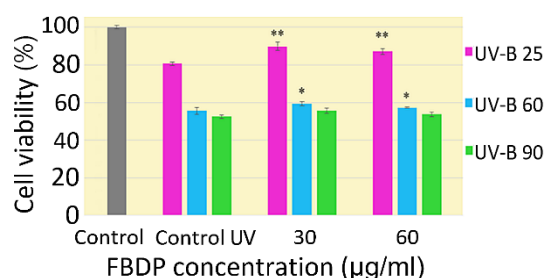


Figure 1. Cell viability of FBDP-treated L929 fibroblasts at different UV-B exposure time, determined by MTT assay (* $p < 0.05$, ** $p < 0.01$, compared to irradiated control).

Conclusions: Biotechnologies applied to fish by-products yielded valuable peptides with photoprotective activity demonstrated by their ability to increase the cell viability in fibroblasts exposed to UV-B and to inhibit cytokine secretion in inflamed macrophages.

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FORMULATION AND EVALUATION OF AN ANTIMICROBIAL CREAM CONTAINING CINNAMON OIL FOR TOPICAL APPLICATION

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Keywords: topical products, cinnamon oil, antimicrobial cream

Introduction: Dermocosmetic products help alleviate certain conditions and have therapeutic advantages regarding skin protection/repairing/prevention. On this subject, the necessity for developing new topical antimicrobial products has increased significantly due to growing concerns regarding multidrug-resistant bacterial, viral, and fungal strains [1, 2]. Due to its antioxidant and antibacterial properties, cinnamon oil improves blood flow to the surface of the skin, helps remove dead skin cells, re-establish the skin softness, and could provide relief from eczema [3, 4]. The aim of this study was to formulate topical creams containing different concentrations of cinnamon oil and evaluate the *in vitro* antibacterial activity and the release behaviour of cinnamon oil from the optimal topical product-based cream.

Materials and methods: Herein we prepare topical creams by melting the waxes at 75°C; the aqueous phase slowly has been added to the oil phase with moderate agitation and was kept stirred until the temperature dropped to 40°C. The emulsion was cooled to room temperature to form a semisolid cream base. Formulation of optimal cream was followed by evaluating its organoleptic characteristics, physicochemical properties, and *in vitro* antibacterial activity against several bacterial strains. The cinnamon oil diffusion from optimal formulation was assessed through Franz cell experiments. The samples were taken at predetermined intervals for 2 days from the receiver solution (50% Ethanol). The released active ingredient in each time point was determined by spectrophotometry using a UV-VIS spectrophotometer. The results were computed by the use of six mathematical models: Zero order, First order, Higuchi, Weibull, Korsmeyer-Peppas and Hixson-Crowell.

Results: Cinnamon oil had a strong antibacterial activity. Release kinetics models: Zero Order, First Order, Weibull, Korsmeyer-Peppas, Higuchi, Hixson – Crowell were applied to predict essential oil release profile. The Korsmeyer-Peppas model best described cinnamon oil release from cream.

Conclusion: This study indicates clear evidence supporting the traditional use of cinnamon oil in treating skin and wound infections related to bacteria.

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NUTRACEUTICAL AND COSMECEUTICAL PRODUCTS CONTAINING LOW MOLECULAR WEIGHT PEPTIDES FROM FERMENTED COLOSTRUM

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Keywords: *fermented colostrum, peptides, nutraceuticals, cosmeceuticals.*

Introduction: Nutraceuticals are food or part of a food that provide medicinal or health benefits, including the prevention and treatment of disease. Cosmeceuticals are the cosmetic products which incorporate biologically active ingredient having therapeutic benefits on the surface applied. Within SC LABORATOARELE MEDICA, fermented colostrum is obtained with enhanced kefir grains by an original method [1]. The fermented product contains low molecular weight (LMW) peptides that have been isolated and characterized [2], [3]. The aim of this paper was to evaluate the potential of these peptides in the prevention of certain diseases so as to be considered active principles in the formula of some nutraceuticals and cosmeceuticals obtained by this company.

Materials and methods: • bovine colostrum fermented with enhanced kefir grains; • quantitative determination of LMW peptides from fermented colostrum using o-phthalaldehyde (OPA) reagent; • the qualitative determination of the peptides was performed by Tricine-SDS-PAGE; • antioxidant activity of peptides using the ABTS method; • angiotensin converting enzyme (ACE) inhibitory potential was evaluated by the method described by Papadimitriou et al. [4]; • emphasizing the healing effect was done *in vitro* through a scratch assay experiment; • the evaluation of the anti-inflammatory effect was performed using a specific ELISA kit for cytokines TNF- α , IL-6 and IL- β .

Results: Bovine colostrum fermented with a consortium of improved kefir, conditioned in powder form by atomization, by its content of bioactive peptides showed the following characteristics: antioxidant effect, ACE inhibitory activity (so blood pressure regulation), biocompatibility, healing and anti-inflammatory effect. Due to these characteristics, it is included in the following nutraceuticals formula: Col-Kefir, Super-Nutrient, Focus 3xbiotics, Pan Verucidin. These nutraceuticals are considered tri-biotic products because their pre-, pro- and post-biotic effect has been determined. The COL-KEFIR MILK THERAPY product line, which is part of the cosmeceuticals category, consists of biocompatible products, with healing, anti-inflammatory and antibacterial effect.

Conclusions: Fermented bovine colostrum, by its content of bioactive peptides is a safe and useful nutraceutical product for use in a wide range of applications. In addition, peptides from this source are useful for the development of cosmetic formulations aimed at treating damaged and dysfunctional skin.

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ASSESSMENT OF BIOLOGICAL CONTAMINATION FROM WOODEN ARTIFACTS OF GOLESTI MUSEUM

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Keywords: *fungi, Aspergillus, Penicillium*

Introduction: Wood, a traditional common material with multiple applications as civil and religious buildings, furniture and artistic objects is subjected to physical, chemical and biological factors which facilitate the growth of diverse microbial community acting through specific and complex pathways. The degradation and biodeterioration of wooden artifacts is influenced by abiotic factors (temperature, moisture etc), specificity of microbial community involved in process and interactions between the organisms and the substrates. Early detection of microbial damages will allow a more rapid intervention for remediation and preservation of artifacts.

Materials and methods: Several experimental procedures for collecting samples and purification of microorganisms isolated were used. The purification of isolates was carried out by culturing on solid medium and periodically transferring hyphal tips. The pure colonies were examined at optical microscope Olympus BX 51 for identification on the basis of their morphology [1-4]. Three commercial biocides were tested against several fungal isolates collected from wooden objects exposed in Golesti Museum.

Results: There were identified fungal strains belonging to common genera, very well known for their ability to colonize wooden substrates, as *Rhizopus*, *Penicillium*, *Aspergillus*, *Alternaria*, *Chaetomium* and *Cladosporium*. In many cases, the contamination of samples collected from Golesti Museum represents the result of a microbial community growing on wooden objects. Preliminary results of biocides tests revealed that compound C1 exhibited a strong inhibitory activity versus *Penicillium*, *Cladosporium*, *Chaetomium* and *Aspergillus* isolates, followed by compound C2 presenting a lower activity, mainly towards *Cladosporium* and *Chaetomium* isolates. Compound C3 was the least effective in inhibiting fungal isolates.

Conclusions: The microbial attack generates loss of dimensions and structural stability, affecting the aesthetical aspect and finally the valor of objects. Understanding the mechanism of microbial degradation of artifacts is relevant not only from a scientific point of view, but also for economic reasons. Identifying the contaminant fungal species and the factors enhancing their growth is an essential step for the success in elaboration of a proper and effective strategy for cultural heritage preservation.

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A BIOTECHNOLOGICAL PROCESS FOR VALORIZING POULTRY FEATHERS THROUGH KERATINOLYTIC *CLADOSPORIUM* ISOLATES

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Keywords: *Cladosporium*, plant growth-promoting fungi, keratin, feathers, protein hydrolysates

Introduction: Protein hydrolysates, as plant biostimulants, have beneficial effects on growth, yield and quality of agricultural crops [1-2]. A good and available source of protein hydrolysates are keratin wastes from agro-industry, especially from poultry industry. Isolation and characterization of keratin-degrading microorganisms with keratinolytic activity and plant growth-promoting activity represent a biotechnological approach for valorizing poultry feathers. In the present study, three keratinolytic *Cladosporium* isolates were investigated for their potential as plant growth promotion agents.

Materials and methods: *Qualitative tests* for production of several secondary metabolites were carried out in Petri plates on solid specific medium [3-4]. In some tests, the response was estimated by measuring the diameter of clear zone formed around inoculation point in solid media. The following tests were carried out: production of phytohormone, namely 3-indole acetic acid (medium with tryptophan), secreting of hydrolytic enzymes, zinc solubilization (medium with insoluble zinc compounds), phosphate solubilization (medium with $\text{Ca}_3(\text{PO}_4)_2$ and brom cresol purple as pH indicator).

Results: Relevant characteristics for the use as plant growth promoting were evidenced at *Cladosporium* sp. T2 which presented a good production of 3-indole acetic acid, a common plant hormone, responsible for various aspects of plant growth and development. Also, *Cladosporium* isolate T2 had the ability to secrete lytic enzymes (eg. chitinases, cellulases, keratinases, proteases), relevant feature as plant biostimulants. The isolate T2 was active in zinc solubilisation, imperative micronutrient for plant growth. The ability for phosphate solubilization has significance through **increasing** the bioavailability of insoluble phosphorus from soil to be used by plants.

Conclusions: Members of *Cladosporium* genus, endophytic fungi in special relationship with plant hosts, have a great potential to improve plants growth and tolerance to abiotic and biotic stresses. In addition to this general behavior of the genus, the experimental results indicated that selected *Cladosporium* isolate T2 presents relevant features as plant biostimulant. Further study will be focused on the effect produced on plants by treatment with feather hydrolysates.

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DEVELOPMENTS OF TERTIARY LEVEL STUDIES IN BIOTECHNOLOGIES AND THEIR APPLICATIONS IN ENVIRONMENTAL BIOENGINEERING

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Keywords: *New curricula, Master & Doctoral Programme, Environmental Bioengineering*

Introduction: To develop a unique block of learning in the field of Environmental bioengineering is need to introduce the pass elements from a linear bioeconomy to a circular bioeconomy. Circular bioeconomy represents an innovative economic model and a regenerative system too, in which resource input, waste emission, and energy losses are minimized by slowing, closing, and narrowing energy and material loops [1-2].

Materials and methods: A methodology based on Survey opinion was applied to acquire the student's preferences regarding courses of Environmental Bioengineering [3-5].

Results: Based on student responses, a new curriculum will be developed for environmental bioengineering courses from the Master or Doctoral program. The proposed content will be divided into 8 Modules respectively: 1) Main development domains in the European bioeconomy-model of transition; 2) From present bio-economy to circular and sustainable bio-economy through waste valorization, based on solving the different categories of requirements to implement the new economic path; 3) Biorefinery for municipal waste processing; 4) Food waste biorefinery: sustainable strategy; 5) Advanced lignocellulosic biorefinery to exploit the forest potential; 6) Improved interest to develop blue bio-economy as future; 7) Development of new business models for circular bio-economy. Innovation and project management; 8) Entrepreneurship and intellectual property in circular bio-economy. Commercialization and marketing of bio-based products.

Conclusions: The new curricula structure will cover all sectors and systems that rely on biological resources (animals, plants, micro-organisms, and derived biomass, including organic waste), the cross-sector of bio-based industries, markets, products, and processes to build a new structure of environmental bioengineering courses for Master and/or Doctoral Programme of European Universities.

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PROPERTIES OF FREE AND EMBEDDED EXTRACTS FROM DIFFERENT GRAPE POMACE INTO MESOPOROUS INORGANIC MATRICES

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Keywords: inorganic matrices, polyphenolic extracts, grape pomace, antioxidant activity, NCTC fibroblasts

Introduction: Grape pomace, a by-product of the winemaking process, is a source of valuable natural compounds like polyphenols, flavonoids or anthocyanin pigments, which can be valorized in cosmetics, nutraceuticals or in food industry [1,2].

Materials and methods: We report the preparation of ethanolic and hydroalcoholic polyphenolic extracts from red grape pomace of two cultivars, Fetească Neagra (FN) and Pinot Noir (PN), from Murfatlar (Black Sea region, Romania) and their characterization through different spectrophotometric methods: total polyphenols, flavonoids and anthocyanin pigments content and radical scavenging activity (RSA) by both DPPH and ABTS assays. The chemical profile of polyphenolic extracts was determined by HPLC-PDA analysis.

To improve the stability of polyphenols, the extracts were further embedded in two inorganic mesoporous matrices, SBA-15 silica with ordered hexagonal pore array and titania with anatase structure. Both inorganic matrices were obtained by sol-gel method, in the presence of triblock copolymer, Pluronic P123 and Pluronic F127 for SBA-15 and titania, respectively. The *in vitro* cytocompatibility of free and embedded hydroalcoholic extracts was assessed in the concentration range of 100-1000 µg/mL on NCTC fibroblast mouse cell line using MTT assay.

Results: The hydroalcoholic extracts exhibited better radical scavenger activity than alcoholic ones, which can be correlated with their higher total polyphenols content. HPLC-PDA analysis evidenced high amounts of polyphenolic acids and flavonoids, especially for the hydro-alcoholic extract from Fetească Neagra cultivar. The embedded extracts preserved the RSA of free ones after several months of storage at 4°C.

Conclusions: The embedding of chosen polyphenols extract in inorganic matrices led to a preservation of radical scavenger activity and showed a good biocompatibility either free (up to 300 µg/mL) or embedded into mesoporous titania (20% wt extract) or mesoporous SBA-15 silica (39 %wt extract) on NCTC fibroblasts cell line (up to 1000 µg/mL and 300 µg/mL, respectively).

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ARONIA MELANOCARPA FRUIT AND LEAVES HOT-ASSISTED ETHANOLIC EXTRACTS ANTIOXIDANT ACTIVITY

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Keywords: *Aronia melanocarpa* L.; hot-assisted ethanolic extracts; antioxidant activity.

Introduction: *Aronia melanocarpa* L. fruit (common black chokeberry) is one of the most abundant sources of antioxidant compounds in the plant world, superior to all edible fruits; chokeberry fruits contain up to 100 g total phenols *per* kg fresh material, predominantly (-)-epicatechin, cyanidin-3-glycosides and procyanidins (60%), added to quercetin and caffeoyl quinic acid derivatives. Alongside, chokeberry leaves contain up to 15 g total phenols *per* kg fresh material, predominantly hyperoside, isoquercitrin, rutin and caffeic acid and chlorogenic acid [1, 2]. Among potential human health benefits, *Aronia melanocarpa* derived products were proved with antioxidant and anti-inflammatory effects, anti-diabetic, anti-lipidemic, cardio-protective, anti-hypertensive and platelet anti-aggregating effects, hepato-protective and gastro-protective effects, cognitive-enhancing and behavioral effects, and antibacterial, antiviral, immunomodulatory and radioprotective effects [1, 2]. The present work aims to study antioxidant activity of two hot-assisted ethanolic extracts from chokeberry fruit and chokeberry leaf plant parts respectively; antioxidant activity was compared with two reference compounds (ref.) and several plant extracts obtained under similar study conditions [3].

Materials and methods: *Aronia melanocarpa* L. fruit and leaves plant parts were collected in 2019 from a plantation situated in Prahova region, Romania. Antioxidant activity screening has been done using chemiluminescence method (CL), luminol – H₂O₂ system, pH=8.9 [3].

Results: The hot-assisted (70%, v/v) ethanolic extraction of chokeberry fruits leads to extracts with low antioxidant activity (IC₅₀=25 µg GAE/mL extract, Figure 1), most likely due to the polymerization of anthocyanins contained resulting in high molecular compounds, less effective as reactive oxygen species scavenging activity. Opposite, the hot-assisted (70%, v/v) ethanolic extraction of chokeberry leaf plant part leads to extracts with very high antioxidant activity (IC₅₀=0.625 µg GAE/mL, Figure 2); by comparison, gallic acid and rutin (ref.) shown IC₅₀=0.85 µg GAE/mL and IC₅₀=2.54 µg GAE/mL.

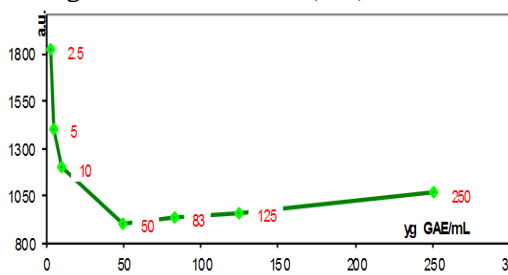


Figure 1. IC₅₀ assay on chokeberry fruit hot-assisted ethanolic extract

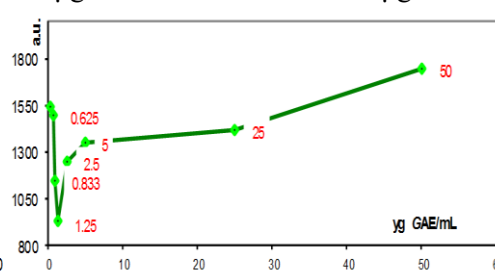


Figure 2. IC₅₀ assay on chokeberry leaves hot-assisted ethanolic extract

Conclusions: Compared to other vegetal extracts [3], *Aronia* leaves ethanolic extract rank as some of the most efficient antioxidant products, suggesting high utility as medicinal and cosmetic ingredient.

Acknowledgements: This work was supported by the ANCSI POC-A1-A1.2.3-G-2015, “New technologies and natural products for human health use”, Contract 60/05.09.2016, ID P_40_406, SMIS 105542, Contract D no. 35/08.11.2019.

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VIRTUAL REALITY (VR) AND MIXED REALITY (MR) IN EDUCATION: A SOLUTION FOR TODAY EDUCATION IN CIRCULAR BIOECONOMY (CB)

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Keywords: virtual reality, mixed reality, circular bioeconomy

Introduction: The updated strategy and action plan for the bioeconomy of October 2018 is part of the European Commission's strategy to make efficient use of natural resources, to stimulate jobs, growth and investment. It aims to improve and expand the sustainable use of renewable resources to address global and local challenges, such as climate change and sustainable development. Ergo, the EC introduces a new direction of integrated development of the bioeconomy - circular bioeconomy with bio-based products. The circular bioeconomy is defined as the “intersection of the circular economy (restorative, regenerative economic model, in which nothing is lost and everything fuels a new cycle, and waste is treated as a resource) and bioeconomy (obtaining bio-based products and services)”.

Material and Methods: In order to educate students and postgraduate students in this new, high level complex and advanced technological field imposes sophisticated up to date education methodology based on online learning and more Virtual Reality (VR) or Mixed Reality (MR) [1]. VR will play an important role in training students and introducing difficult concepts that are easier to explain through strategic experiences in a virtual environment. VR/MR can deliver learning experiences that no longer depend on lectures to teach concepts or the idea of earning a degree to attain just one role in the course of person's lifelong career [2]. In fact, VR can contribute to the creation of learning experiences that extend into several disciplines facilitating the development of multidisciplinary careers, and this is in line with the educational needs imposed by the circular, multidisciplinary and interdisciplinary bioeconomy par excellence. Students can benefit from quasi-real scenarios that will prepare them for real life / various concrete tasks at work. As technology progresses, the best way to explain abstract concepts is through direct demonstration, rather than through ex-cathedra theoretical lectures. [3-6]. With the help of VR, study tools can be adapted to allow students to learn at their own pace and provide learning experiences that lead to a better mastery of information and a deeper understanding of it.

Results and Discussions: The obtained results were focused on: (a) Documentation (technical and pedagogical literature, education curricula and contents, training projects, technical and pedagogical papers) for the elaboration of Curriculum and Content in sustainable CB; (b) Realization of a review study with the recommended MR methods to be chosen and applied; (c) Integration of MR methodology to elaborate the on CB by using these methods. The innovative character of all teaching materials is that is centered to the competences formation to perform in CB outstanding technological and economic domain. The main needed competences to be modeled are: integrative knowledge, systems thinking, ethics and values, action, communication and reflection capacity, vision, planning and organizing potential, networking ability. Finally, the students should actively and independently develop the educational skills that will allow them to process, organize, understand, and evaluate scientific information and to become lifelong self-directed learners by using VR/MR methodology of training / learning.

Conclusions: Due to the fact that CB is still in its infancy, a new industrial paradigm needs to be built in the EU in the coming decades. As a major consequence, the role of education in training future specialists is predominant, and curricula and curricula, especially in universities, need to be elaborated in relation to new IT technologies. At the same time, in order to educate postgraduate students in this complex and advanced technological field, an updated education methodology based on online learning requires a focus on virtual reality (VR) and mixed reality (MR).

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CHEMICAL AND BIOLOGICAL CHARACTERIZATION OF PROTEIN HYDROLYSATES FROM FRESH WATER FISH WASTE

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Keywords: fish waste, peptides, enzymatic hydrolysis, chemical properties, biocompatibility

Introduction: Freshwater fish skin and bones are usually by-products of fish processing industry. These are good sources for obtaining bioactive peptides with high additional value. The aim of this work was to obtain protein hydrolysates by different enzymatic hydrolysis from fish waste (bone, skin and meat) and to assess their chemical and biological properties.

Materials and methods: Protein hydrolysates were obtained by enzymatic methods with papain, flavourzyme, alkalase and a mixture of flavourzyme and alkalase, from fresh water fishes waste (bones, meat, skin). Protein content was determined by Biuret method, peptides molecular weight was assessed by SDS-PAGE in 10-20% tris-tricin gel [1], antioxidant capacity by DPPH method [2] and antihypertensive activity by determining angiotensin converting enzyme (ACE) inhibition [3]. Samples cytotoxicity testing was performed on fibroblast cells (NCTC line) after 48 hours of culture.

Results: The extraction yield values of the four protein hydrolysates varied between 20% and 53%, depending on the type of enzyme used. The protein content was over 50% in all peptide extracts except sample extracted with flavourzyme, which was 32%; the percentage of protein content was over 90% in papain and alkalase variants of hydrolysis. The molecular weight of protein hydrolysates ranged from 3-30 KDa, except the sample obtained by flavourzyme hydrolysis, which contained peptides higher than 30 KDa. The inhibition potential of DPPH free radicals ranged between 49% and 56%, while the degree of ACE inhibition ranged between 22% and 27%. The scavenging effect of fish waste hydrolysates on DPPH free radicals was highest in the case of the protein extract isolated with flavourzyme. The protein hydrolysate obtained with alkalase treatment presented the highest antihypertensive activity. The results of *in vitro* testing on fibroblasts showed that all variants of protein hydrolysates are biocompatible up to a concentration of 6000 µg/ml. Extracts obtained by treatment with papain and a mixture of flavourzyme and alkalase was non-cytotoxic at 8000 µg/ml. The morphology and phenotype of the cultured fibroblasts in the presence of the four peptide extracts remained normal during the tests, proving the biocompatibility of the protein hydrolysates.

Conclusions: Our results demonstrated that protein hydrolysates obtained by enzymatic hydrolysis from fresh water fish waste had high peptides content, with DPPH radical scavenging effect, antihypertensive activity and a good biocompatibility.

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Education and Research, CCCDI - UEFISCDI, project number PN-III-P2-2.1-PTE-2019-0181, within PNCDI III

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PAINTINGS DEGRADATION FROM INSIDE OF WOODEN CHURCHES ACHIEVED IN THE PERIOD 1750-1850

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Keywords: biological degradation, painted wood panels

Introduction: The wooden churches made between 1750-1850 have as decorative elements paintings made on wood or wooden panels. The materials used to make them are generally pigments that existed on the market at that time [1,2]. At present, many of these need restoration and conservation work. For this aim, must be established the type of degradation.

Material and methods. On the wood painted surfaces, the biological degradation was established applying a non-destructive methodology, based on sampling with a cotton swab, and followed by applied on specific culture media and microscopic identification of microorganisms.

Results and discussion. Visual analysis of painted wood reveals the wood panels degradation due to insect activities. The species involved in this process can be *Anobium punctatum*; *Stegobium paniceum*; *Xestobium rufovillosum*; *Dinoderus minutus*; *Euophryum confine*; *Lyctus brunneus* and *Nacerdes melanura* [3,4]. The main microorganisms identified on painted surfaces belong to Dematiaceae Family and respectively to the Phylum Basidiomycetes. In the microbiology lab, only spores of *Epicoccum nigricum* and possible of *Phanerochaete chrysosporium* were identified, without the mycelium presence. No visible infection was observed on the painted wood structure, and for this reason, we concluded that the wood panels painted no exhibit microbiological infections. That is the reason for which we recommend that before painted wood restoration, to be made a treatment against insects. The treatments must be made using a non-destructive method, to keep the painted images from the wood panels. From this point of view, the literature indicates that the treatments with carbon dioxide in concentrations of (50-80%) in the air can able to destroy the insects from the wood in a maximum 96h. In this way, the eggs, larvae, pupa, and the adults of species like *Stegobium paniceum* is destroyed [5]. Other scientists recommend inhibiting the development of the microfungi and insects by using gamma radiations, at a dose of 10 kG [6]. In this case, all species responsible for wood degradation are destroyed. It is important to mention that these treatments do not offer protection in long term; for this reason, the treatments must be repeated at different length times.

Conclusions. The pictures painted on the wood from wooden churches built in the period 1750-1850 exhibit degradation due to biologic agents, main due to insects, and sometimes due to the presence of microorganisms. Physical and/or chemical treatment can be applied for destroyed or inhibit these species but must be repeated from time to time.

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BIOACTIVE COMPOUNDS OBTAINED BY TREATING DAIRY WASTEWATERS WITH PORPHYRIDIDIUM PURPUREUM

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Keywords: Microalgae, Wastewater treatment, Bioactive compounds extraction

Introduction: Annually, 11 million tons of dairy wastewaters are released in the environment worldwide. Over the last decades, cheese whey is considered the most important pollutant belonging to the dairy industry, associated with serious environmental hazards if sustainable treatments are not applied. As a result, several studies have been conducted in order to develop alternative methods for cheese whey valorization [1].

Materials and methods: The purpose of this work is to study the effect of growing microalgae on dairy wastewater. The microalgae strain chosen was *Porphyridium purpureum*. The growth medium (specific ASW), was prepared through the addition of the respective salts that comprise ASW medium in deproteinized cheese whey, used as carbon source. Experiments have been carried out with samples of increasing concentrations of cheese whey, calculated as amount of lactose (0, 2.5, 5, 7.5, 10 g/L). The effects of growing microalgae in cheese whey medium were observed by monitoring the growth curves, biomass productivity after 10 days of growth, and pigment concentration in the dry biomass, specifically chlorophylls and carotenoids, as well as phycobiliproteins.

Results: Cultivation of *Porphyridium purpureum* microalgae strain on dairy wastewaters - cheese whey – have resulted in an increase in the production of exopolysaccharides in the growth medium, proportional to the amount of lactose present. Also, the analysis of the growth medium shows that the microalgae have consumed the lactose present almost completely, small amounts being found in the samples of higher concentrations at the end of the cultivation process.



Figure 1. Cultivation of *Porphyridium purpureum* microalgae strain on dairy wastewaters - samples of increasing concentrations of lactose (0, 2.5, 5, 7.5, 10 g/L);

Conclusions: Continuous work will focus on the extraction, characterization and quantification of the bioactive components present in the microalgae strain. Preliminary results suggest this is a viable route for valorization of whey present in dairy wastes, that are purified through microalgae growth.

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INNOVATIVE SYSTEM FOR CONTINUOUS MICROALGAE HARVESTING BY ELECTROCOAGULATION/FLOCCULATION AND SEDIMENTATION

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Keywords: Microalgae, Harvesting technique, Electro-coagulation

Introduction: Harvesting is an important part of the downstream processing of the microalgae culture and one of the most price demanding [1] and represents more than 30% of the overall production costs. One of the alternatives to high-yield but expensive harvesting methods, such as centrifugation, is electrocoagulation/flocculation, in which an electric current is passed through a sacrificial electrode that releases metal ions which help flocculate the microalgae cells [2].

Materials and methods: The innovative system for continuous microalgae harvesting by electrocoagulation/flocculation and sedimentation proposes the harvesting of microalgae biomass by the use of a prototype equipment for a continuous electrocoagulation/ flocculation system with a total volume of 6.2 L, that can process large volumes of microalgae suspension. The microalgae suspension is pumped through the reactor made of plastic, between the electrodes present inside: 4 aluminum bars placed inside the plastic cylindrical wall of the reactor and one sacrificial anode comprised of an aluminum bar passed through the middle of the reactor. The electrodes are connected to an adjustable electrical current source that goes up to 24 V/10A. The aluminum sacrificial anode releases Al^{3+} ions that attract microalgae cells that are negatively charged and coagulate, finally forming flocks that facilitate separation. The recovery efficiency is about 90%.

Results: Using this system, a concentrated microalgae suspension is obtained (15% v/v), at the bottom of the separation vessel, that contains about 20g/L microalgae biomass. The top liquid fraction still contains small amounts of microalgae biomass.

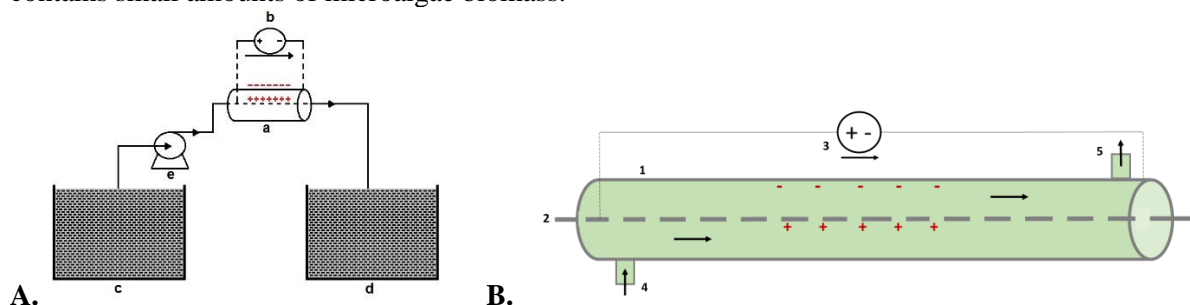


Figure 1. A. Installation for microalgae suspension electroflocculation: (a) electrocoagulation reactor, (b) electric current source, (c) microalgae suspension vessel, (d) coagulated microalgae suspension vessel, (e) pump for suspension circulation through reactor; B. electrocoagulation reactor - simplified view: (1) tubular reactor – plastic cylinder with 4 aluminum bars (cathode), bar aluminum electrode (sacrificial anode), (3) electrical current source, (4) suspension inlet, (5) suspension outlet.

Conclusions: The method described offers significant improvements relating to both time and energy consumption of the EF process, without compromising the recovery efficiency or the culture integrity.

Acknowledgements: 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 and PN 19.23.01.02.

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RDF CHARACTERIZATION FOR MORE EFFICIENT USE IN COMBUSTION SYSTEMS

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Keywords: solid municipal waste, pyrolysis, RDF

Introduction: The main systems for solid municipal waste (SMW) management involve separation of all recyclable materials and the last fraction, named usually refuse-derived fuel (RDF) contains all non-recyclable materials in different particle size and with variable moisture, depending on the efficiency of the management system [1, 2, 3]. Usually, due to its convenient calorific value, the dried RDF is used in cement industry as partial replacement of solid fuels [1].

Answering to specific issues in the Integrated Management Center from Tarpiu, Bistrita Nasaud County, through the CleanTech Project, funded under the frame of POC 2014-2020 Structural Funds Programme, a complete characterisation of produced RDF is under evaluation.

Materials and methods: In this study, the RDF recovered from MSW separation was decomposed in a fixed-bed reactor and the condensable fraction was analysed by gas-chromatography coupled with mass spectrometry (GC/MS) using a Perkin Elmer analyser.

Results: The main compounds in the liquid phase collected during the thermochemical decomposition in oxygen-free atmosphere of tested RDF were identified. In the figure 1 the chemical structure of these compounds and their retention time are presented.

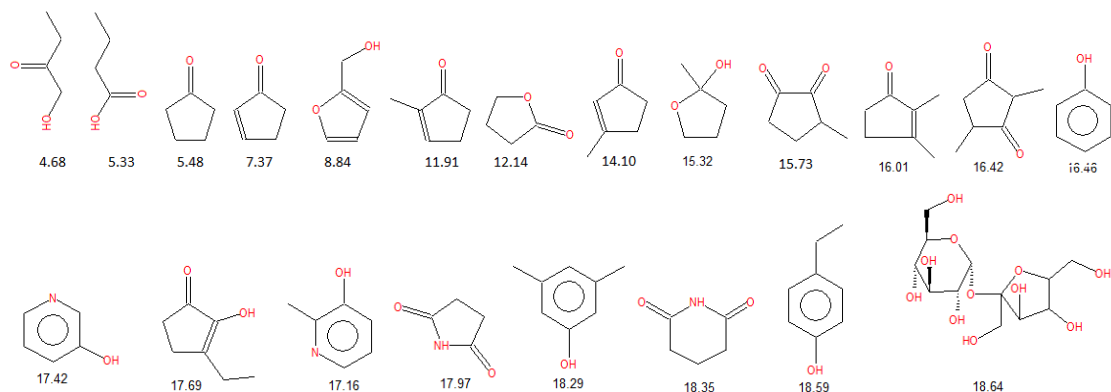


Figure 1. Main compounds identified by GC/MS

Conclusions: By applying GC/MS analyses the main compound released by the RDF in thermochemical applications can be identified, which allows a better control of post-treatment procedures efficiency.

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PROCESSING THE PLASTIC MATERIALS SEPARATED FROM SMW

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Keywords: solid municipal waste, pyrolysis, ATG

Introduction: Solid municipal waste (SMW) may represent a valuable material and/or energy resource if the wastes are well separated. Depending on the management measures and chemical characteristics of the separated materials, dedicated processing paths can be considered [1, 2]. Considering this topic, through the CleanTech Project, funded under the frame of POC 2014-2020 Structural Funds Programme, clean technologies for plastic material separated from MSW within the Integrated Management Center from Tarpiu, Bistrita Nasaud County, are developed and optimised.

Materials and methods: For this paper, plastic materials separated from MSW were pyrolyzed in a laboratory scale pilot system. The technical parameters were established after performing thermogravimetric analyses using SETSYS TG/DTG-DSC apparatus build by SETARAM.

Results: Based on the identified characteristic thermal ranges of decomposition identified through thermogravimetric analysis, applied pyrolysis processes carried out in laboratory pilot plant led to more than 65% (wt) liquid products, 18 – 24 % (wt) solid products and the rest was gas product. In the figure 1, the pyrolysis reactor with catalysis module and thermocouples system is presented, while in figure 2 a typical thermogravimetric analysis diagram (TG and DTG).



Figure 1. Pyrolysis reactor

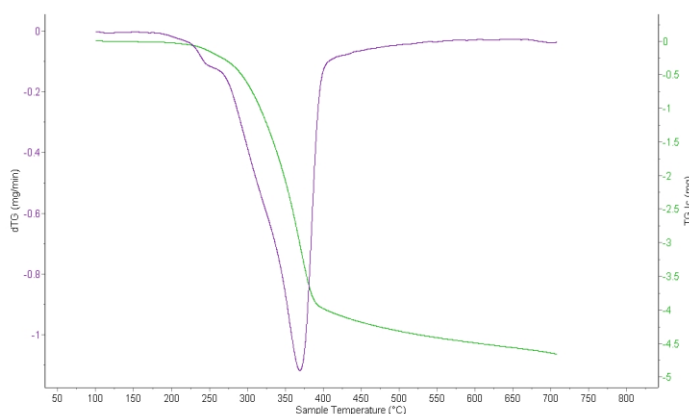


Figure 2. Mass loss (TG) curve and its derivative (DTG)

Conclusions: By applying controlled thermal profile during the specific range of thermal decomposition of plastic materials, selective components can be recovered and further used for specific application.

Acknowledgements: This work was supported by the Romanian competitiveness operational program (POC 2014-2020) through the knowledge transfer project – CleanTech, POC-P40_308, SMIS: 105958 (<http://cleantech.pub.ro/>).

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STEAM-BASED SYSTEM DESIGN FOR SMW TREATMENT

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Keywords: solid municipal waste, steam treatment, ANSYS

Introduction: Solid municipal waste (SMW) represents an environmental problem largely distributed all around the world, that requires urgent management actions. Extensive studies have been performed and dedicated management measures were optimised depending on the country's regulation and specificities [1]. Integrated multistep procedures that involve mechanical, thermochemical, biochemical processes are developed in order to increase as much as possible both mass and thermal efficiency [2]. Within CleanTech Project, funded under the frame of POC 2014-2020 Structural Funds Programme, clean technologies for combustible materials are developed. For this purpose, a thermochemical process using under-pressure solid matter concentration is considered. To do that, the first step was to design the reactor where an adapted hydrothermal treatment will be optimised.

Materials and methods: For this study, a mathematical model in ANSYS has been built in order to design a reactor for SMW processing. Also, on several samples of SMW, immediate and ultimate analyses have been performed in order to ensure the input for mathematical simulation.

Results: Based on the technical characteristics imposed by the technical data sheets of the installation components, the reactor design calculation have been performed by using ANSYS engineering simulation program. In the figure 1, two sections of the designed reactor are presented.

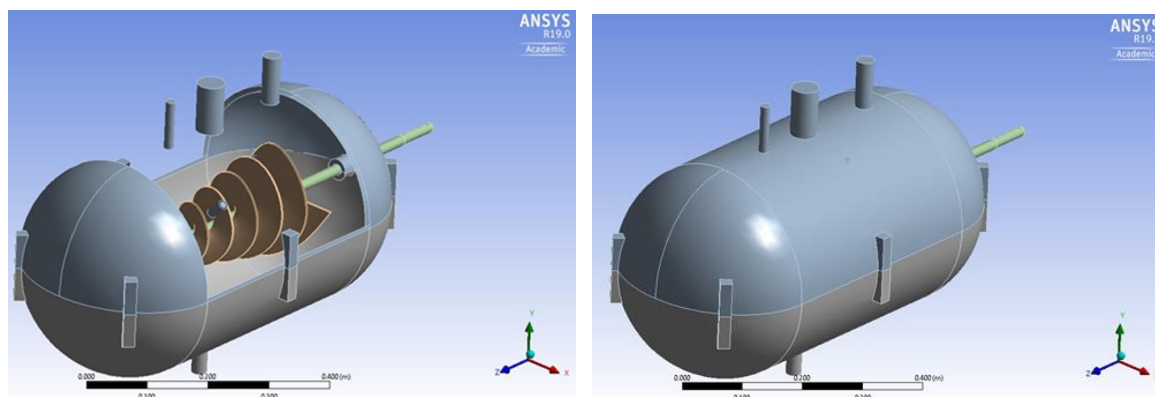


Figure 1. Section of designed reactor for MSW steam-based treatment

Conclusions: By applying the mathematical simulation in ANSYS, reactors for SMW treatment with pressured steam can be designed to operate in secure condition for given technical characteristics of the components.

Acknowledgements: This work was supported by the Romanian competitiveness operational program (POC 2014-2020) through the knowledge transfer project – CleanTech, POC-P40_308, SMIS: 105958 (<http://cleantech.pub.ro/>).

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ADAPTING SPONTANEOUS FLORA FOR IN-SITU SOIL REMEDIATION

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Keywords: spontaneous flora, adaptive mechanisms, contaminated soils

Introduction: The extractive industry faces occasionally incidents that lead to soil contamination with specific products in the proximity of extraction sites. Such punctual problems are treated in general through out-site methods, which involve the excavation of the affected soil and its treatment in dedicated units [1]. Within CleanTech Project, funded under the frame of POC 2014-2020 Structural Funds Programme, clean technologies for remediate contaminated site are developed, by adapting specific biomass types that are able to restore the native soil characteristics [2]. In this paper, remediation of clay-based soil polluted with reservoir water was approached by cultivation of *Salicornia* sp. and *Suaeda* sp. sampled from natural sites like Lacu Sarat (Braila county).

Materials and methods: For this study, the plant species were sampled from Lacu Sarat in three stages of development: early stage, mature stage and at the end of the life cycle.

Results: It was found that, despite the longer time required for effective results, on-site decontamination technologies are not only cleaner, but contribute to the soil microbiome restoring.

Conclusions: Spontaneous flora species such *Salicornia* and *Suaeda* were proved to be effective in managing the level of chlorides in the tested real environment.



Figure 1. Spontaneous *Salicornia* sp. and *Suaeda* sp. from Lacu Sarat adapted on affected soils

Acknowledgements: This work was supported by POC 2014-2020 Programme, CleanTech Project (ctr. no. 56/2016, SMIS 105958) (<http://cleantech.pub.ro/>).

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COUPLING PHYTOREMEDIATION WITH BIOENERGY

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Keywords: soil salinity, adaptive mechanisms, biorefinery

Introduction: The increased salinity of soils may be induced by natural causes and anthropic activities. Salted soils have no suitability for agriculture crops, thus inducing the decline of regional economics. To restore the quality of these soils different remediation practices can be applied, among which the use plant species for salts' extraction seems to be suitable for developing synergic green technologies coupling phytoremediation with biofuel production.

HaloSYS Project – funded within the frame of FACCE SURPLUS Programme aims to develop the cultivation of selected halophytes species in salt-affected soils and explore how to use the obtained biomass in new value chains.

Materials and methods: In order to test the ability of halophyte species to extract salts from soils, laboratory trials have been organised. The plants were monitored from germination to the end of life cycle and the soil analysis through ICP-MS has been performed to determine the decline of salinity. On the biomass side, enzymatic hydrolysis was applied on dried samples and free glucose has been determined by using a UV-VIS spectrometer.

Results: It was found that *Limonium* sp., *Festuca* sp. and *Portulaca* sp. have good adaptability on soils with moderate salinity. In order to produce 2nd generation biofuels, the ability of cellulosic biomass to be hydrolysed is the main step in ensuring sustainable path for fermentation. In our work, it appears that the produced halophytic biomass can be hydrolysed with cellulase and xylanase up to 48% (wt) in 4h.

Conclusions: Halophyte species can be successfully used for salts extraction in phytoremediation practices, and to obtain biomass suitable for biofuel production.

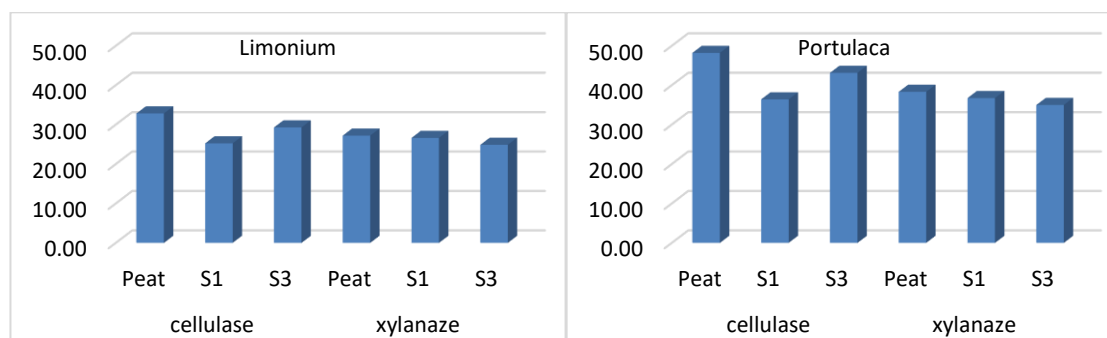


Figure 1. Enzymatic hydrolysis of biomass

Acknowledgements: This work was supported by the ERANet FACCE SURPLUS programme, HaloSYS Project (ctr. no. 44/2018, UEFISCDI) (<http://halosys.eu>).

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SUSTAINABLE USE OF LOCAL BIOMASS RESOURCES WITH THERAPEUTIC POTENTIAL

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Keywords: biomass, bioproducts, bioactive substances

Introduction: Hot peppers (*Capsicum annuum*), *Solanaceae* family, represent the most cultivated species of all 4 known types of peppers. In this sense, the variety of hot peppers is an exception due to the irritating substance capsaicin, [1-3] with multiple therapeutic indications. They are frequently used in therapeutics for their properties: antimicrobial, antiinflammator, peripheral circulation stimulator, content of antioxidants, vitamins (A and C) and minerals [4]. The purpose of this paper is to enhance the valorification of such type of bioresource, by an efficient use of different fractions for the development of bioproducts with input in human and veterinary applications.

Materials and methods: In this work we determined the content of bioactive compounds on different extracts of *capsicum annuum* parts (pulp and seeds powder) in polar and nonpolar solvents (etanol, metanol, hexane, ethyl acetate). The analyses have been performed by gas-chromatography coupled with mass spectrometry.

Results: The experimental results show that the selected natural materials contained important bioactive substances, among which esters of fatty acids and monoglycerides can be further used for developing new sustainable value chains for bioproducts. Furthermore, the chemical composition of the extracts confirms an important complexity of molecular species, useful for the therapy of the cutaneous tissue. Thus, the hot peppers extracts will be further used to obtain a complex bioproduct able to treat pain, inflammations and their complications.

Conclusion: In this study, the chemical composition of *Capsicum annuum* extracts reveals through the complexity of molecular species multiple ways of using the local biomass resources in the field of health and ecology.

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OPTIMIZATION OF CONDITIONS FOR PRODUCTION OF CALCIUM CITRATE FROM EGG SHELLS

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Keywords: egg shell, calcium carbonate, calcium citrate, orthogonal design

Introduction: Eggshells contain high amounts of CaCO_3 (94-97%), some proteins (3-4%), and minor traces of MgO , P_2O_5 , K_2O [1, 2]. Calcium carbonate has the highest concentration of elemental calcium (40%). Its bioavailability is low due to the fact that it is soluble only in strongly acidic environments, and as a result, a low absorption rate of Ca ions occurs in the gastrointestinal tract where the pH is neutral or alkaline [3]. The very high content of calcium carbonate allows the use of these eggshell powders as a raw material for obtaining organic calcium in the form of calcium citrate, which is water soluble, generally regarded as safe, tasteless and has high absorptive properties by the human body. Adequate calcium intake contributes to the prevention of calcium deficiency in the elderly and in children. This study aims to optimize the technological parameters for production of calcium citrate and establish the order of the factors' influence on the yield.

Materials and methods: Ten grams of eggshell powder are mixed with a series of citric acid concentrations (5%- 35%), at different solid: liquid ratio (1:10-1:20), temperatures (25°C - 45°C), and time intervals (2-4 hours), with gentle stirring, according to the experimental design. The filtered solution containing calcium citrate is dried at a temperature of 55°C - 60°C and then grounded. Purification of product was made and the total yield was calculated. The Orthogonal Array Testing Strategy (OATS) was applied to optimize the calcium citrate technology. Four independent variables at three levels were adopted [$\text{L}_9 (3)^4$], namely citric acid concentration (A), solid ratio:liquid (B), temperature (C) and time (D), and the selected levels represent the maximum number of values for each factor determined in preliminary studies, based on experiments with a single factor-design. The yield of calcium citrate is the dependent variant (taken as an indicator). Statistical analysis was performed using Minitab 19 software. Analysis of variance (ANOVA) was performed in Minitab and tested at a significant difference level with $p < 0.05$.

Results: In this study, a total of 9 experimental runs were performed for optimizing the four individual variables and the results were expressed in yield. The yield of calcium citrate exceeded 50%. Range value index shows that the order of influence of the parameters in obtaining calcium citrate is $R_A > R_D > R_B > R_C$. Analysis of variance showed that the contributions of citric acid concentration and time were significant.

Conclusion: Based on the analysis of the experimental results, the optimal conditions are determined for a maximum yield as: 30% citric acid concentration, time 3 hours, solid:liquid ratio 1:16, temperature 30°C . The yield of obtaining calcium citrate prepared under optimized conditions is 88.64%.

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OPTIMIZATION OF LACCASE EXTRACTION FROM SPENT PLEUROTUS SUBSTRATE

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Keywords: solid state fermentation; spent mushroom substrate; laccase activity; respirometer; selenium

Introduction: The spent mushroom substrate (SMS) is a significant source of enzymes and bioactive compounds that need efficient extraction treatments in order to increase its economic value. Mushrooms are multifunctional components used in human diet for their medicinal and nutritional value. Selenium (Se) is a microelement which assures the essential intake of antioxidant enzymes through Se aminoacids[1]. Laccase (EC 1.10.3.2. diphenol:oxygen oxidoreductase) is an enzyme from the oxidoreductase class that oxidize a large variety of phenolic compounds using molecular oxygen as oxidizing agent. The aim of this study was to optimize the extraction of laccase from spent Pleurotus substrate (SPS) varying pH, temperature, and liquid/solid ratio (L/S). We also wanted to see the influence of Se on Pleurotus growth, metabolism, and laccase expression and activity.

Materials and methods: Pleurotus mushrooms were grown in specific tents, in plastic bags, in the presence and absence of 50 and 100 μ M selenium, until formation of fruiting bodies. We used a respirometer equipment (Echo Instruments) to determine the amount of CO₂ produced and the O₂ consumed by mycelium growth in the presence and absence of Se [2]. The substrate was lyophilised, and then subjected to protein extraction in a water bath with agitation (100 rpm) for 4 h. The extraction of laccase was optimized by response surface methodology (RSM) using a face-centered design (FCD) with one nominal factor (the buffer system: acetate and phosphate) and three numeric factors namely pH (6, 7, 8 for phosphate and 3.8, 4.7, 5.6 for acetate), temperature (25, 45 and 65 °C) and L/S ratio (10/1, 30/1 and 50/1). Three center points were added per buffer system to estimate the standard error. The response was the enzyme activity which was determined by measuring the absorbance of ABTS at 420 nm with a UV-VIS spectrophotometer [3]. The design was created with a randomized run order and analyzed using Design Expert® Version 11 software.

Results: Most protein extracts significantly oxidized ABTS, except the extracts obtained at 65°C and at pH \geq 7, parameters that inactivated the enzyme. The oxidating rate increased after concentrating the extract by ultrafiltration, indicating an enzymatic-induced process. The cultivated Pleurotus expressed significant amounts of active laccase which was active at pH < 7, as expected. Preliminary data showed that Se could positively influence the expression of laccases, but the effect is highly dependent on the dose and optimizations are necessary for positive outcomes, as the induction of enzyme expression could be balanced by the toxicity effects of Se. Se did not significantly influence the CO₂ production nor the O₂ consumption by mycelium.

Conclusions: We used solid-state fermentation to obtain fruiting bodies from Pleurotus for dietary supplements or food industry and the SPS as a sub-product for a cost-effective source of ligninolytic enzymes. The influence of Se on enzyme expression needs an in-depth investigation.

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THE EFFECT OF FLUORESCENT STRIGOLACTONE MIMICS ON DEVELOPMENT OF PHYTOPATHOGENIC FUNGI

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Keywords: strigolactone, phytopathogenic fungi, radial growth, hyphal branching

Introduction: Strigolactones (SLs) are organic molecules synthesized by plants that have two main functions, acting as plant hormones and regulating numerous aspects regarding plant development and various stress-related functions, as well as signaling molecules in the rhizosphere [1]. Due to their biological activities, they could be used as plant biostimulants, but the natural SLs have a complex structure that is difficult to synthesize. Therefore, SLs analogues and later SLs mimics that preserve the activity of natural SLs have been synthesized [2]. In this study we tested the bioactivity of new SL fluorescent mimics on two strains of phytopathogenic fungi.

Materials and methods: The fungal strains were *Fusarium graminearum* and *Rhizoctonia solani* which were grown on PDA medium at 28°C, for 5 days. A piece of agar was taken and placed in the center of Petri dishes of either water agar or Poloxamer 407 medium containing different solutions of fluorescent SLs mimics (SL-20 and SL-21) incorporated in different culture media which include agar and Poloxamer 407. To examine the number of hyphal branches and their morphological characteristics in poloxamer and agar cultures we used a stereomicroscope (OPTIKA, Italy). The diameter of the fungal colonies was measured after 3 days.

Results: The radial growth of the two tested fungi was significantly inhibited by GR24, SL-20 and SL-21 at concentration of 10⁻⁵ both in agar and poloxamer. The new SLs mimics, especially SL-21, were as efficient as GR24. The highest effect was obtained against *R. solani*. At lower concentrations, the effect was much less pronounced. No significant effect was observed on hyphal branching for neither SL concentration, but GR24 and SL-21, and to a less extent SL-20 increased the pigmentation of *F. graminearum* in the medium with poloxamer.

Conclusions: We propose new SL fluorescent mimics that have the same effect as GR24, inducing a stress response and inhibiting phytopathogen growth. The synthesised SL mimics can be used for further in depth investigation of SL – plants and SL – microorganisms interactions based on fluorescence analysis.

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OPTIMIZATION OF AROMA COMPOUNDS EXTRACTION FROM WINE LEES USING A TAGUCHI DESIGN

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Keywords: aroma compounds extraction, wine lees, optimization, Taguchi Design

Introduction: In this study we aimed to optimize aromatic compounds extraction from wine lees which are responsible for cognac oil aroma. The concentration of cognac oil represents the sum of the ester concentrations of: octanoic acid ethyl ester (ethyl octanoate - EO), decanoic acid ethyl ester (ethyl decanoate - ED), dodecanoic acid ethyl ester (ethyl dodecanoate - EDD), and hexadecanoic acid ethyl ester (ethyl hexadecanoate - HDE), which are the main organic compounds in hydroalcoholic extracts [1-3].

Materials and methods: The optimization of the extraction conditions necessary to obtain the maximum concentration of cognac oil, from red wine lees, was made by Taguchi design, using the response surface methodology (RSM) with a statistical model with three independent variables (A = solid/liquid ratio, w/w; B = extraction temperature, °C, and C = extraction time, h) and two-levels, to maximize the relative extraction efficiency. The analysis of the experimental program was performed using Design-Expert® Software Version 11 (Stat-Ease, Inc. Minneapolis, MN, USA). The experimental Taguchi model for obtaining volatile organic compounds was performed using the Clevenger hydrodistillation method. Different quantities of red wine lees liquid sediment was mixed with distilled water in the Clevenger installation, at different extraction temperatures and different extraction time, heated in an oil bath on a heating magnetic stirrer with temperature, at 650 rpm. For every experiment, the distillation head was collected separately to remove the odor of pomace. At the end of each experiment, the obtained concentrated hydrodistillate was collected and analyzed by gas chromatography-mass spectrometry (GC-MS) to identify the volatile compounds, by comparing to a standard cognac oil produced by Sigma-Aldrich (Germany).

Results: The main extracted volatile compounds were between 5.8-32.2 mg, where the minimum content obtained was for A = 1/1 w/w, B = 125°C and C = 4 h, and the maximum was for A = 1.5/1 w/w, B = 150°C and C = 4 h. The polynomial equation coefficients were established using the Analysis of Variance (ANOVA) for the selected factorial model. The optimum concentration of aromatic compounds was for A = 1.3/1 w/w at B = 141°C and C = 4.3 h, which is in accordance with the predicted values obtained using RSM. The importance of the factorial model was calculated using ANOVA.

Conclusions: Our study shows that the solid/liquid ratio and the extraction temperature have significant influence on the aroma compounds extraction from wine lees, while the time has less influence. This study could represent a starting point in optimizing the extraction of aroma compounds for a higher valorization of wine lees.

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COMPARATIVE STUDY ON UNSATURATED FATTY ACID EXTRACTION USING GREEN EXTRACTION METHODS

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Keywords: *fatty acid esters, ultrasound extraction*

Introduction: Polyunsaturated fatty acids have a preventive effect on high blood pressure, inflammation, and cancer [1]. The main polyunsaturated fatty acids are eicosapentaenoic acid (EPA, C20:5) and docosahexaenoic acid (DHA, C22:6).

In the last years, green extraction methods based on the use of alternative solvents and low energy consumption are used to obtain high-quality products. These methods improve oil extraction yield and optimize extraction procedures and are recognized as a promising alternative to organic solvents and oil extraction grease. [2]. These methods have many advantages, use nontoxic solvents, time for the extraction and separation process is faster and the lower temperature of the process is much safer.

In this context, this paper presents a comparative study regarding on extraction process (reflux extraction, classic extraction, and ultrasound-assisted extraction) of polyunsaturated fatty acids from different sources using different extraction methods.

Materials and methods: Fish wastes was purchased from fish farms, rapeseed, and soybean seeds were purchased from a national seed producer, ethanol, and hexane grade were supplied by Scharlau (Spain). The analysis of active compounds was performed using GC-MS/MS TRIPLE QUAD (Agilent 7890 A). Ultrasound-assisted extraction and reflux condenser was used for the unsaturated fatty acid extraction.

Results: To improve oil extraction yield and optimize extraction procedures, the influence of various parameters (solvent concentration, the ratio of solvent to solid, time, temperature) was studied. Fatty acid ethyl esters were synthesized to be enriched in PUFA and vitamins by molecular distillation. The analysis of unsaturated fatty acid esters was performed using GC-MS/MS TRIPLE QUAD (Agilent 7890 A).

Conclusions: Regarding the composition of unsaturated fatty acids, fish oil contains the highest amount of eicosapentaenoic acid (EPA, C20:5) and docosahexaenoic acid DHA, C22:6) while rapeseed oil contains a large amount of linolenic acid (ALA, 18:3). These compositions were obtained using hexane as the extraction solvent in the ultrasonic field.

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IN SILICO ANALYSIS OF THE FORMATION OF BIOACTIVE PEPTIDES FROM SILVER CARP (*HYPOPTHALMICHTHYS MOLITRIX*) COLLAGEN

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Keywords: *in silico*, bioactive peptides, silver carp collagen, antihypertensive, antioxidative

Introduction: Due to its unique properties, the study of collagen represents the new trend in medical, pharmaceutical or food sciences [1]. Recently, marine organisms have been considered as potential sources of collagen, as they are not classified as potential spreaders of communicable diseases [2]. This study explores the potential of silver carp collagen protein as a precursor of bioactive peptides using an *in silico* approach.

Materials and methods: A series of *in silico* approaches (BIOPEP database, PeptideRanker database, peptide calculator [PepCalc] database, and toxin prediction [ToxinPred] database) were employed to evaluate the potential of collagen from silver carp as a potential source of bioactive peptides [3, 4]. Furthermore, a number of physicochemical properties, sensory and toxicity characteristics, of the most bioactive peptides with antihypertensive and antioxidant activities were predicted (Figure 1).

Results: Analysis of the profile of the biological activity of silver carp collagen showed possible peptides with antihypertensive and antioxidant activities. Based on the *in silico* hydrolysis simulation of collagen, pepsin and papain proteases can cleave the collagen protein effectively compared to subtilisin, to release ACE-inhibitory peptides. The antioxidant activity was higher for subtilisin-cleaved peptides. PeptideRanker identified the peptides with the best bioactivity scores from the 3 enzymes analyzed. Several peptides showed good solubility in water and all the peptides analyzed were classified as non-toxic.

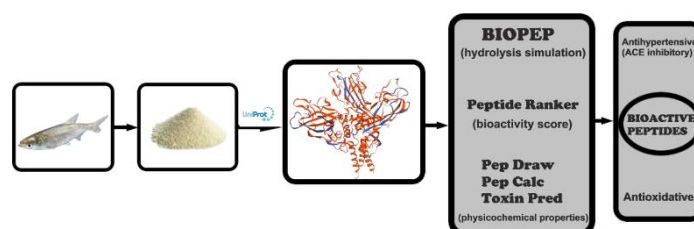


Figure 1. Schematic representation of the steps for the identification of bioactive peptides from collagen

Conclusions: Overall, this study highlights that the silver carp collagen could be a potential source of bioactive peptides with antihypertensive and antioxidant effects and the *in silico* approach is a quick and cost-effective method for analyzing these predicted structures with health-promoting effects.

Acknowledgements: The work on this paper was supported by the Government of Romania, Ministry of Research and Innovation, Project 3PTE -COL-STIM, Project PFE 31/2018.

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BIOSYNTHESIS OF SELENIUM NANOPARTICLES SUPPORTED ON AND WITHIN DIATOMITE THROUGH A CONTINUOUS FLOW METHOD

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Keywords: selenium nanoparticles, diatomite, plant polyphenolic extracts

Introduction: Diatomite, also known as Diatomaceous earth (DE) is a sedimentary rock formed by the deposition of shells of unicellular microscopic algae of the class *Bacillariophyceae* (diatoms). Diatomite-based products are recognized for their significant insect-fungicidal activities and are used in agriculture as a soil improver and for the protection of the aerial parts of crops. Also, diatomite products are characterized by a naturally intricate and highly porous structured composition [1]. Selenium (Se) is a functional element for all living organisms. Selenium nanoparticles (SeNPs) have various biological properties being antioxidant and antimicrobial with applications in diverse industrial fields [2]. The main aim of this work was the bioassisted synthesis of SeNPs within the porous structure of diatomite by a continuous flow method.

Materials and methods: SeNPs were synthesised by the use of plant extracts as a reducing agent of Se from sodium selenite (Na_2SeO_3) to elemental Se, in the porous matrix of diatomite. The plant extract was obtained by mechanical extraction with a ball mill. The AOA of the extract was analysed by DPPH and FRAP methods. The phenolic compounds of the extract were determined by HPLC. The extract was recirculated dropwise through a column with diatomite overnight, after which the remaining extract was removed and 10 mM of selenite solution was added and recirculated in a continuous stream dropwise for 24 h. SeNPs were also prepared in batch as a control sample by dropwise addition of Na_2SeO_3 into the plant extract under continuous magnetic stirring. The samples of SeNPs within and outside of the diatomite were analyzed by TEM.

Results: Our preliminary results indicate that the plant extract has the necessary antioxidant properties to reduce Se from Na_2SeO_3 to obtain SeNPs. TEM analysis indicated the formation of SeNPs both inside and outside of diatomite. The inside NPs should determine a more controlled release of bioactive Se.

Conclusions: We developed a continuous flow method for *in situ* bioassisted synthesis of SeNPs within diatomite pores using plant extracts.

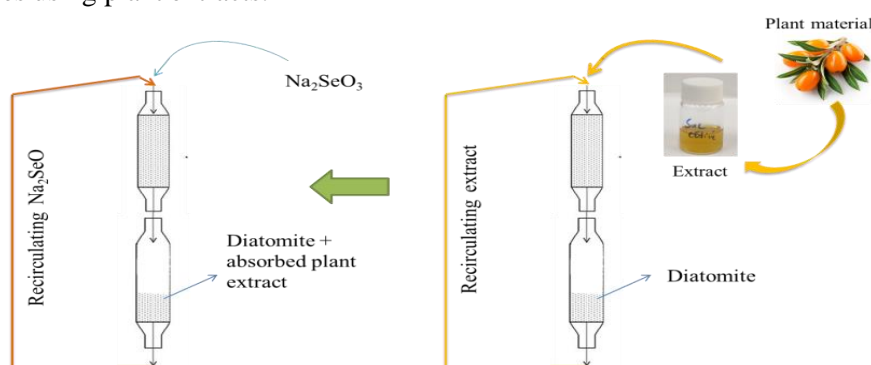


Fig.1 Schematic diagram for obtaining selenium nanoparticles in porous diatomite matrix

Acknowledgements: This work was funded by Romanian Ministry of Agriculture and Rural Development, project ADER 7.3.9. "Research on the biological activity of some nanomaterial-based products on major pest and pathogens of fruit trees and assessment of the ecotoxicological impact of these on useful entomofauna"

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SYNERGISTIC ANTIOXIDANT ACTIVITY BETWEEN HONEY AND PHENOLIC COMPOUNDS

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Keywords: honey, antioxidant activity, polyphenols, plant extracts, synergism

Introduction: Honey is a natural product that has the characteristics of a deep eutectic natural solvent (NADES) due to the intermolecular interactions between monosaccharides and disaccharides, especially the hydrogen bonds formed between them. In previous research, we and others demonstrated that honey enriched in plant polyphenolic extracts presents synergic antioxidant effects. This work shows that specific polyphenolic compounds from plant extracts are involved and responsible for the synergic effects observed.

Materials and methods: The content of phenolic acids from various plant materials (sea buckthorn, raspberry, propolis, tansy and others) was analyzed by HPLC and phenolic acids such as p-coumaric and ferulic acid were found in significant amounts. These phenolic compounds were chosen to test the putative synergy induced between phenolic acids and honey. Ferulic (FA) and p-coumaric (PA) acid were solubilized in 70% ethanol or honey at different concentrations (Fig. 1). The antioxidant activity (AOA) of the samples was assayed using five spectrophotometric methods: radical scavenging activity (ABTS and DPPH) and reducing antioxidant power (CUPRAC, FRAP and PFRAP).

Results: The mixture between individual phenolic acids such as FA and PA, found in plant hydroalcoholic extracts, and honey presented a synergic increased antioxidant activity at all concentrations and for most of the antioxidant assays. No synergic effect was found between different polyphenols indicating that the effect is the result of the interaction between individual polyphenols and honey.

Conclusions Our study shows that phenolic acids such as ferulic and p-coumaric acid found in many plants are involved in the synergic effect between plant extracts and honey. The synergic AOA between honey and the phenolic compounds may be due to the NADES characteristic of honey.

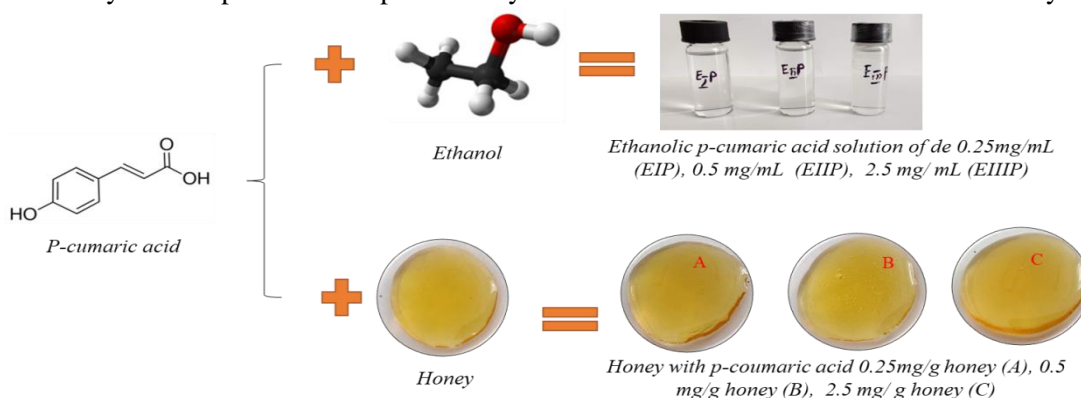


Fig.1 Scheme for obtaining honey with p-coumaric acid

Acknowledgements: The work of this paper was supported by POC-A1-A1.2.3-G-2015- P_40-352 – Secvent, founded by cohesion funds of the European Union, in a subsidiary project 2236/2017 related to increasing polyphenols content into honey.

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ANTIMICROBIAL EFFECT OF MUCOADHESIVE FILMS PREPARED WITH BIOGENIC SILICA NANOPARTICLES

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Keywords: *bioactive films; antimicrobial; biosilica nanoparticles; design of experiments;*

Introduction: Mucoadhesive films can be used to extend the action of different bioactive compounds in the oral cavity. Biogenic silica nanoparticles (SiO_xNPs) release silicic acid that promotes wound healing and connective tissues repair [1]. Due to its mucoadhesive properties, sodium alginate is widely used in the biomedical field, as well as in food industry [2]. The aim of this study was to optimize the preparation of mucoadhesive films with entrapped biosilica nanoparticles and to investigate their antimicrobial effect in order to use them for further applications, such as obtaining oral health products.

Materials and methods: We used three factors-two levels optimization plan for film preparation. The films were prepared with alginate or polyvinyl alcohol (PVA) as a main component and glycerol and sorbitol as additives, as well as biosilica nanoparticles as the active compound. Two of the tested properties of the films were tensile stiffness represented by the Young's modulus or elastic modulus and ultimate tensile strength. Antibacterial activity of the films was assessed through the diffusimetric method. Films with a diameter of 6 mm and sterilized by UV were placed on a previously inoculated medium with a microbial suspension of known CFU (1.5×10^8 colony forming unit). The Petri dishes were incubated at 37°C overnight. Bactericidal effect of the films was quantified by measuring the diameter of the clear circle formed around the spot.

Results: The analysis of the experimental data with Design-Expert pointed out to a link between the Young's modulus and ultimate tensile strength, which represents the desirability factor. The films with entrapped biogenic silica nanoparticles in sodium alginate showed an apparent increase in antimicrobial activity against Gram-negative bacteria in comparison with the films without SiO_xNPs. A similar effect was observed in the case of polyvinyl alcohol. However, there was no noticeable effect against Gram-positive bacteria.

Conclusions: Flexible and elastic yet sufficiently stiff films were prepared using three factors - two levels optimization. Both SiO_xNPs/sodium alginate and SiO_xNPs/PVA films were effective against Gram-negative bacteria.

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BIOPRODUCTS BASED ON MICROENCAPSULATED OILS AND BIOSTIMULANTS USED IN AGRICULTURE CROPS

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Keywords: *microencapsulation, biopesticide, rapeseed treatment*

Introduction: The use of synthetic pesticides creates problems with their toxicity, low-biodegradability, and too high amounts for optimal necessary, which can damage crops and contaminate the environment. Controlled release formulation by microencapsulation of pesticides seems to be the best choice for increasing the efficiency and minimization of environmental damage. The use of essential oils as biopesticides is the subject matter of many investigations in recent years, due to its eco-friendly and biodegradable nature. They are completely non-toxic to mammals, have increased specificity, and pests do not acquire resistance over time due to the intensive use of pesticides. Nevertheless, essential oils are volatile and susceptible to oxidation.

This paper presents a new composition for the rape seeds treatment based on microencapsulation of essential oils and hydrolyzed protein in terms of resistance to drought and pest damage of seeds, during their germination and emergence.

Materials and methods: Microencapsulation of essential oils was performed by the complex coacervation method. Complex coacervation is the separation of a macromolecular solution and is composed of two oppositely charged macro ions into two immiscible liquid phases [1].

Results: The composition of thyme oil was analyzed using gas chromatography coupled with mass spectrometry (GC/MS), using a GC-MS/MS TRIPLE QUAD (Agilent 7890 A). Hydrolyzed proteins from waste have been used as microencapsulation agents. The microcapsules had a central core formed by an essential oil, covered with a shell made of polymeric material, i. e. hydrolyzed proteins and a phase-type which induce coacervation, containing a polyelectrolyte. The new composition used for rape seeds treatment was analyzed in terms of total organic nitrogen (SR EN 15478:2009), ash (AOAC 920.153), density (SR ISO 758:1995), pH (SR EN 10523:2012), total sulfur (SR ISO 10084:1995) by gravimetric methods and Mn, Zn, Cu, Mg by ICP-OES method.

Conclusions: The new composition based on microcapsules as concentrated suspensions containing plant biostimulants based on hydrolyzed proteins were used for rape seeds treatments, in terms of resistance to drought and pest damage of seeds, during their germination and emergence.

The final treatment composition corresponds to the standards regarding the quality and composition of the products intended for seed treatments.

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NEW CONTROLLED RELEASE FERTILIZERS WITH KERATIN-BASED COATING FROM CHICKEN WASTE FEATHERS

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Keywords: keratin, NPK fertilizer, DES, controlled nutrient release

Introduction: Circular economy systems employ minimizing the use of resource inputs and generation of waste, pollution and CO₂ emissions. The new EU regulation [1] advises on the use of urea-based fertilizers and allows only biodegradable coatings, in order to be eco-friendly. In this work, we developed an NPK fertilizer coated with keratin from chicken feathers waste.

Materials and methods: *I. Keratin extraction:* Several methods [2] for obtaining keratin were investigated: (i) solubilisation in natural deep eutectic solvents (NaDESs), (ii) microwave extraction, (iii) extreme pH, (iv) aqueous thermal hydrolysis, and (v) by enzymatic hydrolysis. *II. Fertilizer formulation:* a granular (2-4 mm) NPK type fertilizer was prepared. After milling the raw materials with a centrifugal mill, the powders were mixed together with a longitudinal oscillator mixer with variable amplitude and granulated using a lab-scale rotating pan granulator. *III. Keratin application:* two types of keratin applications were tried: using the Wurster method[3] on a fluidized bed granulator and other trials using the same granulator. *IV. Leaching tests:* The last part was the leaching testing using the Behr system, adapted after [4], [5]. The working conditions were 1680 h - 3 mL/h. The eluent was pumped into the soil cartridge, and the liquid eluate was analysed for N, P, K content (%).

Results: The classical methods for keratin extraction - extreme pH, aqueous thermal hydrolysis - had much higher extraction yields than the greener ones (NaDES and microwave-assisted extractions), at least 100% higher. At 200°C, keratin from feathers was over 90% extracted in an aqueous solution. It was observed that the coated fertilizers had increased nitrogen content, comparative to the untreated sample. The first fertilizer formulation, N/P/K 1/1/1 with keratin coating, released the highest N content, 0.3%, almost three times higher than the uncoated fertilizer. During the first half of the leaching period, the N and K concentrations were at the highest values, with higher values for the coated fertilizers, indicating controlled macronutrient release.

Conclusions: Higher concentrations of N and K were released from the coated fertilizers, P concentration remaining the same. The obtained fertilizer could be used for efficient controlled macronutrient release.

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EFFECT OF FOLIAR APPLICATION OF SILICEOUS NANOMATERIAL ON PHOTOSYNTHESIS PERFORMANCE IN SWEET ALMOND (*PRUNUS DULCI*)

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Keywords: foliar application; natural siliceous nanomaterial; diatomaceous earth; natural zeolites; clinoptilite; foliar fertilizer

Introduction: Siliceous natural nanomaterials, i.e. diatomaceous earth and natural zeolites, are biorational products, generally recognized as safe (GRAS) due to their large utilization as dietary supplement [1] and food/feed additive [2]. Applied as foliar treatment, such siliceous natural nanomaterials (SNNMs) have a plant biostimulants effects, due to a combination of protection against UV radiation, anti-transpirant effect and stimulation of photosynthesis [3]. Stimulation of photosynthesis results mainly from the local concentration effect of the siliceous natural nanomaterials on the CO₂ [4]. Combinations of NPK foliar fertilizer and diatomaceous earth, and, respectively, zeolites, was tested for their influence on the sweet almond (*Prunus dulci*) photosynthesis. Such combinations intend also to generate a slow release formulation of the NPK fertilizer, exploiting the excellent characteristics of the used siliceous nanomaterials as ion exchangers.

Materials and methods: Diatomaceous earth (Adamclisi, Constanza, Romania, marine origin, average dimension 8 µm) and natural zeolites – clinoptilite type (Rupea, Brasov, Romania) were used in this study. An NPK with microelement formulation was included into siliceous natural nanomaterials. The ratio between foliar fertilizer and siliceous natural nanomaterial was of 2 to 1. The foliar fertilizer was a NPK 3.5:15:2 with the following microelement: 20 mg/kg Cu, 25 mg/kg Zn, 17 mg/kg Fe, 8 mg/kg Mn, 3 mg/kg B. Selenium (as biogenic nanoparticles) was included also in the complex formulation, as 2 mg/kg. The adhesion to leaves of the siliceous nanomaterial was enhanced by incorporation of 5% chitosan. The foliar fertilizer complexed with SNNMs was applied in the beginning of June 2018, in a dose equivalent to 7.5 kg per ha. The product was applied to sweet almond (*Prunus dulci*), cv. Preamni, from an orchard located in Valul-lui-Traian (Constanza, Romania), Lat. 44°, 10'38,05" N, Long. 28°C, 29', 4,54", on a soil with significant selenium deficit. Determination of photosynthesis parameters were done by using a portable system LCproT Advance (ADC Bioscientific, Herts, UK), a portable fluorimeter (PAM, Waltz, Effeltrich, Germany) and a porometer (AP4, Delta-T Devices, Cambridge, UK).

Results: The analysis of the experimental data demonstrate that the application of the SNNMs complexed with foliar fertilizer, in dose equivalent to 7.5 kg/ha, enhanced the photosynthesis process in sweet almond, due to a combined effect, optimization of the leaf temperature and increase of the substomatal CO₂ concentration.

Conclusions: Application of siliceous natural nanomaterial enhance the photosynthesis in sweet almond leaves.

Acknowledgements: The work on this paper was supported by the Romanian Ministry of Agriculture and Rural Development, project "Research on the biological activity of some nanomaterial-based products on major pest and pathogens of fruit trees and assessment of the ecotoxicological impact of these on useful entomofauna – ADER 7.3.9."

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THE ANTIBACTERIAL ACTION OF VARIOUS SILVER NANOPARTICLES USED FOR THE STONE TREATMENT

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The antibacterial effect of silver nanoparticles is known from the ancient world. Based on their high antimicrobial effect silver nanoparticles can be used in the stone treatment together with siloxanes as the coupling agent. The application of certain silver nanoparticles on the stone treatment can be used as the protection of stone monuments, claddings, heritages. The antibacterial effect of silver nanoparticles consists in the protection of various surfaces against on the formation of biofilms.

The present work aims to follow the impregnation of various types of stone, usually used in the construction as décor elements, travertine, limestone, marble, with different products as siloxanes and silver nanoparticles solutions in order to protect their surface against aggressive climatic factors and microorganisms. The silver nanoparticles obtained by different methods were chosen, based on their antibacterial effect, for the treatment of the various substrate. It is known the antibacterial effect of the silver nanoparticle acting against the various microorganism strains. The application of silver nanoparticles as the protective film or the impregnation of stone substrates shown an efficiency against the microorganism formation acting not only the surface of the treated substrate also inside of their structure [1-3].

The silver nanoparticles were obtained by chemical methods at room temperature or solvothermal method using silver nitrate and various reducing and stabilizer agents as sodium borohydride, sodium citrate, polyethylene glycol, polyvinylpyrrolidone. The stones surface selected were treated with siloxanes, as the coupling agent with thiol groups containing and various silver nanoparticles synthesized by various routes [4-6]. The impregnated stone were tested by FTIR, SEM EDAX and microbiological tests. All tests were done confirmed the presence of silver nanoparticles both on the stone treated surface also inside of the stone structure. The biological test confirmed the presence and activity of silver nanoparticles against the microorganisms. The figure 1 IR spectra indicated the impregnation of the limestone confirmed by SEM EDAX test.

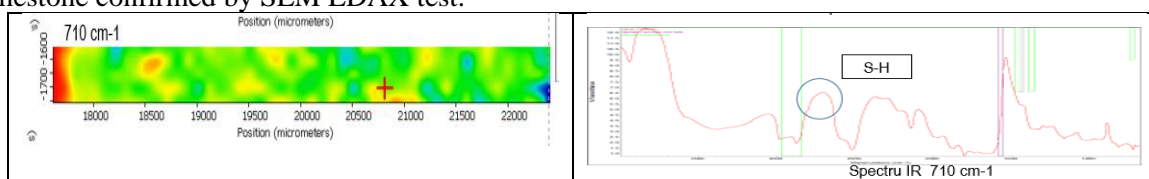


Fig. 1 Limestone impregnated with the COAT O SIL product contain thiol groups and alcohol

The treatment of the stone surface with silver nanoparticle using various type of siloxanes could lead to the high antimicrobial efficiency of the surface with the protection role against the formation of biofilms.

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THE RESTORATION AND CONSERVATION OF A BRONZE ARTEFACT

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Keywords: restoration; conservation; treatment; chromatic integration

The bronze vessel is dated in the Imperial Roman age, during the 1st-2nd centuries. This Italic import item was probably produced in a Campania workshop and reached the territory of the Dacian Kingdom before the Roman conquest. Many such artefacts were discovered in the settlements and fortresses near the capital Sarmizegetusa Regia.

The preservation state of the item was influenced mainly by the nature of the soil in which it rested but also by its composition. We are dealing with the corrosion compounds of the cooper alloy that deeply affected the integrity of the walls. Thus, they became friable and, in some places, the resulting galvanic cells entirely destroyed the metal. The whole surface of the object displays randomly positioned mineral and vegetal depositions. On the outer wall, in the place where the handle was accidentally detached, traces of an empirical interventions are visible, probably a tin patch attempt.

After initiating laboratory analyses and investigations, as well as after running several cleaning tests, the corrosion products were identified and a restoration flux was established and implemented: degreasing, dry and wet mechanical cleaning, local chemical treatment, stabilization, neutralization, filling the missing portions, chromatic integration, and final conservation.

The restoration and conservation of this bronze vessel represented the main method for its salvation and valorization, through exhibiting it for the visiting public.

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FRAGMENT OF A WAGON WHEEL HUB. RESTORATION AND CONSERVATION

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Keywords: wagon wheel hub; corrosion; restoration; desalinization; sodium sulphite

In order to stop the corrosion process which damaged the wagon wheel hub, it was necessary to perform a thorough and laborious restoration process on it.

For achieving this goal, the item was investigated physically and chemically. The results finally determined the diagnosis and the appropriate intervention method.

Therefore, we have selected a restoration flux based on the sodium sulphite (Na_2SO_3) and sodium hydroxide (NaOH) desalinization, as the main stage.

Following the restoration process, the wheel hub was strengthened, regaining its shape and contour. Its aspect resembles the initial one, thus the artefact was introduced in the exhibition circuit.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0413, within PNCDI III.

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ISOLATION OF *MONILINIA FRUCTIGENA* FROM IDARED APPLE VARIETY IN ORDER TO TEST SOME BIO FUNGICIDES

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Keywords: *Monilinia fructigena*; apple disease; fungi isolation; Idared variety; apple fruits

Introduction: To test some bio fungicides, the isolation of *Monilinia fructigena* was carried out. *Monilinia fructigena* is a plant pathogen causing a fruit rot of apples[1-2].

Materials and methods: The fungus strain was cultivated onto potato-dextrose agar from Sigma-Aldrich with next composition: dextrose, 20 g/L agar, 15 g/L, and potato extract, 4 g/L. Chloramphenicol antibiotic was used to avoid the bacterial contamination. Experiences were effectuated with fruits, Idared apple variety, from Research Institute for Fruit Growing Pitesti – Mărăcineni.

Results: Morphological observations were taken based on colony, conidia and conidiophore morphology and other morphological characters [3].



Fig. 1 *Monilinia fructigena* (a), microscope view of *Monilinia fructigena* (b)

Conclusions: *Monilinia fructigena* was isolated from infected apples (fruits) and grown on the potato-dextrose agar culture medium with the goal to test some bio fungicides.

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0332"/Project 3, contract 6PCCDI/2018, within PNCDI III.

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TiO₂ -Ag PHOTOCATALYSTS FOR DEGRADATION OF DYES AND ANTIBIOTICS FROM AQUEOUS SOLUTION

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Keywords: supported TiO₂, silver, photocatalytic degradation, brilliant blue, antibiotics

Introduction

Titanium dioxide, TiO₂, plays an important role due to its catalytic properties and high chemical stability being non-toxic and commercially available. Over time, several synthesis protocols have been established to control the distribution of nanoparticles sizes, surface properties or morphology [1]. In our studies were developed a variety of the synthesis methods in which titanium precursors and surfactants influence the properties of the obtained titanium oxide. Doping of TiO₂ with noble metals such as Ag, Au, Pt or Pd improves photocatalytic efficiency in visible light by acting as an electron trap, promoting interfacial charge transfer and therefore delaying recombination of electron pairs [2]. In this paper TiO₂ mesoporous oxides were obtained by sol-gel method in presence of different surfactants and precursors. TiO₂-Ag photocatalysts were obtained by impregnation of the obtained mesoporous titania and their activity was evaluated in degradation of Brilliant Blue dye and the ciprofloxacin as antibiotic.

Materials and method

TiO₂ was obtained by the sol-gel method using titanium isopropoxide (TP), titanium ethoxide (TE) and titanium butoxide (TB) as Ti precursors and surfactants BRIJ 58 (Bj) and CTAB (Cb). The obtained samples (TPBj, TEBj and TBCb) were doped with silver (1, 2% Ag) by impregnation of TiO₂ with AgNO₃ aqueous solution. The obtained samples were characterized using various techniques, such as X-ray diffraction, N₂ adsorption-desorption, scanning electron microscopy, UV-Vis and photoluminescence spectroscopy. The photocatalytic activity of the obtained samples was tested in degradation of the Brilliant Blue dye and Ciprofloxacin under UV (254 nm) and visible (532 nm) light (laser) conditions.

Results: X-ray diffraction (XRD) of the TPBj-Ag material showed diffraction peaks for anatase without other impurities. A small rutile fraction besides anatase was evidenced for TEBj-Ag and TBCb-Ag samples. Ag species were not detected in XRD. It is probably the result of their well dispersion [3], low concentration and possible formation of amorphous species such as Ag oxide. Adsorption-desorption isotherms showed that TiO₂-Ag materials are mesoporous with typical IV isotherms and hysteresis II type. UV-Vis spectra indicated an insignificant effect of the synthesis conditions on the absorption bands and highlighted the effect of silver with the appearance of plasmonic effect. Photoluminescence spectroscopy evidenced the increase of intensity for the emission peak located at 425 nm, indicating the increasing in time of •OH radical concentration.

Conclusions: The results obtained encouraged the use of TiO₂-Ag nanoparticles for degradation of dyes and the antibiotics under UV and visible light conditions. The best results in Brilliant Blue dye and ciprofloxacin photo-degradation were obtained for TiO₂-Ag sample under UV light irradiation. Thus, the removal efficiency was 98.22% for dye and 90.66% for antibiotic after 150 minutes of irradiation. Photocatalytic tests under visible light showed a good efficiency (90%) after 18 hours in degradation of ciprofloxacin for all the obtained materials.

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NEUTRALIZATION WITH SIMULTANEOUS SEPARATION OF METALIC IONS FROM CONDENSED WATER THROUGH CAPILLARY POLYPROPYLENE AND CELLULOSE DERIVATIVES

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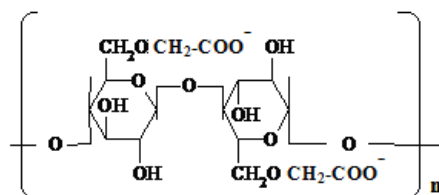
Keywords: composite membranes; neutralization.

An interesting and unpredictable environmental issue raises condensing plants, with an average output of 20-100 Kw, producing thermal energy in individual homes, associations or small public buildings.

Environmental problems arising from acidic waters containing metallic ions from condensing boilers can be adequately addressed using membrane processes [1-3].

This work deals with simultaneous neutralization and separation of aluminum and copper ion from acidic waters containing metallic ions traces through permeation through capillary composite membranes made of polypropylene with carboxymethyl cellulose (PP /CMC) inclusions.

The ionophore from the composite membrane, a cellulose derivative, carboxymethyl cellulose (CMC), is one of the most performing ingredients.



The optimal operating parameters were determined: the flow rate, pH of the receiving phase and working time.

Simultaneously with the quantitative removal of metallic trace ions, an almost neutral pH is obtained, compatible with the natural waters in which it can be dispersed.

It is interesting to note that after 4 hours the performance of the process, especially the neutralization, decreases suggesting an osmotic or retro-dialysis process, generated by lowering the pH gradient.

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MODELING OF SO₂ EMISSIONS IN A THERMAL POWER PLANT BEFORE AND AFTER THE FGD SYSTEM IMPLEMENTATION

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Keywords: flue-gas desulfurization; emissions modeling; SO₂; AERMOD; Gaussian Dispersion Model.

One of the most important problems of modern age is air pollution from the industrial sector. Sulfur dioxide (SO₂) results mainly from volcanic activity or the combustion of fossil fuels. Emissions of sulfur dioxide in reaction with water vapors form sulfuric acid, which generates acid rainfall [1].

The implementation of flue-gas desulfurization (FGD) systems in thermal power plants from Jiu Valley had a significant impact on improving the air quality for the population in that area. Using BREEZE AERMOD / ISC TM, a program based on the Gaussian dispersion model, which can predict the concentrations of particulate matter, NO_x, SO_x, TSP, CO and others from several types of pollutant emitting sources, dispersion maps were generated for a combustion plant with and without FGD system. The modeling considered the topographic characteristics of the thermal power plant's location as well as the climatic characteristics for the analyzed period.

Conclusions: By implementing the FGD system, a major improvement is observed in terms of both the amount of SO₂ emissions and the dispersion of emissions in the analyzed area.

Acknowledgements: The work has been funded by the Operational Programme Human Capital of the Ministry of European Funds through the Financial Agreement 51668/09.07.2019, SMIS code 124705.

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THE INFLUENCE OF AQUEOUS FERNS EXTRACTS ON CUCUMBER (*CUCUMIS SATIVUS* L.) ROOT GROWTH

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Keywords: cucumber; root; ferns; extracts; nanoparticles.

Introduction: In this study we aimed to establish the influence of aqueous ferns extracts on the growth in length of the cucumber root.

Materials and methods: There were tested variants with aqueous extracts obtained from leaves of 2 species of ferns: *Asplenium scolopendrium* L. (As) and *Dryopteris filix-mas* (L.) Schott (Dfm). Some variants with aqueous extracts also contained Ag nanoparticles (As NP, Dfm NP). In this experiment we used two dilutions (1:10, 1:100) for each type of extract.

Results: At the first (Fig.1) and the second (Fig.2) measurement the highest values of root length were obtained at the variants with AgNPs regardless dilution. After 5 days of exposure the highest average root length was 42,73 mm and was settled at As NP 1:100 variant (Fig.3). Generally, at the variants without nanoparticles better results were recorded at 1:10 dilution (Fig.4) than at 1:100 dilution. AgNPs have a positive effect in low concentration [1]. Cui et al. (2014) observed that cucumber root elongation was stimulated after exposure to AgNPs in concentration below 200 mg L⁻¹ [2].

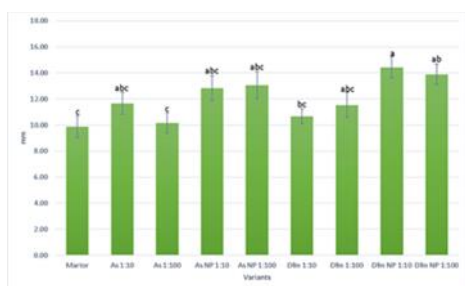


Fig. 1. The influence of extracts on root growth in *C. sativus* - after 3 days of exposure -

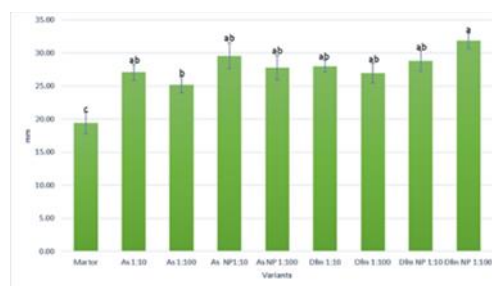


Fig. 2. The influence of extracts on root growth in *C. sativus* - after 4 days of exposure -



Fig. 3. Root growth in *C. sativus* – As NP 1:100 - 5 days of exposure -



Fig. 4. Root growth in *C. sativus* – Dfm 1:10 - 5 days of exposure -

Conclusions: During the experiment, all extracts stimulated the growth of the root length in *C. sativus* compared to the control.

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0332/Project 3, contract 6PCCDI/2018, within PNCDI III.

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CHARACTERIZATION OF PROTECTED AND UNPROTECTED ANCIENT GLASS AFTER ACID CORROSION

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Keywords: SEM; ancient glass; acid corrosion.

Introduction: In the last years the interest to protect integrity of historical objects has increased worldwide. Due to their composition (traces of Cu, Ag, Fe) the risk of deterioration is present [1]. When atmospheric gases (as CO₂, SO_x, NO_x, VOC) come in contact with water in the atmosphere or on the ground they are chemically converted to acidic substances [2] that can attack surface of hiscorical objects. The aim of the work is to coat glass similar with ancient one in order to prevent deterioration of surface by the acetic acid.

Materials and methods: Model glass similar with ancient one with oxide composition 29.23SiO₂-70PbO-0.5CuO-0.15Ag₂O-0.12Fe₂O₃ was prepared by traditional melt quenching route into electrical oven at 1400°C, for 1h. The glass was cast in carbon mold and thermally treated at 500°C for 2h. The covering solutions have been prepared by sol-gel as reported [1,3]. The coated and uncoated glasses were subjected to chemical stability tests in acetic acid. Structure of glass was investigated with FTIR spectroscopy. The morphology was investigated by scanning electron microscopy (SEM) using a microscope, Quanta FEI 200 model. The solutions were investigated with inductively coupled plasma optical emission spectrometry (ICP-OES) method in order to determine elements extracted during tests.

Results:

When the glass surface is in contact with an aqueous acidic medium for long time, the H⁺ ions can replace the metallic atoms in the glass after reaction: $\text{Si-O-M-O-Si} + 2\text{H}^+ \rightarrow 2\text{Si-O-H} + \text{M}$

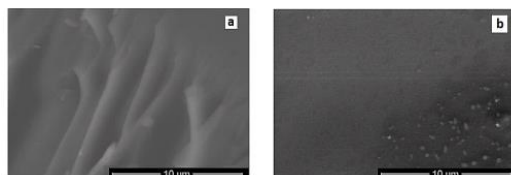


Fig.1. SEM images after acetic acid corrosion
a) uncoated glass and
b) silica coated glass

Figure 1a shows high damage as grooves in the surface of the uncoated glass after acetic acid attack. In the figure 1b can be seen the smooth surface of silica coated glass after acetic acid corrosion. The ICP-OES analysis of solution resulted from corrosion of the uncoated glass show extraction of 52 ppb Pb, 20 ppb Ag, 108 ppb Cu and 40 ppb Fe.

Conclusions: The surface of model glass similar with ancient one was damaged by acetic acid. The silica coating protected glass against corrosion in acetic acid.

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RESEARCH REGARDING USE THE CONDENSED WATER FROM THERMO-BARIC TREATMENT OF MUNICIPAL SOLID WASTE IN CEMENT MORTARS

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Keywords: *municipal solid waste; thermobaric treatment; condensed water; cement*

Introduction: Municipal solid waste management is an important environmental concern around the world. Solid wastes are constantly produced in mega-cities, small towns and large villages, and if residues do not receive the right management, they can cause several affections on the environment and human health. These affections include greenhouse gases emissions, soil contamination, bad odours, underwater contamination, and spread of diseases, among others. Rapid increase in volume and types of solid municipal waste as a result of continuous economic growth, urbanization and industrialization, is becoming a burgeoning problem for national and local governments to ensure effective and sustainable management of waste [1]. Nowadays, the treatment of these wastes is a major environmental issue. A solution for municipal waste treatment is thermobaric treatment. After these type of treatment results a main product (solid product) and a collateral product (condensed water).

Experimental works were carried out to investigate the feasibility of integrating condensed water from the thermobaric treatment of municipal solid waste into road binders. The water of standard consistency, setting time, soundness, flexural and compressive strength were tested.

Materials and methods: A municipal solid waste sample, collected from a Romania historical disposal site, was thermobaric treated at different temperature and pressure. After this treatment resulted in a solid product and condensed water. The quality indices (such as pH, total amount of suspended matter, chlorine, heavy metals and petroleum products) of the condensed water were determined. The determination of the heavy metal content was performed using graphite oven atomic absorption spectrometry, and NovAA 400 hydride generator. Water pH was determined using ORION pH-meter. The quality indices of the condensed water were determined by wet chemistry and atomic absorption spectrometry. For investigate the feasibility of integrating condensed water from the thermobaric treatment of municipal solid waste into road binders was used the following materials: Portland cement type CEM I 42,5R, polygranular quartz sand, condensed water. For this investigation was used methods according to SR EN 196-1, SR EN 196-3 [2,3].

Results: The results obtained show that physical (standard consistency, setting time and soundness) and mechanical characteristics (flexural and compressive strength) prepared with condensed water are comparable with reference mortars performed with water from the national distribution network.

Conclusions: Based on the investigations carried out regarding the possibility to used condensed water from the thermobaric treatment of municipal solid waste into road binders it can be concluded that condensed water could be to perform this type of binders.

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ENVIRONMENTAL MANAGEMENT AND PRECISION AGRICULTURE THROUGH SATELLITE TECHNOLOGIES AND CLASSIC METHODS OF INVESTIGATION

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Keywords: *precision agriculture; environmental management; satellite technologies*

Accelerated advances in Earth Observation technologies determine their successful use in various fields, but especially for natural resources management, ecosystem management and agriculture, providing important information input for monitoring agro-systems and assessing risks to human health. Precision agriculture (PA) is an entire system management approach using information technology, satellite radio navigation (GNSS) data, remote sensing and other associated data sources.

Due to its geographical location, the agriculture in Romania is subject to potential risks caused mainly by natural phenomena but also by anthropic activities. Current climate projections show that all regions will be affected by the global heating phenomenon, by the amplification of regional differences of the main environmental variables as well as by the complex effects of increasing extreme weather occurrences at local level. Due to the limitation of the basic natural resources, an important element in the elaboration of the strategies of agricultural management is the improvement of the knowledge and the capacities for a better management of the variability of the climate, extreme weather and pollution events. The effects of the climatic emergency are significantly reflected in the changes regarding the main environmental variables (air temperature and precipitation), the impact on the growth and development of agricultural crops being more and more obvious [1,2].

In this context, it becomes necessary the development and implementation of an alert system for precision agriculture and environmental management related to identification of air pollution and extreme weather events. The research should be focused on the evaluation of the evolution in time of the physical-chemical characteristics of plants in correlation with the air and of the climatic variables in the area of a pilot site, the estimation of the occurrence of extreme weather phenomena, but also estimation of pollution events during annual vegetative vegetation cycles of the crops with the identification of the influences of long-range transport air masses.

A near real-time alerting system for precision agriculture can be used to assist the management decisions in smart farming since response time is essential to prevent negative effects on crops. Identifying, quantifying, and responding to variability are essential in precision agriculture and environmental management.

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THE ANALYSIS OF A BAYER LIQUOR BY SPME-GC-MS OF DERIVATIZED ORGANIC POISONS

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Keywords: *Bayer liquor; organic poisons; polyacrylate fiber; silylating agent; mass spectra*

Introduction: The aim of this article is the GC-MS analysis of organic matter from a residual liquor sample (S.C. Alum S.A., Tulcea), extracted by the solid phase microextraction method (SPMA) and derivatized with the N-(tert-butyltrimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA) silylating agent. The trace organic matter from Bayer Liquor, known as “poisons”, have the ability to inhibit $\text{Al}(\text{OH})_3$ (gibbsite) crystallisation. The structure of the poisons is essential for understanding how inhibition is induced and consequently, how they can be removed [1-2]. The first step is the extraction of organic poisons from Bayer Liquor by solid-phase micro-extraction (SPME) [3]. Due to the polar functionalized (polyhydroxy compounds, aliphatic and aromatic acids), the derivatization is required to produce more volatile compounds [4]. The most suitable technique of extracted and derivatized organic poisons from Bayer Liquor has been shown to be gas chromatography–mass spectrometry (GC-MS) [1,5].

Materials and methods: The experimental data for this paper were obtained on gas chromatograph coupled with mass spectrometer (GC-MS) produced by PERKIN ELMER, USA. A 50 ml aliquot of the residual liquor sample was acidified to precipitate $\text{Al}(\text{OH})_3$ which was removed by centrifugation. From the supernatant acidified with HCl at pH=2 a 20 ml aliquot was transferred to a test flask. The organic matter (poisons) in the sample vial was extracted by SPME technique on a polyacrylate fiber (PA) of 85 μm . The polyacrylate fiber was immediately exposed in a heated ampoule (700C, 10 min), in nitrogen, to the derivatizing agent MTBSTFA/pyridine (7:3). This was followed by GC injection at 270°C by desorption from PA fiber for 5 minutes. The derivatized components of the residual liquor sample were separated chromatographically on a 60 m capillary column with stationary phase Elite-5 MS (phenyl-methyl silicone). The mass chromatogram (16-40 minutes) of the ions m/z 73+75+147 with derivatized organic components are presented in Fig.1.

Results: The qualitative analysis of the derivatized organic components as tert-butyl-dimethylsilyl (TBDMS) or trimethylsilyl (TMS) derivatives (esters) of the residual liquor sample, separated by gas chromatography, was performed by comparing their mass spectra with the mass spectra in the NIST and NBS mass spectrum libraries; 19 compounds were identified (Table 2). In Table 1, non-derivatized organic compounds with their molecular masses were obtained, subtracting from the molecular masses of the compounds in Table 2 the masses of the tert-butyldimethylsilyl (115-1) and trimethylsilyl (73-1) groups, respectively. For example: glycerin identification in Fig. 2.

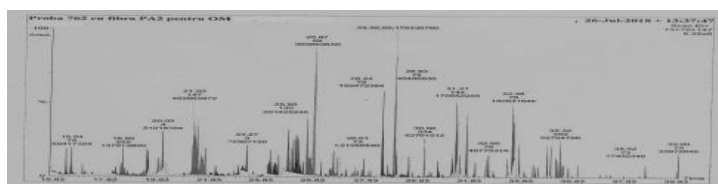


Fig. 1. The mass chromatogram of organic compounds in residual liquor sample.



Fig. 2. The identification of glycerin as TBDMS ester (No. 10 in Table 2).

Table 1. The organic compounds from the residual liquor sample

No.	Name of components	M	Conc. (mg/L)
1	Propanoic acid, 2-oxo- (pyruvic acid)	88	0,3
2	Butanoic acid, 3-methyl- (isovaleric acid)	102	1,3
3	Pentanoic acid, 3-methyl-	116	0,1
4	Propandioic acid	104	2,7
5	Propanoic acid, 2-hydroxy	90	3,1
6	Benzoic acid	122	1,9
7	Carboxylic acid, trans-3- (2,2-dichlorovinyl) -2,2-dimethylcyclopropane	208	0,7
8	Tryptophan	204	1,1
9	Succinic acid	118	0,5
10	Propantriol (glycerin)	92	0,8
11	Acetic acid, 2-hydroxy-2,2-diphenyl- (benzyl acid)	228	0,9
12	5-Nonanol (dibutyl carbinol)	144	0,1
13	2-Methylcyclohexanol	114	0,9
14	Octadecanoic acid	284	1,4
15	9,12-octadecadienoic acid	280	0,3
16	Pimaric acid	302	1,1
17	Isopimeric acid	302	0,6
18	Linolenic acid	302	1,0
19	Cyclopropanecarboxylic acid, 3- (2,2-dichlorovinyl) -2,2-dimethyl -, (3-phenoxyphenyl) methyl ester	390	0,3

Table 2. The derivatized organic compounds from the residual liquor sample

No.	Name of components	M	TR (min.)	P (%)
1	Propanoic acid, 2-oxo-, trimethylsilyl ester	160	16,50	82,7
2	Butanoic acid, 3-methyl-tert-butyltrimethylsilyl ester	216	16,54	91,2
3	Pentanoic acid, 3-methyl-tert-butyltrimethylsilyl ester	230	18,13	90,3
4	Propandioic acid, bis (trimethylsilyl) ester	248	19,51	89,5
5	Propanoic acid, 2- [(tert-butyltrimethylsilyl) oxy] -tert-butyltrimethylsilyl ester	318	21,37	93,3
6	Benzoic acid -tert-butyltrimethylsilyl ester	236	21,50	91,4
7	Carboxylic acid, trans-3- (2,2-Dichlorovinyl) -2,2-dimethylcyclopropane	322	24,50	90,4
8	N, N', O-tris (trimethylsilyl) tryptophan	420	25,00	86,2
9	Bis (tert-butyltrimethylsilyl) succinate	346	25,33	85,9
10	Propane, 1,2,3-tris [tert-butyltrimethylsilyl] oxy] -	434	26,78	95,0
11	Acetic acid, 2-hydroxy-2,2-diphenyl-tert-butyltrimethylsilyl ester	342	29,48	85,0
12	5-Nonanol-trimethylsilyl ester	216	30,88	87,5
13	Silanes, trimeth [(2-methylcyclohexyl) oxy] -, cis-	186	31,45	87,6
14	Octadecanoic acid, tert-butyltrimethylsilyl ester	398	33,76	83,8
15	9,12-Octadecadienoic-tert-butyltrimethylsilyl ester	394	34,38	85,9
16	Pimaric acid, trimethylsilyl ester	374	34,84	80,8
17	Isopimeric acid, trimethylsilyl ester	374	34,97	82,4
18	Linolenic acid, trimethylsilyl ester	350	35,17	82,2
19	Cyclopropanecarboxylic acid, 3- (2,2-dichlorovinyl) -2,2-dimethyl-, (3-phenoxyphenyl) methyl ester	390	36,10	95,0

Legend: M - molecular mass TR – GC retention time (min); P% - Probability of fitting with the mass spectrum from the NBS or NIST libraries.

Conclusions: The 19 organic compounds were identified by comparing their mass spectra with the mass spectra in the NIST and NBS mass spectrum libraries. The calculation of the concentration of the 19 identified components was performed from the area of their peaks in the mass chromatogram of ions with m/z 73+75+147 and from the TOC analysis (854 mg/L) for the residual liquor sample. The concentrations (in mg/L) of the 19 components identified from the residual liquor sample are given in Table 1.

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WATER DECONTAMINATION HYBRID PROCESSES USING PHOTOCATALYTIC ULTRAFILTRATION MEMBRANES

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Keywords: *hybrid water purification processes, ultrafiltration photocatalytic membranes, advanced oxidation processes*

Environmental pollution is a major threat to natural ecosystems, human health and a challenge for the scientific world to adapt to the many side effects of industrialization and development.

The paper presents the results of researches designed to configure innovative water depollution hybrid technologies that use advanced oxidation processes (photocatalysis) combined with membrane separation processes, with synergistic action of degradation of organic pollutants and separation by ultrafiltration, with special purpose of water treatment in the Point of Use (POU). The hybrid processes are based on the development of photocatalytic ultrafiltration membrane systems made on quasi-inert support (PVDF) that incorporate nanostructures based on carbon nanotubes (MWCNT) doped with metal oxides. The laboratory model for the evaluation of hybrid systems is presented. It incorporates the photocatalytic ultrafiltration system in an experimental reactor with automatic control and data acquisition for the analysis of scale processes. The tests performed create the premise of elaborating the design specifications of the processes and their integration in real-scale industrial technologies.

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MONITORING THE STATE OF CONSERVATION OF THE MURAL PAINTINGS IN THE RUPESTRAL CHURCH CORBII DE PIATRĂ

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Keywords: mural painting, rupestral church, degradation, gypsum, biological contamination.

Introduction: The church carved in sandstone rock from Corbii de Piatră, dated in the 14th century, from Argeș County, faces difficult microclimate conditions. The main degradation factors are: humidity (infiltration, capillarity, condensation), migration and crystallization of salts, biological contamination (favored by humidity, temperature, light), temperature fluctuations and relative humidity. These factors led to the degradation of both the mural layer and its support, from the loss of cohesion and disappearance of the painting layer, to the production of gaps in the support, with various extensions, depths and shapes. Within the project 91-001 / 2007 [1] a test of biological decontamination and cleaning of the salts deposited on the mural painting and in the gaps was carried out on the northern wall of the nave. After approximately 11 years, within the 5PS / 2019 project, the decontaminated surface of the nave was evaluated, as well as the whole mural painting from the altar, nave and from the iconostasis.

Materials and methods: The state of conservation was assessed by direct *in situ* observations, humidity measurements and by investigations with specific techniques (X-ray diffraction, scanning electron microscopy and X-ray dispersive energy, optical microscopy) of the samples taken.

Results: The temperature and humidity measurements from November 2019 to June 2020 showed maximums of 20°C, respectively over 95%, and minimums of 4°C, respectively 46%, comparable to those from 2007-2010. The humidity of the rock walls is high (1% -2.6%, often above the detection limit of the device of 3%), and the humidity of the brick wall of the iconostasis is above the detection limit of the device. On direct *in situ* examination no changes of the existing degradations on the walls and vault of the nave and the altar were observed. There has been an increase in degradation (enlargement of gaps) in the case of the iconostasis, especially in the lower area, on both sides of the entrances to the altar and places of worship to the royal icons. X-ray diffraction and electron microscopy determinations performed on the sampled crusts showed the presence of gypsum and calcite. The gypsum comes from the infiltration waters, and the calcite from the lime support of the mural (the calcite from the carbonated lime dissolves partially in the infiltration water and, in optimal conditions of temperature and relative humidity, recrystallizes on the surface of the mural). In the area with mural painting decontaminated and cleaned of salts, from the nave, the reappearance of biological contamination was not observed under the optical microscope. With the help of the electron microscope, traces of biological contamination were observed only on the sample taken from the gap of the mural support. Due to the continuous infiltrations of sulphate-containing waters, in optimal conditions of air temperature and humidity, in the cleaned and decontaminated area they reappeared on the edges of the fresco gypsum and calcite crust.

Conclusions: In the absence of solutions to improve the microclimate, the elimination of infiltration moisture, the degradation process continues through migration and crystallization of salts. Microbiological analysis of samples collected from decontaminated areas demonstrated the absence of identified biodeteriogens before decontamination. Instead, other microorganisms from the aerosphere were identified. The microbial load of the samples was reduced.

Acknowledgements: The authors acknowledge the financial support received from the MCI-Plan Sectorial, contract 5PS/05.09.2019.

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OCCURRENCE AND DISTRIBUTION OF SOME ORGANIC POLLUTANTS IN SEDIMENTS FROM OLT RIVER, ROMANIA

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Keywords: *environmental contamination; organic pollutants; surface sediments*

Introduction: Organic contaminants (OC) accumulate in the environment as a result of anthropogenic activities (industrial, agricultural and household activities and auto traffic) and produce negative effects on the environment and humans. Due to their low solubility in water and their affinity for suspended particles, OC tend to adhere to suspended particles and subsequently remain in sediments [1]. The purpose of this study is to analyze the distribution of the fifteen polycyclic aromatic hydrocarbons (PAHs), twelve polychlorinated biphenyls (PCBs) and nine organochlorine pesticides (OCPs) in surface sediments of the from the middle and lower course of the river Olt, Romania and to determine their sources based on some diagnostic ratio combined with statistical approach.

Materials and methods: Sediment samples were collected on the middle and lower course of the Olt river, including the accumulation lakes and tributaries on its course (28 sampling sites), during three sampling campaigns, in 2019. Microwave extraction protocol was used in order to extract analytes from the sediment samples, followed by quantitative determination of PAHs by HPLC-FLD and PCBs and OCPs by GC-ECD. Some PAHs and OCPs diagnostic ratios were used to suggest the possible contamination sources. Principal component analysis (PCA) was used in order to distinguish the possible sources of specific contamination with POPs and to highlight the locations with considerable ecological risk.

Results: Although OC levels in sediment samples are moderate, some sampling sites show exceeded values for $\Sigma 10\text{PAH}$ and ΣPCB , indicating high contamination. Most of the sites were characterized by Phe/An values < 10 and Flt/Py values < 1 , which correspond to strong pyrolytic input, while some sites show Phe/An values > 10 and Flt/Py values > 1 indicating a petrogenic contamination.

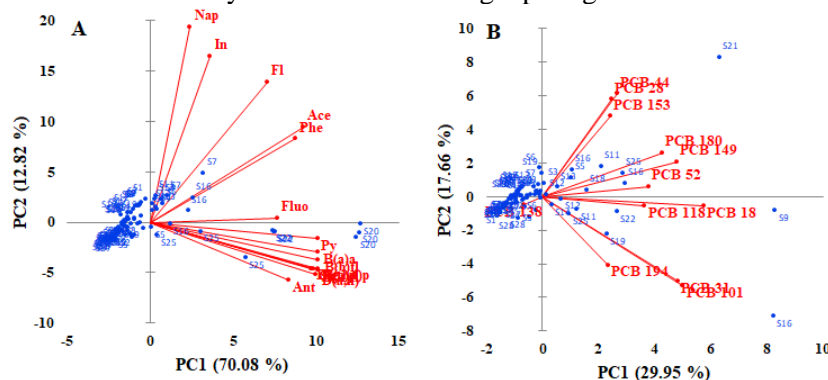


Figure 1. PCA analysis for PAHs (A) and PCBs (B) concentrations in surface sediments of the Olt river

Conclusions: This study provided the first detailed analysis of some OC distributions in surface sediments collected from middle and lower course of the river Olt, Romania. A high spatial variability was observed for the studied OC, with the highest concentrations of PAHs and PCBs near industrial areas and urban agglomerations, while OCPs were identified mainly in rural areas.

Acknowledgements: Romanian Ministry of Research and Innovation, grant number PN 19110303 "Advanced techniques for identifying sources of contamination and biochemical reactions in aquatic ecosystems".

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FROM SPACE TO EARTH – AIRFARE: A PROJECT FOR THE CULTURAL HERITAGE PRESERVATION

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Keywords: artificial intelligence; earth observation; cultural heritage; technology transfer.

Preservation of historic monuments and archaeological sites has a strategic importance for maintaining local cultural identity, encouraging a sustainable exploitation of cultural properties and creating new social opportunities. Cultural heritage objectives are often exposed to degradation due to natural and anthropogenic impacts.

The main aim of the project AIRFARE is to analyze the conservation and the static condition of structures and sites with high historical heritage relevance in Romania, in order to detect critical phenomena that can lead to their deterioration. The project will design, test and promote responsiveness solutions for effective resilience of cultural heritage sites against three types of risks: human activities, climatic impact and structural instability of buildings and their surroundings. In this scope, specific analysis tools will be used in order to construct a catalogue of products for cultural heritage monitoring, by integrating several advanced techniques, such as Artificial Intelligence/Machine Learning and multi-temporal change detection techniques with multi-sensor Earth Observation data.

AIRFARE will focus on assessing and mitigating hazards generated both by natural (severe weather, abundant species, sudden and slow developing geological events, etc.) and anthropic processes (urban sprawl, underground works and material extraction, illegal building and deliberate destruction).

In addition to free EO data, commercial auxiliary EO data and *in-situ* determinations will be obtained, in order to best characterize sites and serve in the validation process.

Probably one of the key points of the project is the consortium, which brings together the know-how and experience of all technologies relevant to the proposed project. The consortium covers the three key segments applicable to the development of services: the economic operator able to exploit the research results by including them in a commercial solution, a university partner with experience in using satellite Earth observation data for cultural heritage monitoring activities and the partner ICECHIM, with experience in the field of cultural heritage conservation, knowledgeable of users' requirements and who will ensure the *in-situ* component of the services.

AIRFARE will focus on assessing and mitigating the influence of natural processes (severe weather, abundant vegetation species, geological events of sudden and slow development, climate change, etc.), as well as anthropogenic ones (urbanization, underground works and resource extraction, constructions illegal and deliberate destruction).

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NATURAL PRODUCTS AS A VIABLE ALTERNATIVE TO CONTROL BIODETERIORATION

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Keywords: *natural products, biodeterioration, cultural heritage.*

Biodeterioration can be considered the one of the most “powerful weapon” that can destroy cultural heritage. Even we talk about stone, leather or other support material, biodeterioration can attack producing irreversible losses. Nowadays a great concern of the scientists is to develop new potential materials which can be used for restoration/conservation without damaging the support and posses longer period of treatment. The study of degradation stages involves transdisciplinary teams based on archeologists, historians, microbiologists, chemists, engineering, materials scientists, etc. when we deal with chemical treatment. Involving natural products as an alternative to classical methods, knowledge from biotechnology or agronomy are required in order to obtain increased yields of active compounds with adequate purity or concentration suitable for these innovative treatments.

Microorganisms present in the environment (both outside and inside) are a permanent risk factor that can damage monuments, pieces of art, but also various other materials, especially when their growth is favored by environmental conditions. The combination of moisture and nutrients favors the development of microorganisms and the deterioration of monuments over long periods of time.

Knowledge regarding natural products has been developed and nowadays pure compounds can be used. The perspective of applying these compounds can be associated with a strong push to create, offering low-cost, environmentally-responsible, sustainable solutions for controlling biodeterioration. Chemical products such as quaternary ammonium, benzalkonium chloride, 2-octyl-2H-isothiazol-3-one were used in order to remove antimicrobial loading [1], but due to their composition based on organic carbon and nitrogen in their commercial formulations families of biodeteriogens that were abundant in the cave (such as *O. lascauxensis* sp., *Aspergillus* sp., *Trichoderma* sp., *Cladosporium* sp., *Alternaria* sp., *Rhodotorula* sp. and *Gymnascella* sp., *Ochroconis* spp., and *Herpotichiellaceae*) had metabolized the organic additives present in the biocide and black spot appeared [2].

In this context, this review paper summarizes different aspects related to the use of natural compounds as viable recipes for controlling biodeterioration of cultural heritage. The literature review was conducted using different databases (Scopus, Web of Science, ScienceDirect, SpringerLink) using as keywords “natural products”, “biodeterioration”, “cultural heritage”, or multiple keywords “natural products for cultural heritage”, “natural products for biodeterioration” within the envisaged time period (2015–2020).

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GREEN TECHNOLOGIES FOR WASTEWATER DEPOLLUTION

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Keywords: *environment, wastewater depollution, green technologies.*

Water pollution remains nowadays a critical issue of our society since in the last decades the pace of industrialization, urbanization and agricultural activities increased rapidly. Consequently, water shortages and water pollution are currently the two major water-related problems experienced by numerous countries worldwide. Long-term adverse effects of these xenobiotics in aquatic ecosystems imply that current water treatment methods have to be improved in order to remove these pollutants at their source or in municipal water treatment plants.

Using a new water treatment technology for NSAIDs (nonsteroidal anti-inflammatory drugs) removal based on catalytic ozonation process with catalytic systems arranged in the form of thin films deposited on a glass substrate is a promising "green technology". Thin-film morphology with phytosynthesized nanosized mixed oxides particles is suitable for catalyst processes since this approach includes advantages from nanoparticles superior properties and avoidance of diffusivity problems (in fixed bed systems) or daunting separation step (in slurry approach). Another important innovative and eco-friendly aspect of this technology consists in the preparation of novel thin-film ozonation catalysts using plant extracts as an environment for nanoparticle formation and stabilization from catalytic starter materials. After preparation, nanoparticles can be used such as (in some cases), but remain the unwanted possibility to agglomerate or deposited in porous structures or on thin films. In porous structures nanoparticles are formed inside pores as a result of a multistep, costly and difficult process without having very good control over their chemical composition, dimensions, and shape. Moreover, after preparation and integration in a chemical process their performances are seriously reduced by diffusion processes, pore blocking, and deactivation.

This type of arrangement brings incontestable benefits comparing with porous supports: a) The deposition of nanoparticles can be accomplished by several methods (spin coating, dip coating, etc.) easy to apply and established technology; b) Composition, thickness, functionalization, and morphology of thin films can be easily modulated in order to obtain desired properties; c) The range of precursors for thin film production is virtually limitless and therefore the number of applications is staggering; d) Thin films can be implemented in all kinds of experimental set-ups and, in the case of chemical reactors, restraints like diffusion phenomena, hydrodynamic behavior of fluid flow inside packed bed and pressure drop associated with fixed bed arrangements do not occur; e) Regeneration of solids and reactor maintenance (if needed) during the life cycle and recycling after total deactivation is easier in case of thin-films approach which makes them a greener choice comparing with porous supports; f) Characterization of thin-films with different techniques is easier comparing with nanoparticles embedded in porous structures. These features make thin films suitable to be used in water treatment processes especially in the oxidation of pollutants and the design of most photocatalytic processes benefits already from the presence of them.

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NANOTECHNOLOGICAL APPROACHES FOR HORTICULTURE: RESULTS OBTAINED IN THE BIOHORTINOV PROJECT

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Keywords: nanotechnology, horticulture, plant extracts, phytosynthesized nanostructured.

Introduction: The BIOHORTINOV component project 3 (Development of plant extracts and innovative phytosynthesized nanostructured mixtures with phytotherapeutic applications in order to reduce biocenotic stress in horticultural crops) goal was the development of nanotechnological approaches for the combating the main fungal diseases that affect the vine and apple cultures.

Materials and methods: During the project, several types of phytosynthesized nanoparticles were evaluated for the application in this area. The recipes developed were tested both at laboratory scale, as well as on field cultures.

Results: From the project emerged, up to this date, several solutions, materialized in three patent applications, awarded at several inventions exhibitions.



Figure 1. Aspect of treated cultures: left – greenhouse tests, right – field tests

Conclusions: Tests are further conducted to evaluate effect of the nanoarchitectures on the horticultural products. The solutions developed were also communicated towards the scientific community by publication in a series of journals (such as *Molecules*, *Coatings*, *Caryologia*, *Journal of Materials Science*, *Journal of Cluster Science*, *Radiation Physics and Chemistry*, *Acta Horticulturae*, etc.), as well as in two books/book chapters.

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WATER TREATMENT USING INTEGRATED CATALYTIC REDUCTION / OXIDATION AND BIOFILTRATION PROCESSES

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Keywords: nitrates; chlorinated organic compounds; water treatment; technology transfer.

Pollution of water sources with nitrogen ions and chlorinated organic compounds (COCl), such as some pesticides or their degradation products, is a major problem, especially in areas where intensive agriculture is practiced [1].

The aim of the project is the transfer and development of a technology for depollution of water from sources contaminated with nitrates and chlorinated organic compounds (pesticides and their degradation products in the environment) efficient and economically feasible, which can be used to obtain drinking water and / or for the remediation of groundwater.

Achieving this goal implies the fulfillment of specific objectives, this guaranteeing the successful implementation of the project: a) Documenting the industrial scale transfer of validated laboratory technology and identifying the possibilities for optimizing the proposed technology (functional, operational and energy) by aligning with the latest scientific discoveries in the field to ensure the success of the transfer; b) Transfer and optimization in the industrial environment of the proposed technology; c) Validation of technology efficiency by independent entities; d) Demonstrating the efficiency of the technology implemented in the industrial environment.

The innovative character of the proposed technology extends on two levels: the level of unitary processes (at the level of the catalytic reduction process will be used innovative catalysts, characterized, tested and selected according to performance and stability and the level of technology (synergistic integration of catalytic reduction processes with catalytic oxidation and biofiltration processes) for the quasi-total conversion of pollutants, in conditions of significant contamination.

The technological maturity reached at the end of the project implementation period will be TRL 6, the project ending with the realization, validation and demonstration in the industrial environment of the functionality and efficiency of the technology on a pilot installation implemented in a water treatment plant.

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EVALUATION OF COMMERCIAL CONSOLIDANT PRODUCTS COMMONLY USED FOR THE CONSERVATION OF WOODEN ARTIFACTS

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Keywords: preservation; wooden artifacts; commercial products; characterization.

Introduction: Wood represents one of the most encountered materials in the Romanian traditional buildings. Exposed to a wide variety of factors (including organic and inorganic pollutants, climatic factors or exposure to microbial colonization), the wood can lose not only its aesthetic characteristics but also its functional and mechanical properties [1].

The present work evaluates three of the most encountered antimicrobial consolidants currently applied on cultural heritage artifacts, by studying their influence on the properties of selected wood models.

Materials and methods: The wooden models used for the experiments consisted of birch wood spatulas with standard dimensions (150x18x1.6 mm), on which the consolidants were applied by immersion. Microscopical aspects of the treated samples were collected using an OPTIKA B-150DBR optical microscope, while the mechanical properties were evaluated using a DMA Q800 (TA Instruments, New Castle, DE, USA), which has a force resolution of 0.00001 N and a strain resolution of 1 nm, operating in multi-frequency-strain mode, samples heated up to 285°C with a heating rate of 3°C/min, in air.

Results: The results obtained suggest the influence of the different consolidants on the properties of the wooden materials.

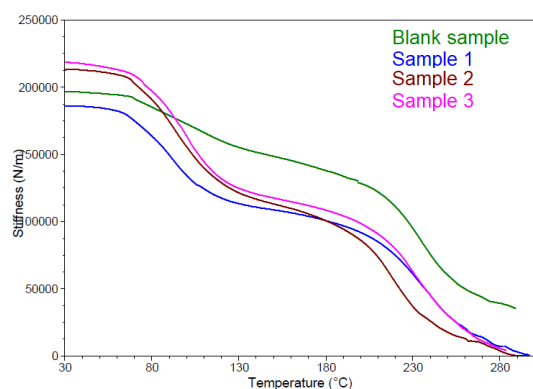


Figure 1. DMA results obtained for the treated samples, compared with the untreated sample

Conclusions: The study of the consolidants influence on the mechanical properties allows the proposal of appropriate consolidants for the selected materials.

Acknowledgements: This work was supported by the Romanian Ministry of Research and Innovation (Romanian Ministry of Education and Research) - Sectorial Program, project 5PS/2018 - Innovative methods and techniques for evaluating conservation-restoration interventions and monitoring the conservation status of traditional constructions in Romania

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PHYTOCHEMICAL COMPOUNDS AND ANTIOXIDANT ACTIVITY OF TWO TYPES OF MEDICINAL PLANTS

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Keywords: antioxidant activity; phytochemical compounds; medicinal plants

Introduction: The present research describes the components of two types of medicinal plants (*Lavandula angustifolia* and *Matricariae flos*). Lavender and chamomile have a variety of therapeutic and curative properties. The aim of our study was to characterize quantitatively (polyphenols, tannins, flavonoids and antioxidant activity by DPPH method) and qualitative (saponins, proteins, terpenoids, steroids) the plant extracts obtained using different types of solvents. The samples were analyzed by UV–VIS and optical microscopy techniques.

Materials and methods: Medicinal plants (*Lavandula angustifolia* and *Matricariae flos*) were collected from Prahova's valley. The solvents (ethanol, methanol, lactic acid and hexane) used for extraction were from Merck. The components and phytosynthesis of extracts were confirmed by UV-VIS spectroscopy and the optical microscopy showed dimensions of grinded plants.

Results: UV-VIS spectroscopy was used to characterize the hydroalcoholic plants extract. The spectrum was registered between 250-750 nm. Specific wavelengths for flavonoids and phenolic acids between 300-350 nm were identified. Another peak appears between 400-420 nm which is specific to carotenoids and another one around 600-650 nm, specific to chlorophyll A and B.

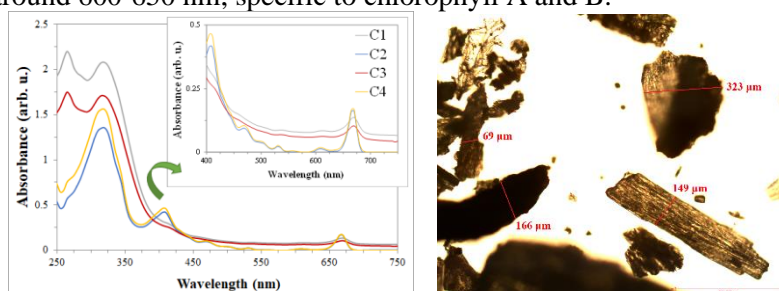


Fig. 1. UV-VIS spectra and optical microscopy image of chamomile (*Matricariae flos*)

Conclusions: UV-VIS spectroscopy showed specific wavelengths for flavonoids, carotenoids and phenolic acids. Optical microscopy allowed to see a structural parallel arrangement of chamomile plant and rods for lavender plant. The tannins content of both extracts decreased in five days between 2-19 %, even in the dark, cold conditions. High values for antioxidant activity represents a good scavenging capacity for free radicals.

Acknowledgements: This paper was supported by a Nucleu Program, project no. P.N. 19.23.03.01, contract no. 23N/2019.

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CONSOLIDATION OF ACRYLIC AND OIL-BASED PAINTINGS WITH CELLULOSE NANOFIBERS

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Keywords: pigments; degradation; consolidation; cellulose nanofibrils.

Introduction: Nowadays, more than ever, the cultural heritage is linking humanity to its history. In order to preserve different artifacts, multiple modern techniques were developed and, under this context, a new method for protect pigments in paintings has been achieved. Over the time, the intensity of the colors tends to fade due to the numerous degradation agents present in the environment. These factors affects the paintings and there is a growing need for new consolidation materials that do not interfere with the original work. Cellulose nanofibers (CNF) has the potential to be a new innovative material for the consolidation of paintings' canvases [1].

Materials and methods: In this work two different types of paints have been used: acrylics and oils (blue, red, yellow and green). CNF 4,5% was chosen as a consolidant and one batch of the samples was treated with this solution on the color layer and another batch on the back surface, directly on the canvas. After that the samples were exposed to direct sunlight for 54h; before and during the exposure 4 types of tests were performed: colorimetry, glossmetry, FT-IR and Raman spectroscopy for the determination of the effects of the sun on the pigment layers [2].

Results: The colorimetric measurements reveal that the untreated samples supported the highest colour degradation, whereas the ones treated with CNF on the colour layer supported the lowest degradation. Glossmetry shows that overall, the samples lost the gloss at the same rate, regardless if the CNF is present or absent. Furthermore, FT-IR and Raman spectroscopy indicate the presence of the functional groups specific to the degradation process, as shown below for the red oil color.

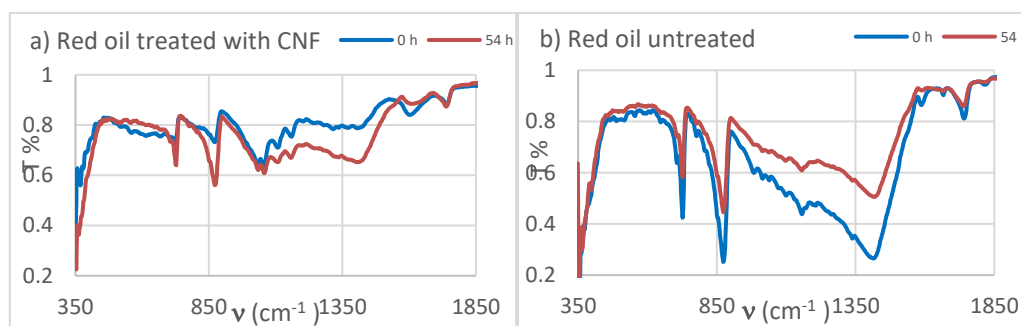


Figure. FT-IR spectrum for red oil before (0 h) and after exposure to direct sunlight (54 h); a) treated with CNF; b) untreated

Conclusions: Following the tests performed so far, it can be said that CNF has a good consolidation effect when applied on the color layer. In the future, the samples will be exposed for longer periods of time to degradation and more detailed tests will be performed.

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LAYERED DOUBLE HYDROXIDES AS CONSOLIDANTS AND ANION ABSORBENTS FOR HERITAGE CONSERVATION

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Keywords: consolidants; layered double hydroxide; anion absorbents; heritage; conservation

Introduction: Knowledge from materials science can be used to design systems that target specific issues in the conservation of cultural heritage, such as the cleaning, consolidation, and anion removal. Layered double hydroxides are a group of anionic clays, that have a several properties of interest in the field of heritage conservations one of them being the property to absorb different anions (sulphate, chloride, phosphate, so on) responsible for the building materials degradation process. In this work, some layered double hydroxides with compositions: $[\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2](\text{Cl})_{0.25}$, $[\text{Mg}_{0.375}\text{Ca}_{0.375}\text{Al}_{0.25}(\text{OH})_2](\text{Cl})_{0.25}$ and $[\text{Ca}_{0.70}\text{Al}_{0.3}(\text{OH})_2](\text{Cl})_{0.30}$ were prepared, characterized and tested as consolidants [1-3].

Materials and methods: The LDH were prepared using the co-precipitation method, starting from the metallic salts [1]. Fourier-transform infrared spectrometry (FTIR), and Raman spectroscopy was used to identify functional groups of the prepared materials respectively DLS were used to analyze the particles size. The relative kinetic stability of the consolidants particles, dispersed in various solvents (ethanol and water) was also determined. The relative kinetic stability (KS) of the suspension was determined from the variation of absorbance over time by UV-VIS spectrometry. KS was calculated using the formula:

$$\text{Eq.1: } KS\% = 1 - \left[\frac{A_0 - A_t}{A_0} \right] \times 100$$

where A_0 represents the absorbance at 0 min, and A_t is the absorbance at time t.

Cubic test bricks measuring 4x4x4 cm were made using gypsum, sand and water 1:2:0.75 w/w. First, the consolidation effect of the LDH was studied by dispersing the solids in water (0.5g/l) and applying the dispersion on test bricks by brush (3 times on every side).

Second, test bricks were made by incorporating 5% (w/w) of every consolidant into the slurry (w/w). The differences in color, mechanical strength and porosity, versus the test specimens were studied, the effect of adding 5% w/w of a calcined LDH (600°C, 4h) on the anion's concentration was also investigated.

The color of the treated sample was measured using a Konica Minolta-Chroma Meter CR-410 colorimeter. The mechanical properties (compressive strength) were determined according to ASTM C805 using a Proceq-SilverSchmidt Concrete Test Hammer Type L. The peeling test was carried out according to the Drdácý method using a 2x2 cm flex tape. Last water absorbtion capacity and the apparent porosity were determined according to STAS 6200/12-73 respectively STAS 6200/12-80.

Results: FTIR and RAMAN spectrum of the synthesized LDH presents several peaks comparable to those in the literature [4]. FTIR: The broad band located at 3438 cm^{-1} arises from the stretching vibration of the hydroxyl groups of the layers, as well as the interlayer water molecules. The band at 1632 cm^{-1} is attributed to the bending vibration of water ($\nu_{\text{H-O-H}}$) a band at 1410 cm^{-1} was also observed, implying a contribution of bicarbonates in the interlayer space. Bands lower than 1000 cm^{-1} could be assigned to

the vibration mode of M–O, M–O–M, O–M–O, and metal hydrogen bond vibration modes. RAMAN: The LDH lattice vibrations in Raman spectra of the samples appear mostly below 600 cm^{-1} . Three bands appeared at ~ 510 , ~ 440 and $\sim 210\text{ cm}^{-1}$ for the MgAl-LDH respectively at 530 and 410 cm^{-1} followed by the band at 1080 cm^{-1} - assigned to CO_3^{2-} vibrations from calcite phase, in case of Ca-Al-LDH. All the LDH dispersions in water and water/ethanol present good kinetic stability, higher than 60% in case of Ca-Al-LDH dispersed in mixtures of water/ethanol. The DLS analysis show that the average particle size varies between 150 and 300 nm, the kinetic studies on the nanoparticles dispersion stability in solvent, confirm that all consolidants dispersions present good stability in water and ethanol/water.

Consolidant testing:

I. **Brushed samples:** The treated samples showed small ($\Delta E^* < 5$) differences in color versus the test specimens. The consolidants did not significantly improved the mechanical properties (compressive strength) of the samples, however, the peeling tests showed that the sample surface is notably (approx. 30%) more stable after the treatment with the dispersion of Ca-Al-LDH. The water absorption capacity and the porosity of the treated bricks showed little differences compared to test bricks, showing that the consolidants applied by brushing did not modify the porosity and water absorption capacities.

II. **Samples with 5% incorporated LDH:** The addition of LDH in the slurry showed little effect on the final color ($\Delta E \leq 5$) or mechanical properties of the samples, however, the porosity and water absorption capacity of test specimens increased, probably due the the high specific surface and mesopores of the consolidants, In order to study the anions absorption capability of the prepared materials, the LDH were calcined and added into the slurry, addition of 5% calcined Mg-Al-LDH showed a good absorption capacity of sulphate anions, absorbing approximately 15% of the sulphate anions.

Conclusions: The consolidants, applied by brushing did not alter the colour of the test bricks and showed promising effect at the peeling test. Incorporating the LDH 5% w/w into the bricks lead to an increase in water absorption capability of 6% and an increase of porosity of about 10%. The incorporation of calcined LDH in the bricks lowered the anion content with about 15%.

Acknowledgements: This paper was supported by the Romanian Ministry of Research and Innovation, Project 51PCCDI/2018 within PNIII and PN 19.23.03.01.04 within the NUCLEU program.

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HYDROXYAPATITE NANOPOWDERS AND NANOCERAMICS

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Keywords: hydroxyapatite; nanoceramic; biogenic waste; microwave assisted method; SPS.

Introduction: Hydroxyapatite is mainly used in biomedical applications because of its very important property – bioactivity. Due to its bioactivity, the stimulation of bone regeneration at the contact between HAp and biological environment becomes possible [1]. A huge amount of eggshells is produced every day, being considered waste. The eggshell consists of 91-94% calcium carbonate. This fact makes it favorable to use them as a source of calcium oxide in the synthesis of HAp [2].

Materials and methods: In this paper we used the microwave assisted method to obtain HAp nanopowders. The powders were lately sintered by Spark Plasma Sintering method to maintain its nanostructure. As reaction precursors there were used orthophosphoric acid solution, calcium hydroxide (obtained from calcinated and hydrated eggshells) and ammonium hydroxide for pH adjustment. In parallel it was realized, for comparison, a HAp synthesis using commercial calcium hydroxide. The obtained precipitate was then placed in a microwave oven for 1 h, dried in the oven and calcinated at 700 °Celsius, then characterized.

Results: As it can be seen in figure 1, there is represented the XRD spectrum of HAp sample (obtained from eggshells). It can be observed that all the diffraction interferences belong to the HAp phase.

The SEM image (fig. 2) presents the microstructure of the HAp powder. From a microstructural point of view, there was obtained a monophasic polycrystalline powder, where the crystalline grains present a needle like morphology, with nanometric dimensions (aprox. 10 nm) and random orientation. The grain boundaries are well defined and the porosity degree is high, the pores being intergranular and interconnected.

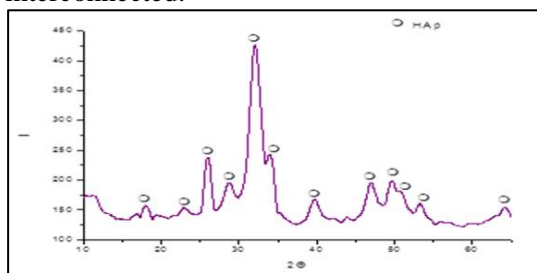


Figure 1. XRD spectrum of HAp obtained from eggshells

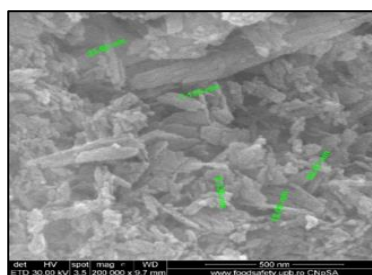


Figure 2. SEM image of HAp obtained from eggshells

Conclusions: The synthesis of HAp using the microwave assisted method leads to the obtaining of a high purity HAp powder, with needle like crystals that present nanometric dimensions. Also, the use of biogenic waste (egg shells) did not affect the final result, so it can be easily used in HAp synthesis.

Acknowledgements: This paper was supported by the Romanian Ministry of Research and Innovation, Project 51PCCDI/2018 within PNIII and PN 19.23.03.01.04 within the NUCLEU program.

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EMBEDDING BIOMATERIALS INTO MORTARS FOR ENHANCEMENT OF SOME PHYSICAL-MECHANICAL PROPERTIES

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Keywords: compressive strength; infrared spectroscopy; mortars; cultural heritage.

Introduction: The history portrays the identity of a culture, of people and various civilizations, which has been preserved by specific images, paintings and buildings over time. In order to carry history forward, but also to preserve the traditional values, cultural heritage reconsolidation is required.

In the last years, biomaterials have gathered attention due to their good compatibility with different materials, and also due to their great potential for applications in various fields. In addition, the low processing costs, availability and the possibility to be used as additives for cement are the advantages that make these materials suitable for preparation of mortars. The aim of the study is to investigate the behavior of biomaterials in combination with sand and white cement for the obtaining of mortars.

Materials and methods: The biomaterials used in this study consists of: alginate (Sigma-Aldrich, low viscosity), chitosan (commercial) and starch (commercial). The mortars were prepared as cubic samples (30 x 30 x 30 mm), according to SR EN 12390-1 standard [1]. In order to characterize the obtained materials, the following tests were performed: determination of mechanical properties by compressive strength using a digital Schmidt hammer, determination of the freezing-thawing resistance according to SR 3518 standard [2], colorimetric analysis using an instrument from Konica Minolta (CR-410 model) under illuminant C and 2 degree standard observer conditions for the calculation of whiteness index [3], and spectral analysis using Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) technique.

Results: The whiteness indices showed the lowest values for sand with white cement and alginate; all materials exhibited a slightly yellow tint (according to the b* parameter) due to the presence of sand in mortars. The infrared spectra showed the presence of sand as major component in the final products, and the white cement as secondary constituent. The lowest value of compressive strength was obtained for alginate as additive, while chitosan and starch showed a slightly better mechanical resistance.

Conclusions: Some biomaterials could be successfully used to improve the mechanical properties of mortars. Infrared spectra analysis was strongly influenced by the sand and white cement materials, which were used in larger quantities than alginate, chitosan and starch. Determination of the freezing-thawing resistance showed promising results for mortars prepared with chitosan and starch. A small improvement of the mechanical resistance, determined by compressive strength, was observed for the samples with chitosan and starch, while the lowest resistance was obtained when using alginate as additive.

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CHEMICAL SYNTHESIS OF MULTI-WALLED CARBON NANOTUBES AND THEIR FUNCTIONALIZATION WITH CARBOXYLATED GROUPS

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Keywords: carbon nanotubes; nanomaterials; chemical synthesis.

Introduction: Carbon nanotubes (CNTs) have attracted attention, due to their structures, as well as to their ability to present multiple walls. CNTs can be synthesized by several methods, such as arc-discharge, chemical vapor deposition, laser ablation and electrolysis. All these methods lead to CNTs with different diameters, lengths, number of layers, but these methods requires high costs of production, high temperatures, high pressures and most of them require repeated procedures for their purification after obtaining. As an alternative to cover these disadvantages, chemical technique seems to be a good option to obtain CNTs easily (at low temperature and without applying pressures) and inexpensively [1].

Materials and methods: Multi-Walled Carbon Nanotubes (MWCNTs) were prepared by chemical synthesis by using graphite microparticles, concentrated sulfuric acid, fuming nitric acid and potassium chlorate. The synthesis parameters were fixed based on the previous work [2]. In order to improve the solubility of the MWCNTs in organic solutions, acid treatment was used (H₂SO₄ (95%) and HNO₃ (65%), in a ratio of 3:1), by functionalizing the surfaces of CNTs with negative charged functional groups (MWCNTs-COOH). The obtained materials were investigated by Fourier transformed infrared spectroscopy (FTIR), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and atomic force microscopy (AFM).

Results: The research focused in analyzing both the MWCNTs obtained by this new method and the functionalized MWCNTs. The major functional groups of the MWCNTs and functionalized MWCNTs were identified by FTIR analysis (Figure 1). Also, in order to estimate the functionalization, the same quantity of MWCNTs was dispersed in water before and after functionalization, for 2 hours in ultrasonic bath and visual observed after that to evaluate their suspension stability (Figure 2).

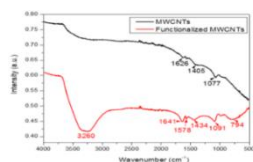


Figure 1. FTIR spectra of the MWCNTs and functionalized MWCNTs

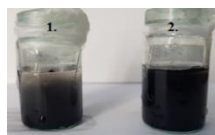


Figure 2. Aqueous dispersion of (1.) pure MWCNTs and (2.) functionalized MWCNTs

Conclusions: By using this chemical route pure MWCNTs were synthesized (sustained by FTIR and EDAX), with a diameter between 9 nm and 43 nm and 500 - 600 nm in length, proved by TEM and AFM analysis. Also, the functionalization of these MWCNTs was successfully done, being confirmed by FTIR and aqueous dispersion of the nanotubes.

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POLYCHROMATIC ARTISTIC COMPONENTS AS INTERIOR DECORATIVE ELEMENTS FROM CONSTANTA CASINO MONUMENT

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Keywords: consolidants; Casino; FTIR; composition

Introduction: The Casino building from Constanta is the most important and characteristic public building built in Art Nouveau style [1]. The stylistic unity of the treatment of the elements is remarkable: the volume, the facades, the shape of the gaps, the modernization, the interior and exterior color decoration (stuccoes), the furniture elements of the interior, the exploitation of the fluidity of the location [2]. The building was designed as a parallelepiped mounted horizontally which gives the impression of stability, but in which each of the 5 visible sides (4 façades and roof), are different from spatial, volumetric and decorative point of view. Besides to the elements of the artistic components described above there are some decorative elements from the repertoire of Art Nouveau style: floral reliefs, curved decorative elements in spirals or waves, painted ceilings, railing and window hardware, lighting fixtures, stained glass (which unfortunately only keeps traces of the original ones) contributing to the harmony of the general composition. In this paper, some compositional aspects of the pigments collected from the Theater Hall of Casino's stuccoes, have been investigated and discussed.

Materials and methods: Fourier-transform infrared spectrometry (FTIR) was used to identify functional groups of the analyzed materials. *Fourier transformed infrared spectroscopy (FTIR)* was performed with single-bounce diamond-attenuated total reflectance (ATR) using a Vertex 80v spectrometer (Bruker Optik GMBH, Ettlingen, Germany), equipped with DRIFT accessory in the range of 4000–400 cm⁻¹.

Results: FTIR spectra of the analyzed samples, presents several peaks comparable to those in the literature [2,3]. The broad band located in the region 3300–3500 cm⁻¹ arises from the stretching vibration of the hydroxyl groups of the layers, as well as the water molecules from the humidity. The band at 1632 cm⁻¹ is attributed to the bending vibration of water (ν_{H-O-H}) a band at 1410 cm⁻¹ was also observed, implying a contribution of bicarbonates in the interlayer space. Bands lower than 1000 cm⁻¹ could be assigned to the vibration mode of calcium carbonate (875 and 712 cm⁻¹) and silica (798 and 779 cm⁻¹) and possibly iron oxides (570 cm⁻¹) for pink colour.

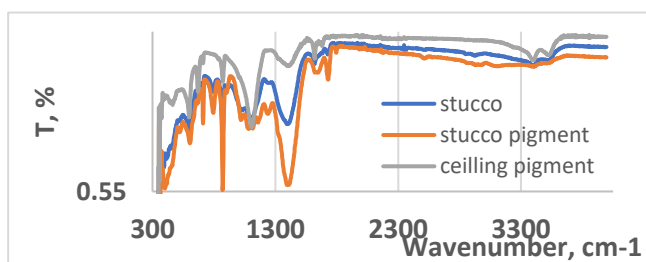


Figure 1. Casino Building (left) and FTIR spectra of some stuccoes from Theater Hall of Casino (right)

Conclusions: The composition identified by FTIR technique is extremely important for the restoration works: a mixture of calcite, silica and iron oxides.

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WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT - PROCESSING AS THERMOPLASTIC COMPOSITES

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Keywords: melt processing, extrusion molding, injection molding, waste electrical and electronic equipment.

Introduction: In the last decades, the waste electric and electronic equipment (WEEE) has increased substantially due to an accelerated development of the economy and the lifetime of electronics. Intensive research was focused on reusing the waste in order to decrease the amount of incinerated or landfill waste. The aim of the paper was to melt process some compositions based on the polystyrene fraction of WEEE and on the non-metallic fraction of waste printed circuit boards (WPCB), compositions that were selected considering the correlation between the mechanical properties of the polymeric composites and the economic advantages arising from the use of a larger amount of waste [1-3].

Materials and methods: For the WEEE composite, the majority component was the polystyrene fraction of the waste, consisting in polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), high-impact polystyrene (HIPS). The WPCB composite contained recycled polypropylene (rPP) and the non-metallic waste. For both compounds, a styrene-butadiene block-copolymer (SBS) and a maleinized and hydrogenated block-polymer (SEBS-MA) were used as modifiers. The composites were processed by extrusion and injection molding, specimens with uniform aspect and reproducible characteristics being obtained (Figure 1). Tensile and impact properties of the resulted composite materials were determined.



Figure 1. Uniform aspect of the injected items

Results: For the studied compounds, it could be observed that some defects appeared at extrusion, like: interior voids, extrudate swelling, shark skin fractures, and variable flow of the polymeric melt. By modifying the processing conditions, defect-free extrudates that can be granulated and used for injection molding could be obtained. The composition influence on mechanical and impact properties of waste composites highlighted that the obtained impact strength, tensile strength and elongation at break are comparable with the characteristics of commercial polymers used in industry.

Conclusions: The processability of the waste composites was verified by obtaining in suitable conditions of extruded and injected items. Their aspect was homogeneous, without surface defects and with high mechanical properties.

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CARBONATED HYDROXYAPATITE SUBSTITUTED WITH MAGNESIUM FOR STONE CONSOLIDATION

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Keywords: carbonated hydroxyapatite substituted with magnesium; nanoemulsion technique; stone consolidation.

Introduction: Carbonated hydroxyapatite (CHAp) is an inorganic compound with various applications that presents a both better homogeneity and consolidating effect than HAp [1]. The insertion into the structure of metallic ions can improve the physico-chemical properties of apatite. In our previous research [2], the inclusion of different dopants (Ag, Sr, Ba, K, Zn) into the apatite structure by replacing the calcium ions was evidenced by a complete characterization of synthesized CHAp substituted with these metallic ions. This paper aims to obtain carbonated hydroxyapatite substituted with magnesium (Mg-CHAp) and to evaluate its consolidation capacity on artificial stone samples.

Materials and methods: Mg-CHAp was synthesized by the nanoemulsion method at room temperature and it was characterized by Fourier Transform Infrared Spectroscopy, X-Ray Diffraction and Optical Microscopy. The effectiveness of Mg-CHAp as consolidate for artificial stone was assessed in terms of mechanical strength, water absorption, humidity, and chromatic parameters.

Results: The XRD spectrum for carbonated hydroxyapatite substituted with magnesium, presented in Figure 1, highlighted the specific apatite structure and Mg presence. The efficiency of the consolidation treatment was influenced by the application method of the consolidating agent, the solution concentration, and the amounts of the absorbed consolidate on the stone surface.

Conclusions: Mg-CHAp was successfully synthesized by the nanoemulsion technique. The treatment with Mg-CHAp of the model samples does not influence the chromatic parameters of the artificial stones. The highest values of compressive strength were obtained on the stone samples treated by brushing with a 0.25 g/L concentration of the consolidate.

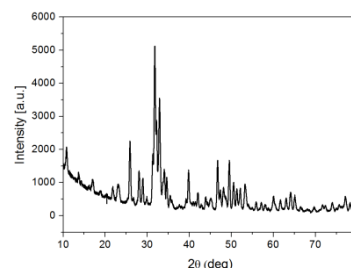


Figure 2 XRD diffractogram for Mg-CHAp

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WORKSHOPS



MATHEMATICAL METHODS APPLIED IN CHEMISTRY.

1. EXPERIMENT PLANNING

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Keywords: *mathematical methods; optimal conditions; factorial plan; statistical analysis.*

Introduction: In the research stage in which it was found that a new technological process is feasible, a systematic and efficient investigation is necessary with the help of quantitative relationships between the established parameters of the process, relationships that ultimately lead to determining the optimal operating conditions. Studying the successive variation of a single variable is disadvantageous because the method is time consuming and may not lead to the overall optimum due to the interactions between the variables. These disadvantages are removed by using experience planning.

Materials and methods: The experimental plan used is carried out in the following stages:

- Setting the objective pursued, the answer of the experimental plan;
- Selection of variables that can influence the studied process (independent variables);
- Fixing the variation interval of each variable, technology permit;
- Choosing points (levels) in these intervals: a lower level (coded -1) and a higher level (coded +1), symmetrical to a central level (coded 0) located close to the optimal value assumed from previous experiences. The set of these points forms the experimental plan;
- Carrying out experiments and measuring the response (determining the value of the dependent variable);
- Calculation of the value of the experimental error: from existing data prior to the plan, or by repeating the experiments for the central level;
- Determining the relationship between independent variables and the dependent variable;
- Statistical analysis of the obtained data and technological interpretation of the results of the statistical analysis.

Results: The case study presented refers to the research of 3 process characteristics (dependent variables Y_1 , Y_2 and Y_3) depending on two process parameters (independent variables x_1 and x_2). The mathematical model corresponding to the factorial plane is: $y = b_0 + b_1 x_1 + b_2 x_2 + b_{12} x_1 x_2$ for which the regression coefficients were calculated:

$$b_0 = (y_1 + y_2 + y_3 + y_4) / 4$$

$$b_1 = (-y_1 + y_2 - y_3 + y_4) / 4$$

$$b_2 = (-y_1 - y_2 + y_3 + y_4) / 4$$

$$b_{12} = (y_1 - y_2 - y_3 + y_4) / 4$$

Conclusions:

- Experiment planning is an advantageous research method, which allows the simultaneous variation of several variables by performing the strictly necessary experiences;
- The factorial plan is the simplest experimental plan, which contains the lowest number of experiences;
- Through the regression analysis of the results of the experiences, a mathematical model of the studied process is obtained, used to determine the optimal operating conditions of that process.

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ENHANCING THE VALUE PYRAMID OF SIDE STREAMS CASCADE PROCESSING THROUGH BIONANOTECHNOLOGIES

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Keywords: side streams, cascade processing, nanostructuration, agricultural inputs, circular approach.

Bioeconomy is still dominated by linear value chains. Sustainable closure of the loop of the value chains involves a value pyramid approach (e.g. recovery of bioactives components from byproducts) combined with a cascading / systemic approach, for re-valorization of co-products from one production cycle, as resources for another production process. Bionanotechnologies bring additional value to such approach, due to conversion of the recovered biologically active components into highly effective products with market demand, such as dietary supplement, cosmeceuticals, plant biostimulants.

One example of bionanotechnological approach is related to the production of agricultural inputs by using carbohydrates recovered from side streams and further nanoformulated. Poly- and oligo-saccharides are active ingredients of different types of agricultural inputs: plant protection products, plant biostimulants, bioactive films for fruit preharvest treatments. The recovery of such bioactive carbohydrates during the initial stage of a biorefinery process should contribute to the development of closed-loop biorefinery, because it produces inputs for the cultivated plants technologies. Also, such approach should improve the recovery of other bioactive compounds (e.g. polyphenols / hydroxycinnamic acids trapped inside the lignocellulose matrix and should better expose for further cascade processing other biomass components. The present understanding of the mode of action of agricultural inputs based on poly and oligo-saccharides supports the selection of the biorefinery feedstock suitable for the proposed active carbohydrate recovery and the development of targeted recovery process. Increased inquiry for sustainable agricultural inputs and additional markets ready accessible for the recovered active carbohydrates (i.e. food additives) should encourage such biorefinery approach. Nanoformulation by using nano carbohydrates (e.g. nanochitosan or nanocellulose) further enhance bioactivity of the agricultural inputs based on recovered carbohydrates.

Another example of side stream processing through a bionanotechnological approach is processing of the spent mushroom substrate. Its processing generate not only plant biostimulants used as agricultural inputs, but also active ingredients for wellness applications - dietary supplement and cosmeceuticals – Figure 1.

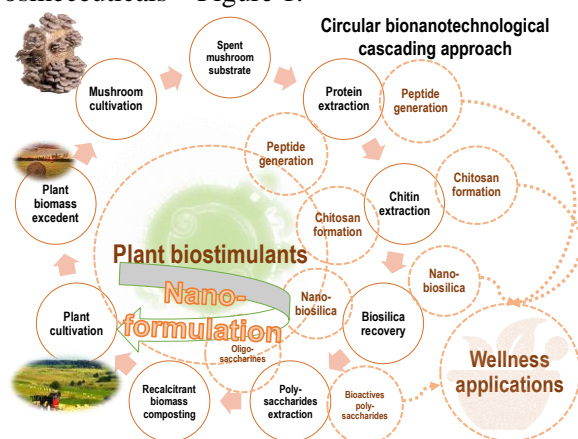


Fig. 1. Bionanotechnological approach for valorization of the spent mushroom substrate. Peptides, chitosan and biosilica are nanoformulated and used as active ingredients for wellness applications, dietary supplements and cosmeceuticals. Nano-biosilica, polysaccharides (including nanocellulose) and nanochitosan are used to produced nano-formulated agricultural inputs. Excess biomass of cultivated plants is used for cultivation of the lignocellulose mushrooms, generating spent mushroom substrate

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COMMON RESEARCH PLAN FOR COMPLEX PROJECT 32PCCDI/2018 (ALGALBIOGASCONCEPT ENERGY)

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Keywords: Biogas; Microalgae.

ROUND TABLE - COMPLEX PROJECT 32PCCDI/2018:

The purpose of this round table is to discuss, within the consortium of Complex Project 32PCCDI/2018, the common program for Research-Development-Innovation correlated with each project Partner's institutional development plan.

Complex project **32PCCDI/2018, Energetic efficiency biogas plants improvement by integrated system: biogas-microalgae-biofuels in frame of biorefinery concept - AlgalBiogasConcept 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. As 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 6 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 (placed at INCDCSZ, Brasov), biogas-microalgae, for demonstration of optimized co-digestion technology functionality and for ensuring the instruction of research personnel from the consortium partner institutions;
5. Setting-up an experimental stand for combustors with gaseous fuels for characterization of the obtained liquefiable gaseous hydrocarbons (Technical University Iasi); 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;

Acknowledgements: 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.

COMMON RDI PROGRAMME FOR COMPLEX PROJECT 6PCCDI/2018 (BIOHORTINOV)

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Keywords: capitalization of vegetal resources; BIOHORTINOV; common RDI programme.

Within the International Symposium PRIOCHEM XVI, the partner National Institute for Research & Development in Chemistry and Petrochemistry - ICECHIM Bucharest organizes the second workshop “Common RDI Programme for Complex Project 6PCCDI/2018 (BIOHORTINOV)” for 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, member of the Consortium, will address technical progress of the complex project in its third 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”, the degree of the fulfillment of the assumed objectives and indicators, as well as technical aspects regarding the finalization of the Common RDI Programme, as required by the contracting authority.

At this workshop will be expected to participate representatives of the Consortium Partners: 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, Research Station for Fruit Growing (SCDP), Constanta.

Acknowledgements: Workshop carried out within the project BIOHORTINOV, financed by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, Complex project PN-III-P1-1.2-PCCDI2017-0332; Contract: 6PCCDI/2018, within PNCDI III.

BIOREGIO – SUPPORTING CIRCULARITY IN THE BIO-BASED ECONOMY

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Keywords: circular bio-based economy; biowaste; sewerage sludge; compost; biogas.

Introduction: Resource efficiency, waste minimization and valorisation, renewable energy, environmental protection are some of the essential elements required for a sustainable development and a safe and clean environment for future generations. A lot of research projects are dedicated to higher valorisation of bio-based materials and side-streams from the agri-food industries. In addition to research, dedicated, efficient policy instruments are required to support the development of circular bio-based economy in the European Union. BIOREGIO project is an inter-regional cooperation project that aims to improve policy instruments in participating regions by sharing experiences and best practices and working closely with stakeholders to boost circular bio-based economy and contribute to the European Green Deal.

Materials and methods: BIOREGIO - Regional circular economy models and best available technologies for biological streams (2017-2021) is an Interreg Europe project coordinated by LAB University of Applied Sciences from Finland. 8 partners from 6 EU countries (Finland, Spain, Greece, Slovakia, Romania and France) are working together towards improving policy instruments to support circular bio-based economy in their regions.

Each region has one policy instrument in focus, and the methods for improvement are exchange of good practices, cooperation models and best available technologies related to circular economy of biological streams (e.g. food waste/biowaste, municipal and industrial sludge and agricultural residues). The activities of the project included roundtable discussions, seminars and site visits, preparation of policy briefs, expert papers and organisation regional dissemination events.

Results: During the first phase of the project (2017-2019), six action plans were developed to improve policy instruments in the participating regions. The action plans are under implementation and progress is continuously monitored. In Romania, the aim of the project is to improve policy instruments to support technology transfer for circular bioeconomy, and the focus was on the Regional Operational Programme, Axis 1. The axis had an initial allocation of 200 mil. Euros, but the call preparation, selection process and contracting were delayed and only around 5 mil. Euros have been contracted so far. The lessons learned from this process were used to design the funding instruments for the next programming period (2021-2027) in order to be more specific and efficient. As a result, the next programme will include dedicated instruments to support the development of circular bio-based economy.

Conclusions: Inter-regional cooperation can be a powerful tool, helping regions to be better prepared to implement new technologies and cooperation models in order to move towards bio-based circular economy. Such projects also contribute to awareness raising and improved communication between stakeholders, empowering them to prepare targeted and efficient instruments, adapted to the needs of the beneficiaries.

Acknowledgements: This project has received funding from the European Regional Development fund under subsidy contract PGI01963/28.11.2016 and from the Romanian Ministry of Regional Development and Public Administration under co-financing contract 93655/14.08.2018.

References: for further information, please visit the BIOREGIO project site <https://www.interregeurope.eu/bioregio/>.

Disclaimer: This abstract reflects the BIOREGIO project's view; the Interreg Europe programme authorities are not liable for any use that may be made of the information contained therein.

APPLICATIONS OF NANOMATERIALS IN ENVIRONMENTAL MONITORING AND PROTECTION

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Environmental pollution is one of the greatest problems facing the world today and is growing every year, causing serious and irreparable damage to the planet [1], and in this respect, the textile industry ranks second after agriculture in terms of clean water pollution.

To remove the organic / inorganic pollutants from wastewater the published studies recommend *biological methods* (aerobic and anaerobic processes that include adsorption by microbial biomass, algae degradation, enzyme degradation, fungal cultures, microbial cultures), *chemical methods* (advanced oxidation, electrochemical destruction, Fenton reaction removal, ozonation, photochemical and UV light irradiation) and *physical methods* (adsorption, coagulation or flocculation, ion exchangers, irradiation, membrane filtration, nanofiltration or ultrafiltration and reverse osmosis [2]. Recent research in the field of environmental protection focuses on the use of the special characteristics of nanoparticles, given that nanotechnology can provide new concepts and materials for this purpose.

The project aimed to approach experimental studies for the removal of organic / inorganic pollutants, existing in wastewater resulting from various chemical processes (e.g. dyeing textile substrates) using nanoscale materials. So far, studies carried out in project aimed the preparing and characterizing new types of nanostructured absorbers and catalysts based on metal oxide nanoparticles / nanostructured ferrites, new types of composite membranes based on polysulfone, with or without metal nanoparticles for use potential in "green" technologies for removing organic / inorganic pollutants from wastewater.

The workshop aims to analyze the stage of fulfillment of the proposed objectives and result indicators, as well as the direction of future research in order to achieve the initially proposed goal.

Acknowledgements: Workshop carried out within the project PN 19.23.03.01 (NanoEnv), Government of Romania, Ministry of Research and Innovation, MCI Core Programme.

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**COMMON RDI PROGRAMME FOR COMPLEX PROJECT 50PCCDI/2018
(RO-CHER)****Radu Claudiu FIERASCU***

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Keywords: cultural heritage; RO-CHER; common RDI programme.

Within the International Symposium PRIOCHEM XVI, the partner National Institute for Research & Development in Chemistry and Petrochemistry - ICECHIM Bucharest organizes the workshop entitled “Common RDI Programme for Complex Project 50PCCDI/2018 (RO-CHER)” 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, member of the Consortium, will address the technical progress of the complex project in its third 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”, the degree of the fulfillment of the assumed objectives and indicators, as well as technical aspects regarding the finalization of the Common RDI Programme, as required by the contracting authority.

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

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