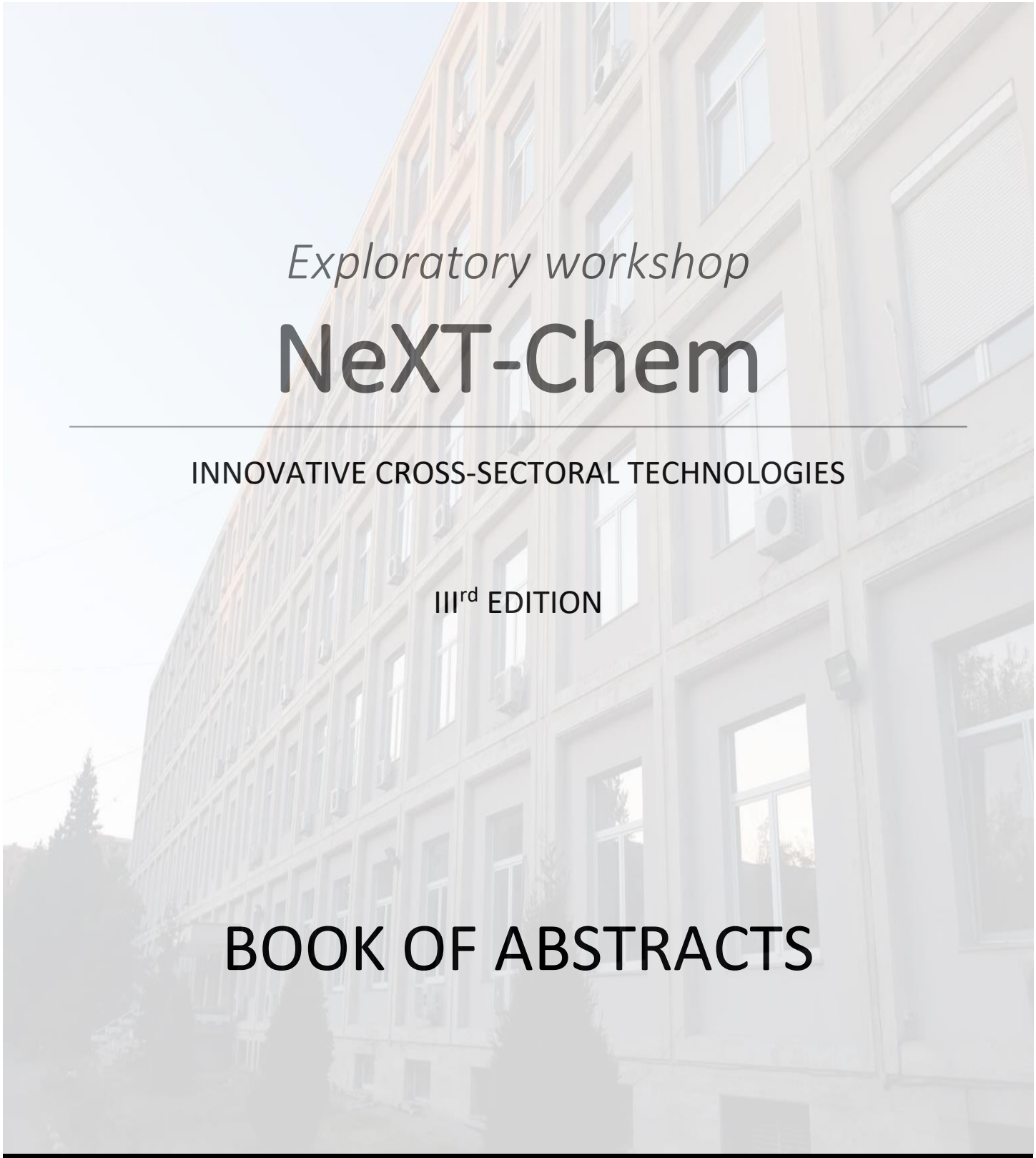

Exploratory workshop

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INNOVATIVE CROSS-SECTORAL TECHNOLOGIES

IIIrd EDITION

BOOK OF ABSTRACTS

Bucharest

MAY 27-28, 2021

INVITED (PLENARY) LECTURES

Thursday, May 27th, 2021

1. Prof. Arben Merkoçi, Institut Català de Nanociencia i Nanotecnologia, Barcelona, Spain ***Nanomaterials-based sensors for diagnostics applications***

2. Prof. Silvana Andreescu, Clarkson University, Potsdam, USA
Advancing environmental sustainability through custom-designed materials and sensors

Friday, May 28th, 2021

3. Prof. Luc Picton, Université de Rouen, France
Smart water soluble polysaccharides for adaptative properties

4. Steve Czapko, Metler-Toledo, Columbus, USA
Safety by design: reaction calorimetry in chemical development

CONTROLLED RELEASE SYSTEMS BASED ON BACTERIAL CELLULOSE AND POLY (ETHYLENE GLYCOL) DIACRYLATE FOR BIOMEDICAL APPLICATIONS

Iulia Elena NEBLEA[1], Ana-Mihaela GAVRILA[1], Tanta-Verona IORDACHE[1], Anita-Laura RADU[1], Andreea MIRON[1], Ana-Lorena CIURLICA[1], Marinela DUMITRU[1], Andrei SARBU[1*]

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Keywords: hydrogels; tissue engineering; cephalexin; PEGDA; bacterial cellulose

Introduction: With current trends leading towards different devices for tissue engineering, hydrogels have been an interesting topic in recent years mainly due to their tunable properties and hydrophilic nature. These interesting properties make their use possible in different fields such as biomedical, pharmaceutical, and technological fields with applications as controlled release systems [1, 2], encapsulation of cells [3], tissue repair [4], electrochemical capacitors and sensors [5]. Among these applications, hydrogel-based drug delivery systems target some important characteristics such as biodegradability, high-swelling capacity and tissue-like mechanical properties. Consequently, the goal of the current study is to synthesize and investigate a series of hydrogels based on different mixtures of poly (ethylene glycol) diacrylate ($PEGDA_{700}$) and bacterial cellulose (BC) in order to determine their antimicrobial activity and suitability for wound healing devices leading to an utterly innovative solution in the field of biomedicine. The samples were synthesized by a cross-linking radical polymerization reaction using potassium persulfate (KPS) and sodium metabisulfite (MS) as redox initiation system. In order to determine the influence of BC concentration upon the degree of swelling and the ability to release the active substance, cephalexin, the new hydrogels were characterized physico-chemically by infrared spectroscopy (FTIR) for determining the composition, by thermo-gravimetric analysis (TGA/DTG) for studying the thermal stability and by scanning electron microscopy (SEM) for highlighting the morphology.

Materials and methods: The hybrid hydrogels were synthesized by radical polymerization reaction using $PEGDA_{700}$, BC (synthesized by our collaborators from University "Politehnica" of Bucharest) and the redox initiating system MS and KPS. Cephalexin was used as active principle in the loading/release process and phosphate buffer solution (PBS) with pH=7.4 as absorption medium.

Results: $PEGDA_{700}$ based hydrogels with variable BC concentration (0%, 20%, 40%, 60%, 80%, 100% wt. rel. to PEGDA) were characterized using FTIR spectroscopy, showing characteristic bands of both the polymer and BC without noticeable differences. TGA/DTG analysis highlighted the influence of biopolymer concentrations, by exhibiting higher thermostability at higher concentrations of BC, and an improvement of the maximum decomposition temperature for diacrylate and poly (ethylene glycol) molecules. Also, the swelling studies indicated that higher concentrations of BC lead to a tight network and, therefore, a higher degree of swelling. SEM images at different resolutions show a disordered network of cellulose fibers with a length exceeding 4 μm and a width greater than 30 nm, in some cases. The size of the bacterial cellulose fibrils is an important factor that may later on determine its performance as a dermal wound healing system. Controlled release studies of cephalexin were investigated by UV-VIS spectrophotometry, which revealed a slow and constant release for samples with higher BC concentrations; the maximum concentration being reached after 24 h.

Conclusions: This study describes the successful synthesis of hybrid hydrogels by radical polymerization based on bacterial cellulose and poly (ethylene glycol) diacrylate. The release profile of the active principle confirms the results obtained in the morphological and thermogravimetric analyzes. This fact encourages the hypothesis of using hybrid hydrogels as controlled release systems of drugs with specific properties for treating dermal wounds. Thus, the proposed concept is intended for developing a biocompatible controlled release micro-vesicular environment, through micro-colloidal hydrogel architectures based on bacterial cellulose, for wound therapy.

Acknowledgements*: The study was funded by the Ministry of Education and Research through the Executive Unit for Financing Higher Education, Research, Development and Innovation (UEFISCDI) [PCCDI project no. 39/2018-INTELMAT]. The authors would like to thank Dr. Eng. Ionut-Cristian Radu from University Politehnica Bucharest for supplying BC.*

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MECHANICAL PROPERTIES OF POLYAMIDE WITH HYBRID 2D REINFORCING AGENTS

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Keywords: bio-based polyamide, graphene, mechanical properties

Introduction: Polyamide (PA) is a thermoplastic polymer with proven advantages involving weight/properties ratio. Due to its exclusive electrical, optical, mechanical, thermal and chemical performances, graphene is a promising nanocarbon filler for several applications.[1] Bio-based polyamide is obtained from natural sources, the main source being castor oil.[2] As seen in literature, polyamides properties can be improved by using different fillers (such as glass fiber). The purpose of this study was the investigation of the mechanical properties of a new class of 2D hybrid nanofillers, obtained through melt processing.

Materials and methods: A full bio-based polyamide 1010 (PA1010) was used as the polymer matrix with a hybrid 2D nanofiller (molybdenum hydrotalcite (HTMo) and different concentrations of graphene oxide (GO) or commercial graphene nanoplatelets (M5)). These composites were obtained in dynamic conditions through melt processing and the resulted samples were analyzed from a mechanical point of view.

Results: The modulus increase depends on the percentage of GO. An increase of the modulus (over 45%) of the sample with the highest percentage of GO demonstrates the reinforcing effect of the 2D hybrid agents.

The same trend was observed in the case of tensile strength. An important decrease in axial strain at break for all sample with 2D hybrid agents was observed. The results obtained by DMA analysis correlate very well with the results obtained after the tensile test.

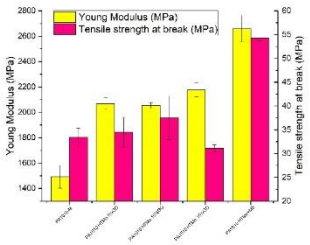

Figure 1. Mechanical properties of PA1010 composites filled with HTMo and GO (0-15%)

Conclusions: These new classes of hybrid 2D reinforcing agents, represent a promising way for the reinforcement of bio-based PA1010. These 2D hybrid agents proved their efficiency as reinforcing agents through the increasing of PA1010 strength and stiffness.

***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-2017-0387/80PCCDI Emerging Technologies for the industrial application of 2D structures (graphene and non-graphene) Acronym EMERG2IND, within PNCDIIII.*

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ON THE BIOBASED POLYAMIDE WITH FLAME RETARDANT PROPERTIES

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Keywords: bio-based polyamide, thermal analysis, flammability

Introduction: Polyamide was proven among polymer thermoplastic materials to be as one of the most important engineering thermoplastics where mechanical, thermal and chemical properties such as high strength, high stiffness and good temperature resistance are required in specific applications [1]. Bio-based polyamides are obtained from renewable sources and are promising alternatives for fossil-based ones [2]. Graphene types of fillers as well as double layered hydroxide (LDH) were proven as interesting choices for improving polymer properties [3]. The purpose of this study was to improve fire behaviour of polyamide materials with a new class of halogen-free flame retardants (based on hybrid structure containing both graphene and LDH structures). Some flame retardant agents may induce strong decrease of the thermal stability of the polymer material. Therefore, in this study we verified in a complete picture both thermal and flame retardant properties of the composites with 2D hybrid fillers.

Materials and methods: A bio-based polyamide 1010 (PA1010), hydrotalcite with molybdate anions (HTMo), graphene oxide (GO) and graphene nanoplatelets (M5) were used to obtain composites with different graphene oxide concentrations (5%, 10% ,15% wt). The obtained samples were processed under dynamic conditions by melt processing fallowed by injection moulding. Thermal analysis was done with TGAQ5000 and DSC Q2000. The flammability of PA1010 composites was performed by means of the limiting oxygen index (LOI) and vertical burning tests according to the ASTM D3801.

Results: Flame retardant properties have been enhanced by the inclusion of the nanofillers. In the case of TGA analysis we observed that the nanofillers showed a modification of the degradation mechanism. The glass transition temperature, determined by DSC, was around 40°C for the neat polymer and increased in the presence of the nanofillers. The addition of HTMo-GO in the polymer matrix showed important increases of the LOI value. The best improvement was found for the sample with HTMO-15%GO with LOI value close to 30%. The results were in good corelation with the results from vertical burning tests and TGA.

Conclusions: Thermal properties and flame retardant properties of polyamide have been enhanced by the inclusion of nanofillers based on HTMo and graphene/graphene oxide. The LDH structure has contributed the most to the flame retardant properties of the hybrid structure. The best improvement in the case of LOI was found for the sample with HTMo-15%GO. All sample with a reduced content of GO was classified at the highest level of vertical burning test (V-0) compared to the neat PA1010 with V-2 level.

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-2017-0387/80PCCDI Emerging technologies for the industrial application of 2D structures (graphene and non-graphene) Acronym EMERG2Ind, within PNCDIIII.*

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THE PROPERTIES OF RECOVERED POLYPROPYLENE FROM FACE MASK WASTES

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Keywords: polypropylene, face mask, mask cords, recovery

Introduction: In the last decades, the world governments have shown more interest into the capability of recycling polymeric composite materials due to the dangerous increase of waste and the pollution it causes to both nature and human health [1][2]. Face masks represent such a waste material, especially in recent years with the start of the pandemic [3][4]. The objective of this study is to analyze and correlate results between mechanical, thermal and nanomechanical properties of polypropylene recovered from face masks in order to valorize the studied materials and to find an application in an industry.

Materials and methods: Face mask waste (PP) and mask cords (E) were used. Two samples (PP and PP+E) were prepared in dynamical conditions by melt processing method, one made out of neat face mask waste and the second made of face masks and mask cords. The mechanical properties (modulus of elasticity, tensile stress at yield, axial stress at yield and Charpy impact strength) were tested with Instron and Charpy devices, thermal properties were performed with DMAQ800 and TGAQ5000 and the nanoindentation and nanoscratch tests have been performed at room temperature on a TI Premier system (Hysitron Inc., USA) using a three-side pyramidal Berkovich tip.

Results: From mechanical point of view the polypropylene from the waste masks has shown similar values to industrial used polypropylene. With the introduction of mask cords, an increase of elasticity was observed, which can be noticed in mechanical tests. DMA results show a decrease of stiffness for the PP+E composite compared to neat PP from masks. Thermal analysis showed a slight decrease of thermal stability for the PP+E composite compared to the neat PP from masks. Nanomechanical analysis showed higher values of reduced modulus and hardness for the composite with mask cords compared to the neat polypropylene from worn masks.

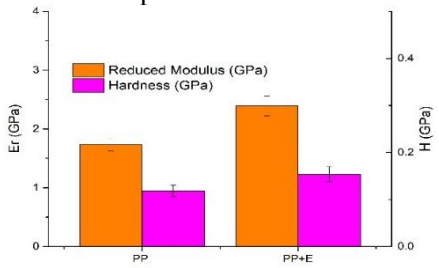

Figure 1. Nanomechanical properties of PP and PP+E

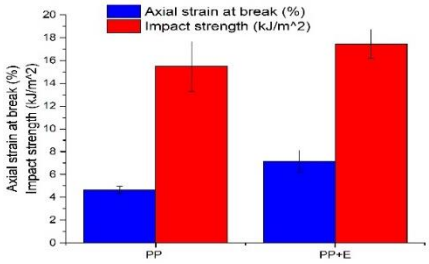

Figure 2. Mechanical properties of PP and PP+E

Conclusions: This study has shown that worn masks can be used in order to obtain a viable polymer matrix for further use in the industry. The addition of mask cords leads to an increase of elasticity when it is mixed through melt processing with the polypropylene from face masks. Further investigations are needed in order to valorize the studied materials and to find an application in an industry.

Acknowledgements: The work on this paper was supported by UEFISCDI Romania through the framework of project POC 2016 SECVENT, P_40_352, MySMIS: 105684.

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SPECTRAL CHARACTERIZATION OF MACRO-HETEROCYCLIC COMPOUND NiTMPyP / ZnTSPc / MC

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Keywords: macro-heterocyclic compound; FTIR; RAMAN

Introduction: Due to their important physical and chemical properties, macro-heterocyclic compounds, such as porphyrins and phthalocyanines, are widely studied [1]. They are used for many applications because they have the ability to absorb light across the spectrum and self-organization [2]. The spectral properties investigations of the supramolecular assembly NiTMPyP / ZnTSPc / MC - 5,10,15,20 nickel tetramethylpyridyl porphyrin / 2,9,16,23 zinc tetrasulfonated-phthalocyanine zinc / methylcellulose are registered by FT-IR and Raman spectroscopic techniques.

Materials and methods: NiTMPyP, ZnTSPc and MC have been used as pure materials, without any supplementary procedures from Aldrich company, while their heteroaggregate has been prepared in the laboratory after a standard procedure. The infrared spectra were measured using an FT-IR spectrometer (VERTEX 80) with ATR, in the following conditions: range 4000 cm^{-1} to 580 cm^{-1}, 32 scan, resolution 4 cm^{-1}. The Raman spectra were recorded with a portable Xantus-2 TM Raman analyzer equipped with two laser sources (i.e., 785 nm and 1064 nm) and two detectors (i.e., TE cooled CCD and TE cooled InGaAs).

Results: FTIR and Raman spectroscopy are complementary techniques, which are commonly used for analysis of different states of samples (solid, liquid, and semi-solid). These methods are rapid, non-destructive and real-time analytical method for analysis, without any excessive sample pre-treatment.

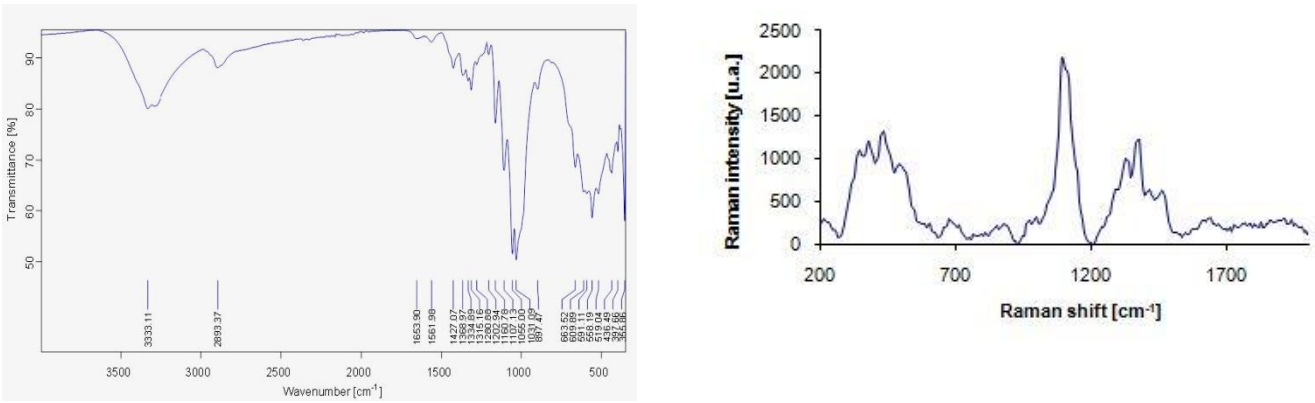

Figure 1. FT-IR and Raman spectra of the NiTMPyP / ZnTSPc / MC compound

Conclusions: To develop new sensitizers based on macro-heterocyclic compounds, in this paper were studied the NiTMPyP / ZnTSPc / MC compound. Spectral properties of the studied materials indicated that these could be perspective for many applications, due to their versatility to change their central metal valence and to attach new substituents. Under this context, NiTMPyP / ZnTSPc / MC is a special compound with proper properties. Their capacity of association has been identified by FT-IR and Raman spectral techniques, which identified their internal bonds, their capacity to add new axial ligand and to create larger and versatile spatial structures.

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ADDITIVE MANUFACTURING OF ZnO-CNT BASED STRUCTURES FOR WASTEWATER TREATMENT

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Keywords: zinc oxide; carbon nanotubes; nanocomposites; 3D printing; wastewater treatment.

Introduction: Developing composite nanostructured materials for the field of water and wastewater treatment is one of the research trends nowadays. Zinc oxide nanoparticles (ZnO NP) had shown great promise in the area of water and wastewater treatment due to its high BET surface area, strong oxidation ability and good photocatalytic capability. The main drawbacks of ZnO NP are related to its limitations to absorb light only in the near UV region and its wide band gap which implies a reduced ability to use solar energy efficiently. Carbon nanotubes (CNT) can be modified easily by functionalization of the material surface and it presents large specific surface area, high chemical stability and the capability to adsorb a great variety of contaminants. CNT poor dispersion ability and problematic separation process prevents the use of this adsorbent material by itself. Reinforcing ZnO with CNT could be an interesting strategy to overcome their limitation. The aim of this study was to obtain 3D porous structures from hydrothermal synthesized ZnO-CNT nanocomposite powder with an additive manufacturing technique for potential application in wastewater treatment [1-3].

Materials and methods: In this study ZnO-CNT powder previously synthesized by in situ hydrothermal method was used. The nanocomposite powder was mixed with different commercial organic additives using a centrifugal mixer in order to obtain a printable paste. Square cuboids with dimensions of 10x10x5 mm were designed with a CAD software, SolidWorks 2019. The designed sample had a line-based pattern with a distance between strands of 1.7 mm. The rotation angle between 2 consecutive layers was of 45° and 135°. ZnO-CNT 3D structures were obtained with a robocasting technique using the 3D-BioPlotter Starter system by dispersing the paste trough a 0.4 mm nozzle. The morphology of ZnO-CNT 3D structures was analyzed using scanning electron microscopy (SEM).

Results: In this study ZnO-CNT based 3D structures were obtained by additive manufacturing technique. In order to obtain the printable paste different polymeric additives were tested and the optimum composition was based on PEI (polyethyleneimine), HPMC (hydroxypropyl methylcellulose) and Tween 80 (polysorbate 80, polyoxyethylene sorbitan monooleate). An example of CNT-ZnO based 3D samples, obtained by 3D printing process, can be seen in figure 1a. In figure 1b the SEM image of the 3D printed structure is presented. Strand thickness is between 390-430 µm and the distance between strands varies between 1.665-1.706 mm, in accordance with the printing parameters which have been set [4].

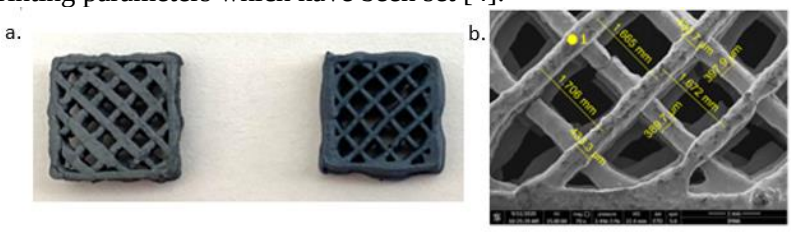

Figure 1. An example of the CNT-ZnO 3D structure (a) and SEM micrographs of CNT-ZnO printed sample (b) [4].

Conclusions: Using hydrothermally synthesized nanocomposite powder and polymeric binders CNT-ZnO 3D structure were fabricated by robocasting technique. Additional work will be conducted in the near future in order to determine the potential of ZnO-CNT based 3D structures in wastewater treatment applications. Different organic additives were tested in order to obtain homogenous and printable paste for the 3D printing process. The combination of organic additives and their quantities influences the paste printability, thus not all compositions can be printed due to their inappropriate properties.

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STUDIES ON PARAMETERS INFLUENCING THE MECHANICAL RECYCLING OF SOME RENEWABLE POLYESTERS

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Keywords: PLA-based materials; melt rheology; degradability; drying

Introduction: With the growth of interest towards the use of biobased materials, the importance of mechanical recycling and the decreasing the incineration activity become more and more obvious. In a circular economy, the mechanical recycling is one of a good solution to reduce the dependence on the fossil resources [1 - 3]. The aim of the present paper was to study the parameters influencing the mechanical recycling of some renewable polymers. In this study the influence of the drying as a pre-recycling treatment on the PLA melt rheological properties was studied.

Materials and Methods: The influence of the shear rate and of the humidity on the melt degradation of PLA was studied. Neat PLA, dryed and undryed, ρ = 1.24 g / cm³, ICT = 7-9 g / 10 min (210º C / 2.16 kg) was used. The melt rheological properties was studied using the flow index method (ISO 1133: 2012 / ASTM 1238: 04). Based on the obtained result the the degradation factor (DF $\approx \frac{\dot{\gamma}_{undryed}}{\dot{\gamma}_{dryed}}$) was calculated.

Results: The shear rate is higher the lower the molecular weight is. Because the shear rates are higher (fig.1) , it results that the molecular mass of the un-dryed polymer is smaller consequence of the degradation during the extensional flow through hydrolysis (fig.2). The degradation generates the decreasing of the molecular weight and increasing of the content of carbonyl and carboxyl end groups. Measurements are underway to identify the content of hydroxyl, carboxyl and end vinyl ester groups.

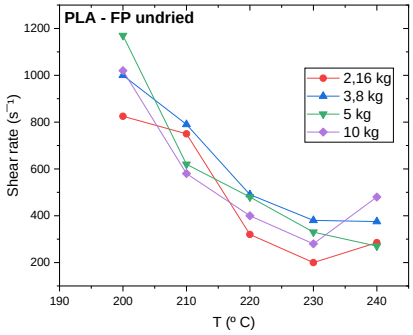

Figure 1. Dependence of the shear rate of the melted PLA on the flowing conditions

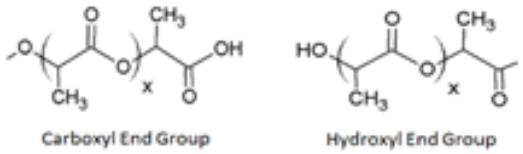

Figure 2. Functional groups formed through PLA hydrolysis during melt preocessing

Conclusions: Experimental results complete the literature data in that, above 200º C the hydrolytic degradation of PLA in the melt decreases in importance. The shear speed and humidity directly and decisively influences the degradation of the renewable polyesters which must be very well controlled in view of their mechanical recycling.

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STUDY OF THE INTERFACE IN NEW PRACTICAL INTEREST COMPOUNDS BASED ON RENEWABLE POLYMERS

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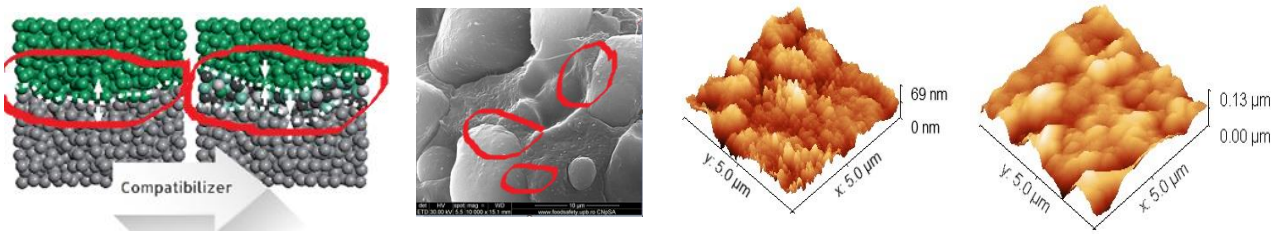
Keywords: renewable; starch; interface; compatibility; melt processing technique

Introduction: Continuous efforts are being made currently in developing sustainable polymeric materials that can replace the polluting petroleum-based ones [1,2]. In most cases, because of poor functional properties, lower than that of the conventional those, in most cases, renewable polymers cannot be used as such without improving through different methods as compounding with other polymers their properties. Due to the hydrophobic nature of poli(ε-caprolactone) (PCL), its blends with starch (S) are immiscible and cannot be converted into different issues without being compatibilized. The aim of the present study was to identify the changes that occur at the PCL-S interfaces due to the presence of the compatibilizer.

Materials and Methods: After melt compounding of starch (amylose/amylopectin: 30/70) with poli(ε-caprolactone) (PCL-Mw=85000–105000, g*mol) and a compatibizer, in order to clarify how the used characterization methods highlights the interfaces changes because of the compatibilizer's presence, the resulted compounds were characterized by various methods (DSC, XRD, SEM, FTIR, AFM, etc.).

Results: The results (figure 1) show that the presence of the compatibilizer generated the modification of the PCL-S interfaces which are responsible for the level of the measured properties by each used method. All the obtained results are in good agreement with the changes at the interfaces of PCL-S compounds.



a) b) c) d)

Figure 1. The highlighting the theoretically changes at the same blends interfaces (a), at the PCL-S blends interfaces (b) and the dependence of the surface appearance on the compatibilizer amount (c, d).

Conclusions: Because of the compatibilizer's presence, the PCL-S compounds were turned on from an immiscible in partially miscible type. The research will continue to increase the degree of compatibility between the two polymers in order to reach compounds for different applications.

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DESIGN OF CARBOXYLATED GRAPHENE OXIDE-CONTAINING CHITOSAN COMPOSITE ELECTROSPUN BIO-SCAFFOLDS

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Keywords: chitosan; carboxyl-modified graphene oxide; composite scaffolds; nanofibrous architecture

Introduction: The present research brings to the fore the design of chitosan/carboxylated graphene oxide (CS/GO-COOH) composite scaffolds with nanofibrous architecture, as biomaterials to be used in biomedical applications. The concept of designed composite fibrous material is based on bringing together the biological properties of CS [1], mechanical, electrical, and biological characteristics of GO-COOH [2] with the versatility and efficiency of ultra-modern electrospinning technique [3]. The outstanding properties of electrospun nanofibrous structures, such as large surface area-to-volume ratio, high degree of porosity and permeability make them be perceived as important biomaterials with extensive applications in tissue engineering, controlled drug delivery and wound dressing.

Materials and methods: Three different concentrations of GO-COOH were added into a CS/PEO solution (the ratio between CS/PEO was 3/7 (w/w)). The resulted mixtures were subjected to electrospinning process in order to obtain CS/GO-COOH composite nanofibrous scaffolds, which were further crosslinked in the glutaraldehyde (GA) vapors. The obtained nanofibrous composite scaffolds were investigated: structurally (FTIR and Raman spectrometry), morphologically (SEM microscopy), wettability by means of water contact angle measurements; in addition, *in vitro* cytocompatibility (MTT assay) and cytotoxicity (LDH assay) of the materials were also studied.

Results: FTIR results revealed the non-covalent and covalent interactions that appear between different functionalities of system components. Raman spectrometry highlighted the exfoliation of GO-COOH layers into the CS/PEO polymeric matrix. The SEM micrographs showed the nanofibrous architecture of scaffolds, and the presence of GO-COOH sheets along the composite CS/GO-COOH nanofibers. Contact angle measurements depicted a strong correlation between the surface wettability degree of the scaffolds and both the GO-COOH content and the crosslinking step.

Conclusions: The obtained CS/GO-COOH composite scaffolds with nanofibrous structure were designed using the electrospinning technique. The effect of GO-COOH concentration on the spinnability, morphological, wettability and biological properties of engineered scaffolds was investigated. The composite CS/GO-COOH 0.1% and CS/GO-COOH 0.2% nanofibrous scaffolds exhibited the highest cytocompatibility and therefore they may be considered suitable for biomedical applications.

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DEVELOMENT OF BIOSENSORS FOR THE HYDROXYCINNAMIC ACIDS ANALYSIS

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Keywords: hydroxycinnamic acids, cyclic voltammetry, ferulic acid, tyrosinase

Introduction: Due to its antioxidant properties, hydroxycinnamic acids are often used in the cosmetics industry. Among these, ferulic acid (FA) is an active ingredient in antiaging products or depigmented creams because it supports intracellular anti-antioxidant defense systems [1] and has the ability to inhibit the main enzyme of melanogenesis [2]

Materials and methods: In this study a new electrochemical method using a voltamperometric enzyme sensor based on nanomaterials has been developed for the detection of FA in various cosmetics. To obtain the biosensor, a screen-printed electrode based on carbon nanofibers and gold nanoparticles modified with tyrosinase it was used.

The immobilization of the enzyme was carried out by the casting technique followed by crosslinking with glutaraldehyde. Carbon nanofibers and gold nanoparticles give the sensor good mechanical properties and high conductivity. They facilitate the immobilization and maintains high activity of the enzyme. Tyrosinase has the role of increasing sensitivity and selectivity for FA detection. Preliminary studies were performed with several solutions such as phosphate buffer solutions, potassium ferrocyanide and in model FA solutions.

Results: The cyclic voltammograms showed electrochemical signals representative of the redox processes on the electrode surface related to presence of active compounds from the solutions. The biosensor showed good sensitivity for a broad range of FA concentrations with low detection limit. Following the qualitative and quantitative analyzes of the cosmetic products, the peaks related to the present FA were observed. According to the features observed in the cyclic voltammograms the concentrations of FA were calculated from the analyzed samples. To validate the voltammetric method, the quantities of FA in cosmetics were analyzed by infrared spectrometric method, and the results obtained were similar with those obtained by electroanalysis.

Conclusions: The method developed in this study has a number of advantages, such as feasibility, simplicity and low cost. Also, the precision and versatility of the method, a suitable face for routine analysis in the quality control of cosmetics, nutraceuticals, pharmaceuticals and other types of samples.

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DETECTION OF AMINO ACIDS L-PHENYLALANINE, L-TYROSINE AND L-TRYPTOPHAN WITH BIOSENSORS BASED ON POLYPYRROLE

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Keywords: biosensor, polypyrrole, L-Phenylalanine, L-Tyrosine, L-Tryptophan

Introduction: New generation material, with important thermal, electrical and morphological properties, polypyrrole has utility in various fields of activity: chemistry, medicine, pharmacy, biology[1,2]. In the present study, polypyrrole was used for the modification and development of screen-printed carbon electrodes, and further to enzyme for the purpose of easy, rapid and accurate detection of three amino acids, namely L-Phenylalanine, L-Tyrosine and L-Tryptophan. The three selected amino acids represent for humans the basis of the functioning of a nervous system within normal limits, existing an interdependent relationship among them[3]. They are responsible for the prevention of neurological diseases and affective disorders some of them increasing as number ad intensity during the pandemic, such as: Parkinson's disease, depression, attention deficit hyperactivity disorder (ADHD), insomnia, phenylketonuria (PKU)[4].

Materials and methods. The method for the developing of polypyrrole modified biosensors was chronoamperometry, and the electrochemical method for the amino acids detection was cyclic voltammetry.

Results: The biosensors developed in the present work demonstrated an increased sensitivity and a good selectivity, and the results were validated on pharmaceutical products from different manufacturers containing different concentrations of the amino acids under study.

Conclusions: Following the experiments, it was concluded that polypyrrole modified biosensors showed electroactivity in all studied environments, which demonstrates that these biosensors are useful for the detection of the amino acids L-Phenylalanine, L-Tyrosine and L-Tryptophan.

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PHOTO OXIDATIVE DEGRADATION OF ORGANIC SUBSTRATES OVER NOBLE METAL-MODIFIED TiO_2

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Keywords: photocatalytic oxidation, TiO_2 modified with noble metals, phenol oxidation

Introduction: Photocatalytic oxidation of organic matter conducted by sunlight is of great importance in several respects: (i) it involves low costs, (ii) it is able to clean water and air [1-3], and (iii) is an alternative route relative to selective synthesis of high value-added oxygenated products [4-5].

Materials and methods: Materials used: phenol aqueous solutions, TiO_2, Pt/TiO_2, Ag/TiO_2 and Au/TiO_2 powders (obtained by laser pyrolysis). The reaction products of liquid phase oxidation processes were analyzed by liquid and gas phase chromatography (GC, HPLC).

Results: Both support and noble metals play an important role in light absorption, charge separation and the formation of $\cdot OH$ and O_2^- (ROS) which are analyzed for light-induced oxidation of phenol (Ph) on the noble metal (Ag, Au, Pt) loaded with TiO_2. The results show that noble metals help separate photos and reduce O_2 to O_2^- and act as a visible light absorber. The role of O_2^- is to slightly oxidize the phenol to oxygenated products (hydroquinone, benzoquinone and 1,2-dihydroxybenzene).

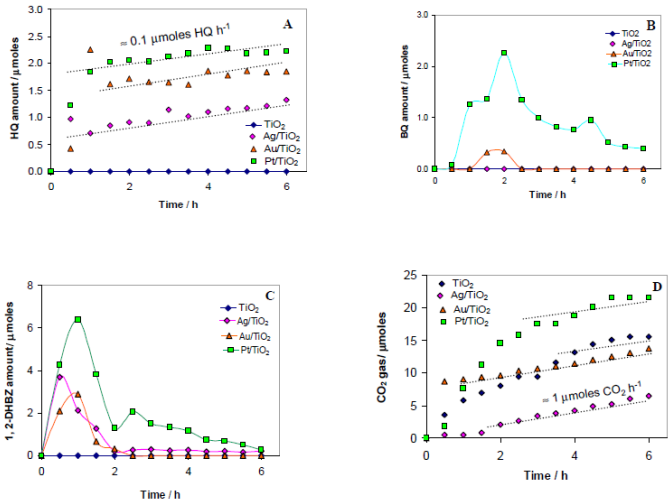

Figure 1. Solar light-driven phenol oxidative conversion

Conclusions: This study reveal the light-initiated photooxidative pathways for an organic substrate with-aromatic ring (Ph) over TiO_2 charged with noble metal. The analysis of the complex phenomena associated with the photocatalytic reactions focuses on the formation of ROS ($\cdot OH$ and O_2^-), the separation of the light generated charges, as well as on the oxidative conversion reaction mechanism of Ph.

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3D PRINTABLE INK BASED ON ALGINATE AND LAYERED SILICATES

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Keywords: alginate, layered silicates, nanocomposites, ink, 3D printing

Introduction: The main purpose of this research was to obtain 3D printable nanocomposite-based inks. In this respect, alginate and different types of commercial clays were used.

Alginate is one of the most widespread polysaccharides in nature. It is derived from brown algae and forms a viscous paste when hydrated. The inorganic fillers used in the present study were commercial clays namely, montmorillonite (MMT) and organo modified montmorillonites (OMMT) with the following general formula $[(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O]$.

The obtained nanocomposite-based scaffolds were characterized structurally (FTIR, XRD), morphologically (SEM, Micro CT), and mechanically (Rheology, Nanoindentation).

Materials and methods: Alginic acid sodium salt (Sigma-Aldrich, Norway), layered silicates with commercial name Cloisite (Southern Clay Products Inc. Gonzales, TX, USA). Ultrapure water and Phosphate buffered saline (PBS) solution pH=7.4, were prepared in our laboratory.
The mineral clay powder was dispersed in ultrapure water and maintained a period of time under magnetic stirring. A homogenous viscous paste was obtained after alginate was added. The system was kept overnight for system stabilization. 3D constructs were printed using alginate-clay based ink and the scaffolds were crosslinked using a $CaCl_2$ solution.

Results:
Printable nanocomposite inks and further 3D printed scaffolds based on alginate and several types of commercial clays were successfully obtained. The 3D printed scaffolds maintained their shape fidelity and presented modified properties as function of the nanocomposite ink used in the synthesis process.

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PHYCOCYANIN – A POSSIBLE SOLUTION FOR NATURAL BLUE PIGMENTS

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Keywords: spirulina, phycocyanin, ultrasonication, antioxidant activity

Introduction: Spirulina (*Spirulina platensis*) is a blue-green microalga (filamentous cyanobacteria) originated from the lagoons in Latin America and Africa [1]. Spirulina is an important source of valuable compounds: proteins (55-70%), carbohydrates (15-20%), lipids (7%), vitamins, minerals, γ-linolenic acid, chlorophyll, carotenoids, and phycocyanin [2], which is why it is currently used in the functional food and nutraceutical market [1]. It has a high antioxidant activity, due to the presence of the blue pigment, phycocyanin [3]. Spirulina blue can be a substitute to Brilliant Blue FCF and an environmentally friendly coloring solution [4]. The aim of this study was to establish the best extraction conditions of phycocyanin from spirulina, in order to utilize it as a natural blue pigment.

Materials and methods: Powdered spirulina was subjected to conventional and unconventional extraction methods. The phycocyanin extractions were carried out using a 0.1M sodium phosphate buffer solution (pH = 7.4), a 1/15.6 (w/V) ratio of vegetal material to solvent and 600 rpm, ensured by a heating plate equipped with a temperature control unit and magnetic stirring. The conventional extractions (CE) were performed in an air bath at different temperatures (RT, 30, and 40 °C) and at different extraction times (up until 330 min, using 30 min increments). The ultrasound assisted extractions (UAE) were performed in a controlled-temperature jacketed reactor, using the UP200H Ultrasonic Processor at a 30% amplitude and different cycles (0.5 and 1), for different extraction times (5, 10, 15, 20, 25, and 30 min). After the extractions, the mixture was centrifuged at 4000 rpm for 15 min at RT and the supernatant was further analyzed. The extracts were analyzed in order to determine the phycocyanin concentration using a spectrophotometric method developed by Munawaroh et al. [3]. The antioxidant activity of the extracted phycocyanin was also determined using the CUPRAC method [5].

Results: Phycocyanin is a thermolabile compound, being stable at increased temperatures (maximum 70 °C) for reduced periods of time. Thus, the influence of temperature and time on the extraction efficiency was studied. The CE provided a high phycocyanin content at long extraction times, obtained more rapidly at higher temperatures (comparative results were obtained at RT for 270 min and 40 °C for 120 min). Compared with CE, a higher extraction yield in a shorter time was achieved using UAE. Better results were obtained when a cycle of 1 was established. However, at long extraction times, the degradation of phycocyanin occurs. A high antioxidant activity was determined.

Conclusions: Spirulina is an important functional food with a possible future in the dyeing industry. The aim of this study was to establish the best extraction conditions for phycocyanin – natural blue pigment – from powdered spirulina. The extraction was highly efficient using UAE, where important quantities were extracted in shorter periods of time than compared with the CE.

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CASCADE BIOTRANSFORMATION OF MONOTERPENES USING CO-IMMOBILIZED ENZYMES

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Keywords: monoterpenes, biotransformation, biocomposite

Introduction: Monoterpenes are a class of compounds with wide occurrence in nature, acting as natural defense against herbivores, and to attract pollinators. Terpenoids are the corresponding oxygenated derivates and are used as flavor and fragrance products [1]. Therefore, an increased interest for developing methods for monoterpenes valorization, and previous studies showed the bioconversion of limonene to limonene-1,2-diol is achievable using whole cell biocatalysis [2]. However, this method has some drawbacks, such as: difficulty of controlling the process, low tolerance of substrate concentration, and high chances of side reactions [3]. Therefore, we propose a bienzymatic cascade pathway that overcomes the mentioned disadvantages.

Materials and methods: A sample contains the following components: 1.6 mols/ L substrate, 1.6 mols/L octanoic acid, 0.1 mols/L phosphate-buffer saline with pH of around 8, 11 mg biocomposite, 0.3 milimols trisodium citrate. Gas chromatography was used for analysis.

Results: We tested the bienzymatic cascade system using lipase – hydrolase enzymes couple for different substrates transformation, eg (R)-(+)-limonene and α-phellandrene. The tests were performed with

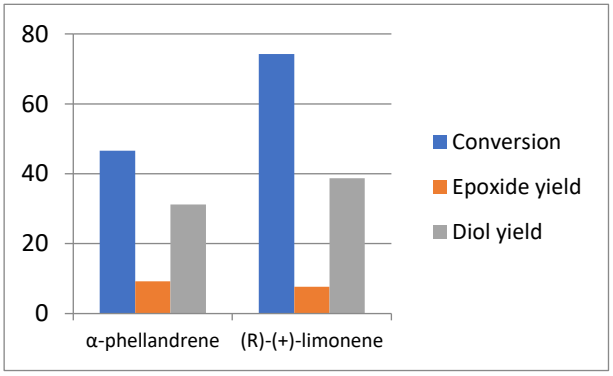

Figure 1. Biocomposite efficiency

Novozym®435 (Candida antarctica B lipase immobilized on acrylic support), Novozym®435 in the presence of free hydrolase, and hydrolise@Novozyme®435 biocomposite. Novozym®435 in the presence of free hydrolase (CH55-LEH) allowed to achieve a conversion of 45% (R)-(+)-limonene and a diol yield of 27%. On the other hand, the biocomposite transformed 74% of (R)-(+)-limonene with 39% yield in limonene-1,2-diol. Additionally, the biocomposite offered 47% of α-phellandrene conversion with 31% yield in p-menth-5-ene-1,2-diol. In all the cases, the enantiomeric excess was above 90% for (1S, 2S, 4R)-(+)-limonene-1,2-diol and (1S, 2S, 4R)-p-menth-5-ene-1,2-diol.

Conclusions: The developed bienzymatic system exhibited an efficient enantio-biotransformation of (R)-(+)-limonene/ α-phellandrene into diol derivatives which find many applications in the industrial field.

Acknowledgements: *This work was financially supported by PNCDI III PED project (contract no. 376PED/2020) from UEFISCDI, Romania.*

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TREATMENT OF LIQUID DIGESTATE FROM ANAEROBIC DIGESTION BY ELECTROCOAGULATION-FLOCCULATION IN BATCH MODE

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Keywords: liquid digestate; electrocoagulation-flocculation; wastewater; anaerobic digestion.

Introduction: Anaerobic digestion is a multi-stage biological process used in organic waste management practice, which simultaneously limits the wastes and produces biogas, a clean and important biofuel for energy generation. One of the side streams from biogas production, liquid digestate, requires treatment, as it is high in nutrients and total organic carbon (TOC), meaning it cannot be released directly into the environment [1,2]. The aim of this study is to evaluate the performance of the electrocoagulation-flocculation (ECF) process for treating liquid digestate by reducing the content of phosphorus and nitrogen from liquid digestate, to values low enough for its use in crops irrigation systems or discharge directly in the environment, without further contamination with toxic flocculants. For this purpose, ECF in a batch system was studied as a treatment for turbidity reduction and total nitrogen content (TNC), total phosphorus content (TPC) and TOC decrease by using as process factors electrode distance and applied voltage onto the electrodes, as well as the ECF time.

Materials and methods: The batch ECF unit used in our experiments was a glass reactor with a total volume of 1 L and two aluminum electrodes, connected to a direct power supply (MATRIX MPS-6003S laboratory power supply, 0-3 A, 0-60 V)). Both electrodes (anode and cathode) were made of high purity electrolytic aluminum (99.99 %), each having an active area (the surface of the electrode immersed in the liquid subjected to ECF) of 38 cm2 ¬ and a total area of 72 cm^2. The material subjected to ECF experiments was a liquid fraction resulted from a 5 m^3 batch horizontal fiberglass pilot-scale system of AD of mixtures of biomass (potato and sugar beet waste, corn silage) and farm waste (poultry and cow manure).

Results: Applied voltage and especially ECF time present a positive influence on turbidity (OD) whereas electrode distance and the combined interactions between electrode distance and ECF time negatively affect this parameter. The amount of aluminum in the supernatant increases directly with the applied voltage and ECF time and decreases with the distance between electrodes. Even if the influence of ECF time is less important for aluminum content, its influence becomes important through the combined interaction between the electrode distance (ED) and ECF time. Applied voltage and ECF time are important both through main interactions as well as binary interaction on TNC. Even if the applied voltage seems to be less important for TPC and TOC through the main interaction, it becomes important through the relative influence together with ECF time.

Conclusions: A batch system for electrocoagulation-flocculation was used in this study as a treatment for turbidity reduction and decrease of nitrogen, phosphorus and carbon content, using as process variables the electrode distance, applied voltage, as well as the ECF time. The maximum turbidity reduction (about 89%) was obtained at an EC time of 90 min, an applied voltage of 12 V and the electrode distance of 5 cm.

***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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PROCESS INTENSIFICATION TECHNIQUES FOR BIODIESEL PRODUCTION IN CONTINUOUS FLOW SYSTEMS

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Keywords: process intensification; biodiesel; acoustic cavitation; hydrodynamic cavitation; microwaves

Introduction: Following many years of research, the use of process intensification techniques for the production of biodiesel is well documented. This work has focused more on a study of biodiesel production using continuous flow systems assisted by acoustic cavitation (ultrasonic or hydrodynamic) or microwaves [1,2].

Materials and methods: Hydrodynamic cavitation was obtained using a hydrocavitation generator which consists of two symmetrical plates facing each other, one stationary and one connected to a 2.2 kW engine. The plates' geometry exerts strong enough forces on the fluid in the space between the rotor and the stator to lead to the formation of bubbles and the occurrence of the cavitation phenomenon. In the case of the ultrasound assisted probe system process, the transesterification reaction was carried out in a cylindrical shaped metal reactor with a cooling jacket. The ultrasonic probe (Vibracell 750 ultrasonic processor) is placed inside the reactor through the top section, the reagents are pumped into the reactor through an inlet on the bottom of the reactor. Another type of acoustic cavitation equipment was used, with experiments carried out using an ultrasonic processor incorporating MMM Clamp-on (AMMM-400 W, Frequency 20 kHz-100 kHz). To study the influence of microwaves on the transesterification process, a mono-mode device – Miniflow (Sairem) was used.

Results: Two of the processes involving an ultrasound probe or the MMM clamp-on, used ultrasonic vibrations and were the most promising, as seen in figure 1. The improvements were due to higher mass transfer between the two non-miscible reactants via the formation and collapse of asymmetric cavitation bubbles. Both types are promising equipment for a small-scale production of biodiesel. The main drawback to the upscaling of this type of process could be the potential limitation to reactor volume due to the penetration depth of the ultrasonic waves. This would not be the case for a hydrocavitation reactor and there are several types which could be used to develop a larger scale hydrocavitation assisted process.

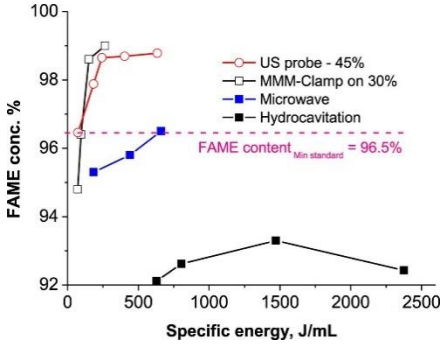

Figure 1. Comparison of intensification techniques for biodiesel production

Conclusions: Continuous flow ultrasound and microwave assisted transesterification processes were developed and compared in terms of fatty acid methyl ester (FAME) concentration and specific energy consumption. Using these types of process intensification methods proved to be beneficial for FAME production yielding higher conversion rates than a control system in shorter reaction times.

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BIFUNCTIONAL AL_2O_3 BASED CATALYST FOR THE HYDROTREATING/HYDROCRACKING REACTION OF BIO-OIL

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Keywords: hydrocracking, dehydrogenation, bifunctional catalyst

Introduction: Hydrocracking is a catalytic hydrogenation process in which high molecular weight raw materials are transformed and hydrogenated in low molecular weight products. The catalytic catalysts used in hydrocracking are bi-functional, composed of a metallic part that promotes hydrogenation and an acid part that promotes cracking. Catalysts used in hydrocracking have a cracking function and a hydrogenation-dehydrogenation function. The cracking function is provided by acid support, while the hydrogenation-dehydrogenation function is provided by active metals. The acid support used in our case is alumina. [1]

The objective of the present work was to synthesize and characterize bifunctional Al_2O_3 based catalysts and to test them in the hydrotreating/hydrocracking reaction of pyrolysis bio-oil.

Materials and methods. Al_2O_3 based catalyst was prepared by impregnation method using granulated ɤ-Al_2O_3. The impregnation solution was prepared by dissolving the salts of the catalytic precursors in the solvent. In order to obtain good homogeneity of the metals deposited on the support, successive impregnation and drying of the catalysts were performed. Drying has been carried out at room temperature for 24h and in a air recirculation oven at 160 °C for 4 hours. After final drying, the catalysts were calcinated in a oven for 6 h at 450 ºC. The textural properties of the synthesized catalysts were determined (specific surface area, volume of pores and distribution of pores size) using a Nova 2200 nitrogen porosimeter.

Hydrotreating/hydrocracking reactions were performed in a pilot plant in a continuous flow system consisting of a fixed bed catalytic tubular reactor with an descending flow of liquid and gas, Series 5400, coupled with 4871 process controller, produced by Parr Instrument Company USA. The tubular reactor is provided with three independent heating zones. The catalysts are positioned in the appropriate area using the metal spacers and the required volume of glass balls. The composition of the final product (liquid phase) resulting in the pilot plant by hydrotreating-hydrocracking processes of the conditioned pyrolysis bio-oil was determined by gas chromatographic analysis (GS-MS/MS triple quad from Agilent Techn. USA)

Results: The textural characteristics of the bi-functional catalyst indicate the obtaining of a mesopore structure, which is confirmed by the specific area value as well as the average pore diameter and total pore volume. The acid-center distribution was calculated on the basis of the temperature-desorption curve of the diethylamine. From the data obtained, a balanced ratio between weak and medium acid centers and a lower concentration for strong acid centers is obtained. The performance of the hydrotreatment-hydrocracking processes has been assessed by determining the liquid phase efficiency and the composition of the resulting liquid product.

Conclusions: In this study we synthesized Al_2O_3 based catalyst for the hydrotreating/hydrocracking reaction of bio-oil and tested in mild reaction conditions. Chromatographic analysis reveals the reduction of oxygenate content, and in particular cyclic oxygenates, and the increase in linear, branched or cyclic saturated hydrocarbons content.

***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.*

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GRAFTING NATURAL LIGNIN WITH ANILINE USING BIOCATALYTIC APPROACH

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Keywords: lignin, peroxidase, aniline, derivatization

Introduction: Lignin is one of the most abundant natural polymer with large perspective of industrial applications nowadays. Due to the presence of reactive –OH groups, lignin can be modulated using different processes.This paper presents a biocatalytic method for grafting lignin (grafting bioprocess) with aniline, leading to an amino-derivatized polymeric product with controlled properties (e.g., conductivity, acidity/basicity, thermostability and amino-functionalization) [1-2]. The grafting bioprocess has been developed in different configurations by varying the source of peroxidase, the enzyme concentration and the type of lignin.

Materials and methods: Different types of lignin and peroxidases from various sources were tested in the grafting process. A phosphate buffer saline was used as buffer solution (10 mM pH=7.4) and 30 wt % solution of hydrogen peroxide (H_2O_2), methanol (MeOH), Na_2CO_3, F-C reagent of analytical purity were purchased from Sigma-Aldrich.

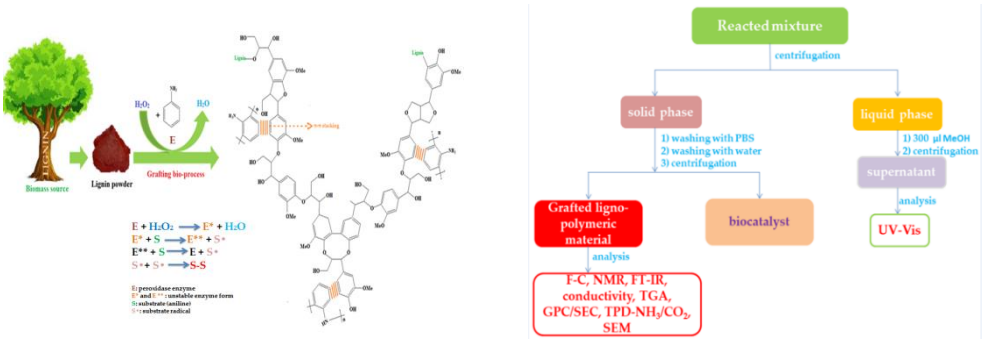

Fig. 1. Grafing process of natural lignin and the protocol for the characterization of polymer [2].

Results: The insertion of the amine groups was checked by ^{1}H-NMR technique, where NH protons were detected in the range of 5.01–4.99 ppm. The FTIR spectra collected before and after the grafting bioprocess evidenced as well the lignin modification. Additionally, the grafted lignin was characterized using conductivity measurements, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), temperature-programmed desorption (TPD-NH_3/CO_2) and scanning electron microscopy (SEM) analyses.

Conclusions: New strategy for lignin derivatization using enzyme biocatalysis has been set up for insertion of -amino groups in the lignin structure. Derivatized lignin exhibited lower acidity and conductivity according to the chemical structure of the derivatised ligno-polymer. Very important to notice, the resulted grafted lignins exhibit suitable characteristics for industrial applications, such as ion-exchange resins, cationic surfactants, flocculants, coagulants, heavy metal adsorbents or support for protein immobilization [3].

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NEW APPROACHES FOR OBTAINING LIGNIN FROM LIGNOCELLULOSIC BIOMASS

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Keywords: DES, BSG, lignin, extraction, solubility

Introduction: DESs (Deep Eutectic Solvents) represent a modern variant, with applicability in different extractions, having multiple beneficial characteristics in terms of toxicity, biodegradability, vapor pressure, thermal stability, synthesis, with an important involvement in Green Chemistry [1]. The foundations of this new concept were laid in 2004 by Abbot and collaborators, with the aim of using new sustainable ionic liquids to support Green Chemistry due to the advantages mentioned above. Thus, we have developed several types of deep eutectic solvents, in order to extract and solubilize the lignin present in the lignocellulosic mass derived from brewer spent grain (BSG), which is a by-product of beer processing. Lignin is an abundant class of heteropolymer, consisting of three main monomers (p-coumaril, coniferyl and synapyl alcohols) with multiple roles in plant products, the most representative being the mechanical support [2]. Because the lignocellulosic mass has three main components (cellulose, hemicellulose, and lignin) [3] it is imperative to designate the percentage of these components. In order to characterize BSG, several steps were taken, namely: determination from the substrate of the quantities of extractables, hemicellulose, lignin, cellulose. The methods used are described further. DESs consist of two or more components, which act as acceptors of hydrogen bonds (HBA) and donors of hydrogen bonds (HBD), respectively [4]. Several types of binary, ternary and quaternary DESs based on choline chloride, betaine hydrochloride, glycine (HBA) and lactic acid (HBD) were prepared.

Materials and methods: High purity reagents (over 98%) purchased from various manufacturing companies, such as Merck, Sigma Aldrich, were used for DES synthesis. To characterize and confirm DES formation, FT-IR analyzes were performed, which highlighted the presence of hydrogen bonds formed following the homogenization of the eutectic mixture. The density, the refractive index, the surface tension were determined, as well as the quantification of lignin solubility by UV-VIS spectrophotometric analyzes. For characterization of DES, duplicate and triplicate experimental analyzes were performed.

Results: The highest extraction yield of lignin was obtained using the DES composed of Be*HCl (betaine hydrochloride): LA (lactic acid): W (water), with the molar ratio 1: 5: 6,7 (69,9 %), followed by Be*HCl: LA: W, 1: 2: 6.5 molar ratio (34 %). Lignin solubility assays were very effective when the quaternary solvent based on Be*HCl: LA: W: PEG-400 (polyethylene glycol) = 1: 2: 6.7: 2 (96.6 %) was used, followed by the solvent based on ChCl (choline chloride) : LA : PEG-400 = 1: 2: 2 (95.0 %).

Conclusions: Several DESs were synthesized, four of which showed good results in the process of lignin extraction and solubilization. Green extraction and solubility methods have allowed to obtain good results, promising for industrial applications. More research is needed to optimize the extraction of lignin using DES.

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ACTIVITY OF THYME ESSENTIAL OIL ON PLANT PATHOGENES AND PLANT SEED GERMINATION

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Keywords: phytopathogenic fungi, phytotoxic, essential oil, plant germination

Introduction: Synthetic pesticides are considered a real problem who increased interest in the development of biodegradable and non-toxic compounds [1]. Essential oils are used in agriculture, medicine and the food industry, due to their antimicrobial, antiviral, insecticidal and antifungal properties [2]. Due to the fungicidal activity, essential oils are an alternative in combating phytopathogens of agricultural crops, while being safe for the environment [3]. The aim of this study was to test the antifungal activity of the volatile compounds of thyme essential oil on 2 strains of phytopathogenic fungi and evaluate the phytotoxic activity of the oil on the germination of plant seeds.

Materials and methods: Testing antifungal activity of thyme essential oil was tested *in vitro* on *Fusarium graminearum* and *Rhizoctonia solani* which were grown on PDA (potato dextrose agar) medium at 28ºC, for 5 days. A piece of fungi with growth medium was taken and placed in the center of Petri dishes, on the PDA medium and sterile paper disc was placed on the lid (testing volatile compounds method). After that, 10 µL of different concentrations of essential thyme oil was added over it. The phytotoxicity test kit (for liquid samples) containing 3 species of plant seeds *(Sorghum saccharatum; Lepidium sativum; Sinapis alba)* was used to determine the phytotoxic activity of thyme essential oil at 0.1% concentration. It was evaluated: seeds germination, roots and shoots length, percentage effect, proton pump, coloring with nitro blue tetrazolium (NBT) stereomicroscope analysis. These measurements were performed with the aid of an Image Analysis program.

Results: Different percentage concentrations (%) of thyme essential oil, dissolved in DMSO, were tested: 0.5; 1; 5; 10; 25; 40; 50; 75; 90. An inhibitory effect was observed on *Fusarium graminearum* strain starting at 50% oil concentration and on *Rhizoctonia solani,* 40%, respectively. Also, thyme essential oil at 0.1% concentration shows a significant inhibitory action on *Lepidium sativum* seed germination (34%), *Sorghum saccharatum* (24.73%) and less for S*inapis alba* (4%). The highest phytotoxic action was manifested on the length plant roots: 96.88% (*Lepidium sativum*), 87.11% (*Sinapis alba*) and 97.47% (*Sorghum saccharatum*). Measurement of the rhizosphere pH after 24 hours from placing the plants in the bromocresol purple medium indicated a major discoloration in the oil sample, which means activation of proton pump. The method of staining plant roots with NBT in the oil sample indicated an accentuated intensity of the color, especially at the top of the roots.

Conclusions: The volatile components of thyme essential oil inhibited the growth of both fungal strains studied, demonstrating a strong antifungal effect. According to the results obtained, thyme essential oil at 0.1% concentration has inhibitory action on the plant seeds germination, especially affecting the appearance of the primary, lateral roots and damage their architecture.

Acknowledgements*: This work was funded by Subsidiary contract 1229/2020 of project SECVENT 81/2016 "Sequential processes of closing the side streams from bioeconomy and innovative (bio)products resulting from it"*

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BIOSTIMULANT ACTIVITY OF YEAST PROTEIN HYDROLYSATES ON *VIGNA RADIATA* SHOOTS

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Keywords: Biostimulant activity, yeast extract, Vigna radiata.

Introduction: Biostimulants are a type of agricultural inputs, used originally in ecological agriculture, but which had spread widely in traditional agriculture as well, due to their abilities to promote plant resistance to abiotic stress, such as desiccation or salinity [1]. Among the frequently used types of biostimulants one can list humic and fulvic acids as well as seaweed extracts and protein hydrolysates. Protein hydrolysates are usually obtained through chemical or enzymatic hydrolysis of a substrate, such as animal waste (skin, bone, feathers), plant biomass or some other substrate high in proteins [2].
One such substrate could be spent brewer's yeast (SBY) as it contains a variety of bioactive components, among which chief are proteins with a concentration between 40 and 60% (w/w) [3]. The yeast used in this study is a lager-type used in a local brewery.
The aim of this study was to test the biostimulant activity of these protein hydrolysates and determine their potential in mitigating the effects of salinity.
Materials and methods: Yeast protein extracts were obtained through a novel method involving high pressure homogenization coupled with an enzymatic pre-treatment. Hydrolysis was carried out using an enzymatic approach involving Alcalase (Novozyme).
Mung beans (*Vigna radiata*) were used to test the biological activity of the yeast protein hydrolysates. Mung bean seeds were incubated with the yeast protein hydrolysates for an hour. The treated seeds were germinated in Petri dishes, with sterile water or sterile NaCl 200mM to induce saline stress. In the 4th day, the plants were measured, in order to assess the biomass accumulation under the effect of yeast hydrolysates.
Results: Biomass accumulation was assessed through measuring the weight, root length and shoot length of the seedling. Across the data series we could observe the stunting effect the saline stress had over the seedlings. While treating the seeds with yeast protein hydrolysates led to an increase in all the measured parameters, compared to the control, it could not mitigate the damaging effects of the saline stress.
Conclusions: Yeast extracts present potential in functioning as biostimulants, due to their effects on biomass accumulation.

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THE ACTIVITY OF THE LIGNOLYTIC ENZYMES FROM THE SPS OBTAINED BY ENRICHING THE SOLID STATE FERMENTATION PROCESS.

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Keywords: enzyme activity, spent pleurotus substrate, selenium

Introduction: Solid state fermentation (SSF) is a fermentation process that takes place in the absence or very low amount of free water leading to significant quantities of products. This process has aroused interest due to its economic benefits and to its implication in the green chemistry concept employing industrial residues. In this direction, white rot fungi (WRF) have demonstrated great capacity to degrade organic substrates because of their two types of extracellular enzymes: the hydrolytic system (α-amylase, xylanase) and the lignin degradation system (laccase-Lac, manganese peroxidase-MnP, lignin peroxidase-LiP and aryl alcohol oxidase-AAO)[1]. The aim of the study was to investigate the influence of selenium enriched substrate on Pleurotus growth, the ability of mycelia to accumulate this microelement and the enzyme activity of lignolytic enzymes[2].

Materials and methods: The *Pleurotus ostreatus* mycelia were obtained from La Breccia Trading Company and were grown in plastic bags, using two final concentrations of selenium of 50 µM (Se1) and 100 µM (Se2), by treating with solution of Na_2SeO_3 (Sigma-Aldrich). The spent pleurotus substrate (SPS) was lyophilized and the proteins were extracted in a water bath with agitation, at 25 °C, for 4 h. The liquid:solid ratio was 10:1 (w/w) and the pH of the liquid phase was 3.80 (optimum for lignolytic enzymes). The enzymatic activities were determined using spectrophotometrical methods[3].

Results: Selenium induced a small delay on the fruiting process. The fruiting bodies of the mycelia grown on selenium enriched medium had different sizes (Se2 induced bigger fruiting bodies than Se1 and standard medium). We obtained protein extracts with significant laccase activities, selenium at the concentrations applied inducing a decrease in enzymatic activity.

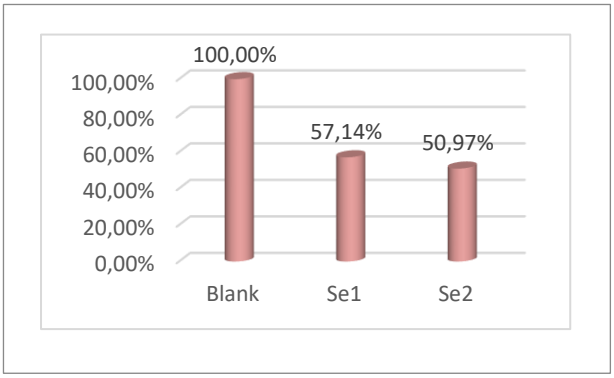

Figure 1. Relative activity of laccase from *Pleurotus ostreatus* grown on selenium augmented medium vs standard medium

Conclusions: Selenium salts can be used to transform SPS into a valuable sub-product enriched in selenium for nutraceuticals applications. The influence of Se on the lignolytic enzymes needs an in-depth investigation.

***Acknowledgements**: This work was funded by Project PN.19.23.01.01 Smart-Bi and Project 10PCCDI / 2018 – PRO-SPER supported by the Government of Romania, Ministry of Education and Research.*

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THE EFFECT OF A STRIGOLACTONE MIMIC ON PHYTOPATHOGENIC FUNGI DEVELOPMENT

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Keywords: strigolactone mimics, hyphal branching, plant hormone, signaling molecules

Introduction: Among living organisms there are plants that can interact with some above- and belowground species [1] and release chemical compounds such as strigolactones (SLs). Initially, upon their discovery, strigolactones were thought to have two main functions, acting as plant hormone [2] and regulating numerous aspects regarding plant development and various stress-related functions, as well as signaling molecules in the rhizosphere. SLs can stimulate the branching and metabolism of pre-symbiotic hyphae in arbuscular mycorrhizal fungi (AMF) [3,4]. In this study we tested the bioactivity of a new strigolactone mimic on *Colletotrichum acutatum* and *Sclerotinia minor* development.

Materials and methods: The fungal strains were represented by *Colletotrichum acutatum* and *Sclerotinia minor* which were grown on PDA following the standard procedure. The stock solutions were prepared by dissolving in acetone GR24 and synthetic SL mimic 5, characterized according to Oancea et al., 2017 [5]. Micelial disks excised from the edge of old cultures were taken and placed in the center of Petri dishes containing different solutions of SLs incorporated in agar medium. After 3 days, the developed fungal colonies were observed and the Petri dishes were examined under a Leica DM 1000 LED microscope. The observations were focused on the diameter and also on the arrangement and number of hyphae. Statistical analysis was applied on the data using IBM® SPSS® Statistics, version 26.

Results: Both GR24 and SL synthetic mimic 5 compounds induced an increase of branching activities. GR24 treatment with various concentrations (5×10^{-6}, 10^{-5}, 5×10^{-5}) increased the hyphal branching and determined the formation of fourth-order branches which were lacking in the controls. The responses of tested fungal strains to compound SL mimic 5 were relatively similar to the response to GR24. The presence of these compounds in the culture media appears to inhibit the growth of both fungal plant pathogens.

Conclusions: We present a new SL mimic compound that has similar effect as GR24, inducing stress response and inhibiting phytopathogen growth.

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IN SILICO EVALUATION OF THE ABILITY OF SOY PROTEINS (*GLYCINE HISPIDA*) TO RELEASE ANTIOXIDANT AND ANTIHYPERTENSIVE PEPTIDES

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Keywords: in silico, bioactive peptides, soy proteins, antihypertensive, antioxidative

Introduction: Bioactive peptides encrypted in various protein sources can become active during gastrointestinal digestion, exerting a number of physiological effects on the human body [1]. The aim of this study is to see if two high-quality soy proteins can be precursors of bioactive peptides, when they interact *in silico* with various proteolytic enzymes [2].

Materials and methods: The FASTA sequences of alpha and beta subunits 1 of Beta-conglycinin were extracted from the UniprotKB database. Analyzing entries from a series of databases such as: BIOPEP-UWM, PeptideRanker, PepCalc, ToxinPred and AllergenFP v.1, we observed the scope in which soy proteins can be used as potential sources of bioactive peptides (Fig. 1) [3]. Through computational prediction, we managed to generate the aforementioned peptides and our goal was to analyze the physico-chemical, sensory, toxicity and allergenic characteristics.

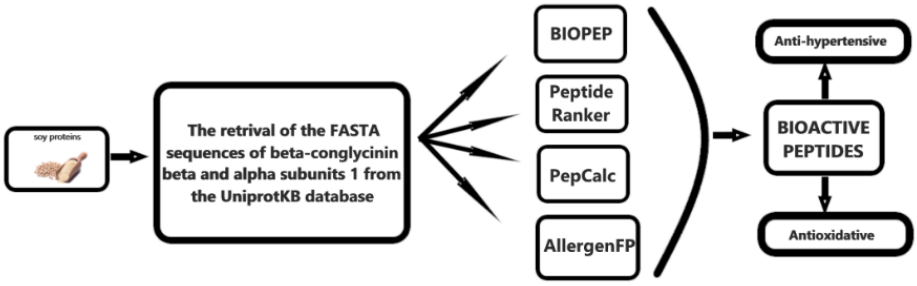

Fig.1. Schematic workflow representing the process of evaluating soy proteins as precursors of bioactive peptides

Results: The peptides from both proteins showed antihypertensive activity, which was evidenced due to the action of pepsin, followed by papain and subtilisin but also showed low levels of antioxidative activity. The alpha subunit 1 proved to contain the highest number of bitter ACE-inhibitory peptides, under the influence of pepsin. From the analyzed soy proteins, the RF peptide was predicted to have a high score of bioactivity and represents a good target for further analysis.

Conclusions: Overall, the study shows that a major source of health-promoting bioactive peptides with non-toxic and non-allergenic effects can be outsourced from soy proteins. These results were generated based on *in silico* approach, which shows that it represents a cost efficient and effective method for further studies.

***Acknowledgements**: The work on this paper was supported by the Government of Romania, the Ministry of Research and Innovation, Project PN.19.23.01.01 Smart-Bi.*

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ULTRASOUND-ASSISTED EXTRACTION OF PHENOLIC COMPOUNDS FROM QUINCE LEAVES USING BOX BEHNKEN DESIGN

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Keywords: polyphenols, response surface methodology, ultrasound extraction

Introduction: Many plants are known to contain biologically active compounds, which offer health benefits and could be used to obtain bioproducts with nutraceutical/fortification properties. Several studies [1, 2] show that quince, fruits, seeds and leaves are sources of bioactive compounds such as phenolic acids, flavonoids, organic acids, amino acids, procyanidins, with various beneficial effects on human health.
The main aim of the study was to determine the optimal parameters for the extraction of phenolic compounds.
Materials and methods: Ultrasound-assisted extraction of phenolic compounds from quince leaves was optimized using Response Surface Methodology (RSM) from Design-Expert software ver.11. A three-factor BBD (extraction time, liquid to solid ratio, ethanol concentration) was applied to obtain the optimum conditions for the highest yield of total polyphenolic compounds (TPC) and antioxidant activity (AOA). AOA was evaluated by three colourimetric methods, namely FRAP, ABTS and DPPH. The optimal extract was analyzed by HPLC to identify the phenolic acids.
Results: Highly significant factor for the content of polyphenols and AOA was the concentration of ethanol, while the other two were marginally significant for the extraction of the maximum total polyphenolic compounds and the maximum AOA of the extracts. The phenolic acids from the optimised extract of the quince leaves were identified by HPLC, as caffeic acid and chlorogenic acid.
Conclusions: We have determined the optimal conditions for TPC extraction from quince leaves and identified that caffeic acid and chlorogenic acid are the main phenolic acids present. High content in these active ingredients of hydroalcoholic extracts from quince leaves make them usable as a nutritional supplement and/or as an active ingredient in some cosmetics.

Figure 1. The schematic diagram for obtaining and application of a bioactive compound from the by-product of quince

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GREEN SOLVENTS BASED ON CHOLINE CHLORIDE FOR CO_2 CAPTURE

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Keywords: Deep eutectic solvents, green solvents, CO_2 absorption, CO_2 desorption

Introduction: Today, the awareness for CO_2, the most important greenhouse gas, has increased, due to the rapid climate change [1]. The most applicable methods for CO_2 capture are the processes based on solvent-separation. They have the capacity to reduce the energy input for CO_2 absorption, comparing to the distillation technique, unfeasible for large CO_2-pollutans (e.g. power plants). The solvent-processes must be environmental-friendly, biocompatible, customizable just by tailoring their properties, and used in mild separation systems. The state-of-the-art CO_2 capture method is the post-combustion [2], which separates CO_2 from the combustion gases, usually using amines-solvents. This work aims to bring new green solvents (*DES - deep eutectic solvents*) with amines, solvents that are more stable, reusable, and safer than the classic aqueous amine solutions.

Materials and methods: As HBA (hydrogen bond acceptor) choline chloride [3], and as HBD (hydrogen bond donors) three amines: monoethanolamine MEA, diethanolamine DEA and triethanolamine TEA were used. The molar ratios were 1:5, 1:6, 1:8 and 1:10. The reagents were weighed and then mixed at 300 RPM, 60°C for 2 hours. The reaction is over when the solution becomes clear [4]. Each solvent was characterized (pH, density, viscosity, refraction index, electrical conductivity) and used for CO_2 absorption tests on a lab-scale installation, in which pure CO_2 was bubbled.

Results: Most of the CO_2 was absorbed in the first 5 minutes using ChCl:MEA, after which the rate dropped sharply. The same happened to the ChCl:TEA, after 10 minutes. While ChCl:MEA had the exponential growth in just a few minutes, ChCl:DEA was more constant, showing a slower absorption rate with maximum absorption after 15 minutes. This fact can be explained by their viscosity, 15 cP for ChCl:MEA, while ChCl:DEA has more than 450 cP and ChCl:TEA around 500 cP. For the present tests (fig. 1), ChCl-DEA 1:10 absorbed over 120 mg of CO_2 per gram DES, 1:6 and 1:8 ratios with 8-10% less and 25% less for 1:5 ratio. ChCl:MEA absorbed CO_2 from 70 mg/g (1:5, 1:6), up to 88 mg/g for the other ratios (1:8, 1:10). ChCl:TEA absorbed only 10 mg/g CO_2, due to its higher density and viscosity, with a slightly increase at 1:8 ratio – 17 mg/g. Desorption tests have proven than these solvents have the tailoring property [5], but also with simultaneous partially amine volatilization (MEA and TEA), or very slow CO_2 release (DEA).

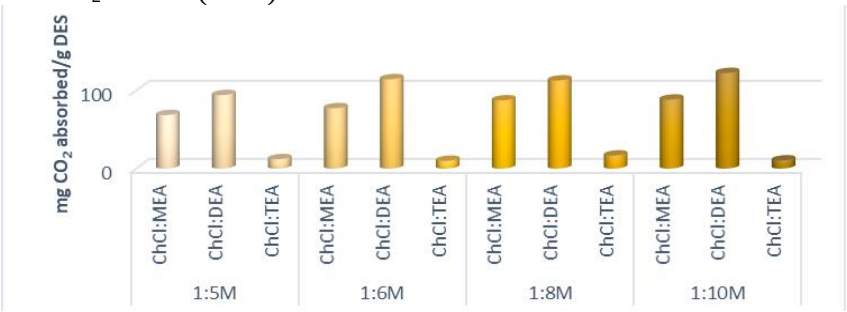

Fig. 1. CO_2 absorption in ChCl:Amines, at four molar ratios

Conclusions: The absorption tests have shown that ChCl:MEA, ChCl:DEA, ChCl:TEA are a promising solution for CO_2 capture, especially because they are more environmental-friendly than the aqueous amine solutions. Further optimizations are needed, according to the desorption tests.

***Acknowledgements**: The work on this paper was supported by the Government of Romania, Ministry of Research and Innovation, Project 296PED/2020 ASOCIAT*

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MORPHOLOGICAL CHARACTERIZATION OF VERO CELLS TREATED WITH BIOGENIC SILICA NANOPARTICLES

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Keywords: biocompatibility; nanobiosilica; rice husk

Introduction: Rice husk (RH) is a valuable source of biosilica [1]. Silica nanoparticles (SiNPs) represent one of the most efficient forms of controlled release of silicic acid. It has been shown that silicic acid can promote wound healing and connective tissue repair [2]. The aim of the present study was to detect any morphological changes induced by silica nanoparticles from rice husk in the Vero cell line in order to show their suitability to be used in different applications, such as medical devices.

Materials and methods: In order to study cell morphology, Vero cells were incubated for 24h at 37ºC in Dulbecco's Modified Eagle's Medium (DMEM) supplemented with 10% FSB (Fetal Bovine Serum) Subsequently, the cells were exposed to 10 µg/mL SiNPs dose. Cell morphology was evaluated after 24h and 48h using fluorescence microscopy. Cytoskeleton was observed by labeling the actin filaments with phalloidin conjugated with Alexa Fluor 488 and the nuclei were marked with DAPI (4',6-diamidino-2-phenylindole).

Results: Fluorescence microscopy images revealed no significant changes in cell morphology. Thus, the cells showed an elongated polygonal shape, which is typical for the epithelial phenotype of the Vero cell line. The cytoskeleton is highly organized in a fibrillar structure, with abundant actin filaments (arrows), which improves the mechanical stability of the nucleus (Fig. 1).

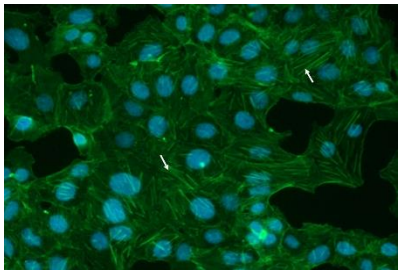
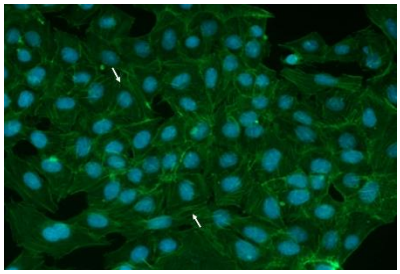
A)  B) 

Figure 1. A) Untreated cells (control) and B) SiNPs treated (10 µg/mL) cells after 48h exposure.

Conclusions: The study shows that no significant morphological change was found in the tested cell line, which suggests that biogenic silica nanoparticles have no harmful effects at low concentration. This is the first step in proving that they are a potential candidate for various biomedical applications.

***Acknowledgements**: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number 366PED/2020, within PNCDI III*

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BIOREMEDIATION OF HYDROCARBONS POLUTTED WATERS USING MICROALGAE

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Keywords: bioremediation, microalgae, hydrocarbons, Chlorella sp., Chlorella sorokiniana, Desmodesmus communis

Introduction:
Oil and gas industries generate approximately 250 million barrels of produced water per day. More than 40% of these waste streams are introduced into the environment, significantly contaminating it with hydrocarbons and heavy metals [1]. In this context, engineered bioremediation techniques such as biostimulation and phycoremediation are gaining popularity because of their faster remediation rates. It has already been demonstrated that phycoremediation offers cost-effective, nonintrusive, and safe cleanup technology in which macro- or microalgae are used to treat a large group of pollutants [2]. Some microorganisms have hydrocarbons degradation abilities. [3]. Therefore, in this study, we evaluated the microalgae`s bioremediation capacity of heptane as a hydrocarbon pollutant from wastewaters.

Materials and methods:
Axenic culture species of microalgae (*Chlorella* sp., *Chlorella sorokiniana*, and *Desmodesmus communis*) originates from the Norwegian Culture Collection Algae, NORCCA. The microalgae were cultivated in a growth chamber using BBM medium, under stable conditions of light 100 μmol/m^2·s, temperature of 25°C and 130 rpm orbital agitation [4]. Two parameters (optical density and cells number) were measured as indicators of microalgae growth rate. The effect of heptane concentrations between 0.01% and 0.1% was investigated. The degradation activity of the microalgae was determined by analyzing the residual hydrocarbon from the medium using a GC-MS method [5].

Results:
All three strains showed increased optical densities and cell number values after 14 days of incubation, indicating high biomass productivity. The effect of n-heptane on *Chlorella* sp., *Chlorella sorokiniana*, and *Desmodesmus communis* growth rate was studied. H-heptane concentrations up to 0.1% did not present any inhibitory effect on the three microalgae tested. The experimental data showed that the growth of *Chlorella sorokiniana* and *Chlorella* sp. was the highest at 0.01% heptane, the optical density (OD) being 2.5x higher than in the absence of heptane (control) in the case of *Chlorella sorokiniana*. This trend is confirmed by cells number. *Desmodesmus communis* registered the best growth at the highest concentration of 0.1% n-heptane, with the OD being 73% higher than control.

Conclusions:
The present study indicated that *Chlorella* sp., *Chlorella sorokiniana*, and *Desmodesmus communis* microalgae could bioremediate the produced water.

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THE ANTIOXIDANT ACTIVITY OF HONEY WITH PROPOLIS EXTRACT

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Keywords: antioxidants, polyphenols, honey, propolis

Introduction: Both honey and propolis have been recognized as functional foods with health benefits. Based on such ethnopharmacological heritage, many scientific studies demonstrate the health effects of honey and propolis: protection against cardiovascular diseases and metabiolic syndrome and anti-inflammatory, antioxidant, and antibacterial activities. Honey is a mixture of mono- and disaccharides, with water pockets wherein are crowded proteinS and polyphenols. Propolisis a resinous mixture produced by bees by collecting parts of plants. Propolis mainbioactive components are polyphenols. This study aimed to realize a new productbased on honey enriched with polyphenols from a propolis extract and compare its antioxidant activity with a commercial mixture of honey with propolis.
Materials and methods: The polyphenols were extracted from propolis by ultrasound-assisted extraction with 75% ethanol solution and the ratio powder to solvent 1:5, for 30 min. at room temperature. The extract was split equally intotwosamples andconcentratedusing a semi-automated evaporation system, MultiVap54 (Lab tech), at 40°C. One of the two samples was resuspended in honey(ratio 1:20 (w/w) and the other was resuspended in 75% ethanol solution. The extract in honey was solubilized in an ultrasonic bath, mixed thoroughly, and the polyphenols were left to diffuse overnight. The antioxidant activities (AOA)of the samples were assayed using three spectrophotometric methods: two based on radical scavenging activity (ABTS and DPPH) and one based on reducing antioxidant power (CUPRAC). The total phenolic content (TPC)was determined with Folin-Ciocalteu.
Results: Honey with polyphenols extracted from propolis showed an almost 4-fold increase in TPC compared with honey simple and a nearly 2-fold increase compared with honey with propolis commercial. These trend data can be observed in the case of AOA by all methods. The data of AOA indicated that the addition of polyphenols extract in honey was enhanced AOA by all methods a fewtimes more.
Conclusion: Our results show that the solubilization of polyphenols extracted from propolis in honey can increase the AOA of honey more than that of thesimple polyfloral honey simple or the commercial mixtures ofhoney with propolis.

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RESPONSE SURFACE METHODOLOGY FOR MAXIMING THE BIOSTIMULANT EFFECT OF SODIUM ALGINATE COATING ON MUNG BEAN SEEDS

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Keywords: biostimulants, alginate, phlorotannins, response surface design

Introduction: A plant biostimulant is any substance or microorganism applied to plants with the aim of enhancing nutrition efficiency, abiotic stress tolerance and/or crop quality traits, regardless of its nutrients content. The purpose of this work was to test different compounds or classes of compounds, for example sodium alginate (an acid polysaccharide salt), which could be potentially biostimulant on Mung bean seeds. Possible biostimulant effects can be estimated in a number of ways such as the measurements of morphological plant growth characteristics (for example stem length and radicle length) or biochemical assays related to biostimulation (plant growth hormones: auxin and gibberellin, α-amylase). Various conditions can be tested which, at times, could lead to a synergistic interaction between these conditions. One such situation could be the use of phlorotannins (polyphenolic compounds in brown macroalgae) [1] extracted from *C. barbata*, a brown seaweed which is naturally available on the Romanian coast at the Black Sea and was shown to include a relatively high amount of phlorotannins as compared to other species [2]. The simultaneous extraction of both classes of compounds would demonstrate a potentially useful application in agriculture of these extracts from *C. barbata*.

Materials and methods: The first step was to determine sufficient conditions for the proper growth of seeds (the blank test) against which commercial alginate, *C. barbata* alginate and other extracts could be tested. The independent effect of commercial alginate was tested in a first Response Surface Methodology (RSM) design by looking at modified levels of concentration for both alginate and agar gel (a usual sterile growth media). The cell viability, the root length and following storage at – 80 °C, α-amilase determination. Furthermore, seeds were coated with sodium alginate using a Mini-Glatt fluidized bed system and crosslinked with $CaCl_2$ solutions at certain concentrations for a known amount of time following another RSM design. After another rapid sterilization in Ethanol 70%, the seeds were planted on agar gel and measured after 4 days. The seeds were grown in an Algaetron system using an 8 hours day cycle alternating with an 8 hours dark cycle.

Results: Alginate delivered directly in the growth medium did not have a significant effect on the growth of the seeds although a higher concentration of agar gel lead to a low seed viability. The second design has shown possible effects of $CaCl_2$ interference for the coating of the seeds, although otherwise the cells were viable.

Conclusions: These initial tests represent the first part of a larger subject which will eventually lead to a better understanding and development of relevant seed growth tests. The final objectives is to determine a) if CBA has reproducible biostimulant effect on Mung bean seeds; b) if the seed coating process represents a more efficient way to deliver the bioactive compounds.

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OPTIMIZATION OF 3D BIO-INKS COMPOSITION FOR BIODEGRADABLE FISH BAITS FROM INDUSTRIAL BYPRODUCTS

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Keywords: 3D printing; biopolymers; sport fishing; bioeconomy; fish baits; biodegradable;

Introduction: The industrial market presents a high request for biodegradable fish baits because of the contamination of fresh waters and salt waters with the microplastics from the classical plastic-based fish baits. This is a real problem nowadays, affecting both the environment and underwater life. Using organism-based baits (such as worms) for sport fishing goes against the sport itself. Involving biopolymers from different industrial byproducts encourages closing side-streams of bioeconomy and creating innovative bioproducts, such as biodegradable 3D printed fish baits (that will protect the environment). The printability of the biopolymers requires specific rheological properties (as shear-thinning), high viscosity and/or hydrogel formation, influenced by the nature of the ingredients and their concentration. Herein, we propose the optimization of a bio-ink for biodegradable fish baits by studying different properties that influence the printability [1].

Materials and methods: pectin, carboxymethylcellulose (CMC), calcium carbonate ($CaCO_3$) and chitosan were used for optimization of the composition of the 3D bio-ink, in 1% acetic acid solution (using Design Expert tool). The bio-ink was extruded manually through a 1 ml syringe to observe the printability of the ink.

Results: We have obtained an optimal concentration domain for all the proposed components in the bio-ink, as a complementary composition (by studying the desired properties using a statistical valuable model). The total desirability study of our purpose, as well as the height of the object (Figure 1) involve a high amount of pectin and chitosan, to the detriment of acetic acid. The elasticity of the object requires high amounts of pectin and the antifungal property is increased by a higher amount of pectin and especially chitosan (Figure 2). Chitosan is known to have antimicrobial and antifungal activities and cellulose reinforces the object (at an optimal concentration). Calcium carbonate and chitosan could provide a natural strength [2] and provide insolubility of our 3D printed desired fish baits.

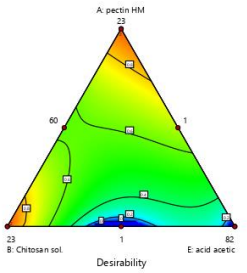

Figure 1. Desirability and height of the 3D printed object.

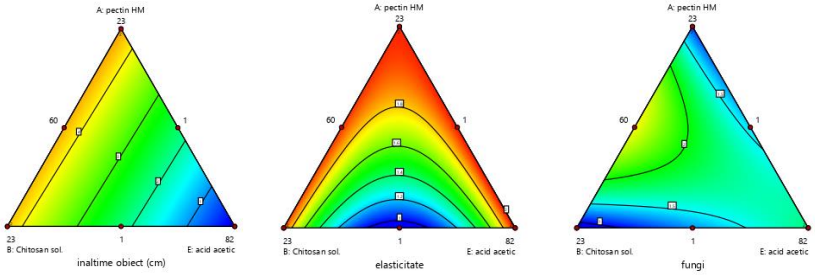

Figure 2. Elasticity and fungus content of the 3D printed objects.

Conclusions: The optimized composition for fish baits were designed using Design Expert, considering the homogeneity, viscosity, the height of the desired 3D object, elasticity/plasticity of the object, antifungal and antibacterial properties of the bio-inks.

***Acknowledgements**: This work was funded by the project POC-A1-A1.2.3-G-2015- P_40_352-SECVENT, "Sequential processes of closing the side streams from bioeconomy and innovative (bio)products resulting from it", contract 81/2016, funded by cohesion funds of the European Union, subsidiary project 1488/2020 3D-4Fish.*

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SOLID STATE SYNTHESIS, CHARACTERIZATION AND COLOR PROPERTIES OF Co, Mn-DOPED KARROOITE $MgTi_2O_5$ CERAMIC PIGMENTS

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Keywords: ceramic pigments; karrooite; pseudobrookite; chromophores

Introduction: Recently, the traditional ceramic industry showed an increased interest on research of new ceramic dyes, presented as fine powders that are integral part of many decorative and protective coatings and are used for the coloration of glazes, ceramic bodies, and porcelain enamels [1]. Those ceramic pigments must have some characteristics, including: high thermal stability, high chemical resistance and must be inert to the action of molten glass. Karrooite, $MgTi_2O_5$, can be considered a potential ceramic pigment due to its refractoriness and high refractive indices[2]. Moreover, it is possible to develop different colors and shades because karrooite can be a host lattice for several transition metal ions. The purpose of this paper was to develop and study 4 karrooite solid solutions doped with transition metal chromophore ions (Co and Mn), according to the stoichiometry: $Mg_{1-x}Co_xTi_2O_5$ and $Mg_{1-x}(Co_{0.5}Mn_{0.5})_xTi_2O_5$, x = 0.1 and 0.3.

Materials and methods: Firstly, there were obtained the oxide precursors MgO and Co_3O_4. MgO was obtained by sol-gel route using $Mg(NO_3)_2 \cdot 6H_2O$ and NaOH. Co_3O_4 was obtained using $Co(NO_3)_2 \cdot 6H_2O$ and NH_4HCO_3, molar ratio of 2:5. After that, the samples were prepared by the classical ceramic route from mixtures of oxide precursors (TiO_2, MgO, Co_3O_4 and MnO_2), fired at 1200°C. The resulted powders were then characterized.

Results: The pigments color range from light green to a darker shade once the Co^{2+} content increase, and turn brown when MnO_2 is added.

The XRD spectrums of the Co-doped karrooite samples are represented in figures 1 and 2. The diffraction interferences confirmed the effective formation and relative stabilization of karrooite solid solutions in all samples, although with decreasing quantities of residual TiO_2 (rutile) and $MgTiO_3$ (geikielite) the higher the Co content.

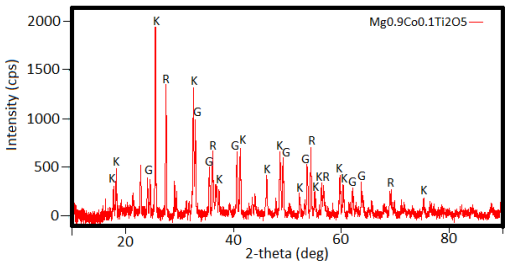

Figure 1. XRD spectrum of karrooite solide solution ($Mg_{1-x}Co_xTi_2O_5$ with x = 0.1)

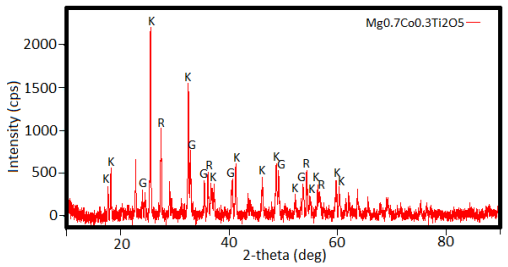

Figure 2. XRD spectrum of karrooite solide solution ($Mg_{1-x}Co_xTi_2O_5$ with x = 0.3)

Conclusions: XRD characterization confirmed the formation of karrooite solid solution with residual TiO_2 and $MgTiO_3$ phases, by a conventional ceramic route. The color characterization revealed that the resulted colors are more saturated or darker (lower L values) the higher the cobalt and manganese content, and that the Co-doped samples are less yellow (lower b values) than the Co,Mn-codoped samples.

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COMPOSITIONAL INVESTIGATIONS OF AN MEDIEVAL STONE CROSS – 1656

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Keywords: medieval cross, XRD, WDXRF, FTIR.

Introduction: The area of Targovishte has a rich history, with countless vestiges of the historical past. The parish church "Pious Parascheva", located 8 km from the voivodship fortress of Wallachia, was documented on July 5, 1705, according to the Dâmboviţa Archival Treasury 1526-1848. But the church is much older, from the text carved in stone on a stone cross, being inscribed January 11, 1656, placed next to the place of worship. This paper aims to address one of the major challenges of conservation state of stone artifacts surfaces.

Materials and methods: In our study from the X-ray investigation methods (XRD and WDXRF) and FTIR spectroscopy methods could be observed the stone composition and its degradation proccess.

Results: Some weathering processes are visible, as follows: porous structure, with cracks, alveolar formations and detachments, effusive, unevenly located gypsum deposits accompanied by microbial population development. By XRD, WDXRF and FTIR measurements the composition of the stone and of the weathering layers from the sample surface have been detected. By WDXRF some major metallic oxides have been identified as: CaO, SiO2, Al2O3, Fe2O3, well correlated with XRD results, where the following species have been quantified, as follows: Calcite, Calcium carbide, Perlikite (with specific bands in FTIR spectrum, Fig.1) and minor quantitities of Fe, Sr, Si, Al, Mg derivatives.

Conclusions: In order to establish the importance of the cross in the historiography of the monuments of Targoviste and its surroundings, we want to pay due attention and highlight the monument of real significance.

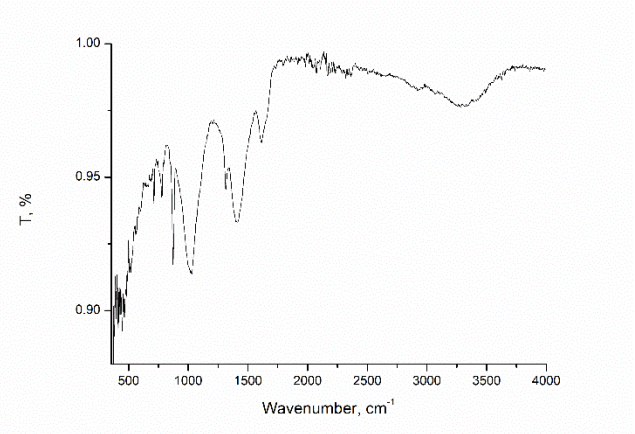

Fig.1. FTIR spectrum of Medieval Stone Cross

EVALUATION OF NEW AND OLD BANKNOTES USING HYPERSPECTRAL IMAGING

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Keywords: hyperspectral imaging; evaluation of banknotes;

Introduction: The application of hyperspectral imaging techniques in the science of cultural heritage conservation has come to the attention of researchers in recent years due to its non-destructive characteristics. Face to the colour image which has only 3 bands, the hyperspectral image contains much more information being composed of a very narrow continuous band that consists of hundreds of bands. The spectral band covers all spectral bands of visible and near-infrared light. [1]

Materials and methods: It was used to identify hyperspectral images chamber VNIR InnoSpec Greeneye with the spectral domain 373.52-1102.61 nm and the resolution of 10 nm. The quality of the spectrum is influenced by parameters such as light intensity, distance between object and camera, the quantity of light which goes to camera. The method used consisted in the analysis of multivariate image in a reflectance spectrum [2].

Results: Evaluation at different points (with abbreviations pa= dot blue, pm= mauve, pp=orange, pr=red, pv=green) led to the identification of the wavelengths corresponding to the maxima: i_{pa}=0.2724 (λ_{pa}=474.54 nm) I'_{pa}=0.2107 (λ'_{pa}=871.32 nm); i_{pm}=0.4548 (λ_{pm}=541.24 nm), i'_{pm}=0.4674 (λ'_{pm}=898.86 nm); i_{pp}=0.6392 (λ_{pp}=540.54 nm), i'_{pp}=0.6615 (λ'_{pp}=961.59 nm); i_{pr}=0.5489 (λ_{pr}=476.630 nm), i'_{pr}=0.6200 (λ'_{pr}=902.21 nm); i_{pv}=0.5045 (λ_{pv}=546.09 nm), i'_{pv}=0.7347 (λ'_{pv}=373.52 nm).

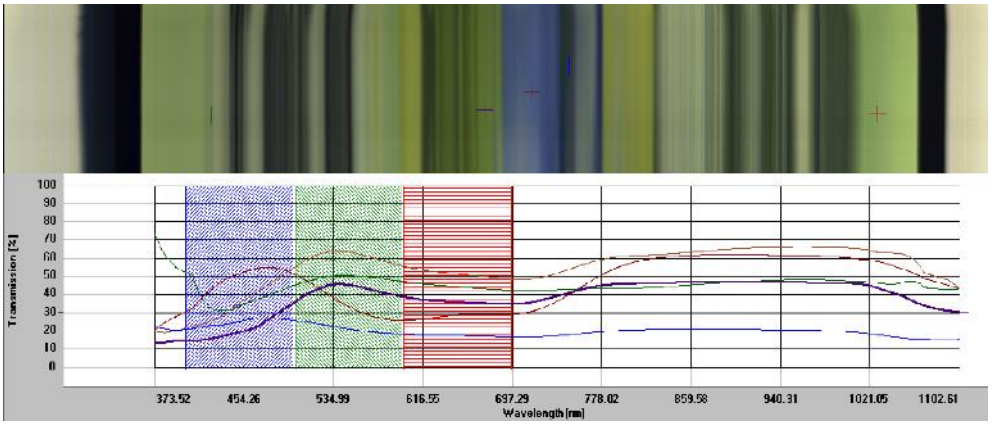

Fig.1 Diagram 3D of surface analyse

Conclusions: Analysis at different points of the banknotes and the comparison between the spectra can be a method of verifying the authenticity of the respective banknotes. A wider spectral library can be built if banknotes of other values or old banknotes are registered. With this methodology of HIS we can help in forensic science and cultural heritage science to authenticate and counterfeit of currency.

***Acknowledgements**: The work on this paper was supported by the Government of Romania, Ministry of Research and Innovation, Project 51PCCDI/2018.*

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CaAl - LAYERED DOUBLE HYDROXIDES FOR HERITAGE CONSERVATION - PREPARATION, CHARACTERIZATION AND KINETIC STABILITY OF THEIR DISPERSION IN SOLVENT

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

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 the heritage conservation, depending on the synthesis method implied, notably, bacteriostatic properties and anion absorption [1], [2]. However, the literature lacks a comprehensive study of their properties as consolidants in cultural heritage.

The LDH-like materials were prepared using two different co-precipitation methods, derived from Z. Y. Qu et al. [2], and S. Xu et al. [3]. The materials obtained were characterized by X-ray diffraction, FT-IR spectroscopy, and XRF. The kinetic stability, of the material dispersion in water and water-ethanol mixtures were determined from the variation of absorbance over time by UV-VIS spectrometry. KS was calculated using the formula:

$$KS\% = 1 - \left[\frac{A_0 - A_t}{A_0}\right] \times 100 \qquad (1)$$

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

XRD patterns of both materials corespond to a well crystallized Ca-Al-LDH phase (JCPDS 31–0245) with monoclinic symmetry and chemical formula $Ca_8Al_4(OH)_{24}(CO_3)Cl_2$ [3]. The FTIR and XRF analysis showed that the interlayer space consists of carbonate anions, water and chloride anions [4]. During synthesis, no significant amounts of cations were lost. The kinetic stability of these materials presents good values – of about 50% or higher, both in water and water ethanol mixtures (figure 1).

Both the coprecipitation methods lead to pure LDH-like materials with slightly different properties. When dispersed in water and water/ethanol these materials can form relatively stable dispersions which make these materials interesting for further studies in heritage conservation.

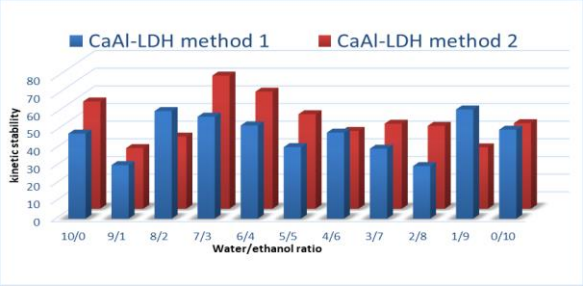

Figure 1. Kinetic stability of materials dispersions in water/ethanol mixtures

Acknowledgements *The work on this paper was supported by the Government of Romania, Ministry of Research and Innovation, Projects 51PCCDI/2018 and 567 PED/2020.*

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CHARACTERIZATION OF MORTARS PREPARED WITH DIFFERENT BIOPOLYMERS AND YELLOW IRON OXIDE

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Keywords: cultural heritage; yellow iron oxide, biopolymers

Introduction: The preservation of the national heritage has become a main concern for the present times. Materials such as stone, bricks and mortars are subjected to damage mostly due to meteorological factors and harsh environmental conditions (acid rains, the presence of salts, sulphate attack, the action of frost and thawing, causing serious degradation processes over the time in the artifacts' structure [1]. Hence, the emphasis is focused on finding new materials that could be used for restoration of old constructions in safe conditions. Because pigments of natural or synthetic origin have an ability of colouring the materials they are applied on [2], using pigments in mortars could lead to changes of some properties. The objective is to study the combination effect of yellow oxide and different biopolymers on some physical-mechanical properties of mortars in the preservation process.

Materials and methods: Various biopolymers were used in this study: sodium alginate (Sigma-Aldrich, low viscosity), chitosan (commercial) and starch (commercial). Also, the yellow iron oxide pigment was purchased from S.C. Alfa Chim S.R.L (Buzău county, Romania). The mortar references were prepared in the shape of cubes (30 x 30 x 30 mm) using white cement, sand and water. The following analyses were performed in order to evaluate the physical-mechanical properties of the prepared samples: determination of mechanical properties by compressive strength using a digital Schmidt hammer, determination of freezing-thawing resistance by measuring the variations of the resistance strength [3], analysis by optical microscopy using a Primo Star ZEISS optical microscope at magnification of 40x, and colorimetric analysis performed using an instrument from Konica Minolta (CR-410 model) under illuminant C and 2 degree standard observer conditions. The yellowness index was calculated to evaluate the chromatic changes when using different biopolymers [4].

Results: The compressive strength of mortars is highly influenced by the water content at the time when performing the analysis [5], therefore the specimens were tested at a minimum age of 28 days. The analysis of freezing-thawing has shown a resistance up to 47 cycles for the samples prepared with different biopolymers and yellow iron oxide. The surface morphology was investigated using an optical microscope. Therefore, the mortar samples with yellow iron oxide and various biopolymers have shown a particle size distribution between 224 μm and 447 μm. The colorimetric analysis pointed out that high values of the yellowness index are obtained when using the sodium alginate.

Conclusions: The mortar samples prepared using biopolymers and yellow iron oxide have shown important changes in the physical-mechanical properties. The colorimetric analysis indicated that higher values of the yellowness index are obtained when using sodium alginate, compared to starch and chitosan. The compressive strength determination revealed that the samples with chitosan and starch exhibit a good durability while a slight decrease of the compression resistance for the samples with sodium alginate was noticed. Depending on the purpose, the prepared materials could be suitable for restoration of mortars.

***Acknowledgements**: This work was supported by the project no. PN-III-P1-1.2-PCCDI2017-0476 - "New diagnosis and treatment technologies for the preservation and revitalization of archaeological components of the national cultural heritage", ctr. no 51PCCDI/2018.*

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