Institutul National de Cercetare-Dezvoltare pentru Chimie si Petrochimie - ICECHIM

Book of Abstracts

No. 17/2021

The International Symposium PRIOrities of CHEMistry for a sustainable development

PRIOCHEM

www.icechim.ro

Partener: Societatea de Chimie din România

Volume of Summaries Technical Page

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Cover, graphics and conception of the edition:
INCDCP - ICECHIM

The International Symposium
"PRIOrities of CHEMistry for a sustainable development"
PRIOCHEM
XVIIth Edition, ICECHIM - Bucharest – ROMANIA
October 27 - 29, 2021

The original title (in Romanian): Simpozionul international „PRIOCHEM”
Edited by: ICECHIM Bucharest, Romania

ISSN 2601 - 419X and ISSN-L 2601 - 4181 - English ed., CD-ROM, other Electronic Supports;
ISSN 2601 - 4181 and ISSN-L 2601 - 4181 - English ed., Print;
ISSN 2601 - 4203 and ISSN-L 2601 - 4181 - English ed., Online;
ISSN 2285 - 8334 and ISSN-L 2285 - 8334 - Romanian ed., Print;

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FOREWORD

Making complex scientific topics accessible for the public while maintaining scientific accuracy requires placing science and research in a larger narrative context. In the current modern society - in which anti-scientific tendencies are winning a certain weight - communicating the social role of science is fundamental and responsibility lies with the specialists themselves when they relate to the broader public. Society has become more and more dependent on the scientific work and experts have to be aware of their social role. When scientists can communicate effectively beyond their peers to broader, non-scientist audiences, it builds support for science, promotes understanding of its wider relevance to society, and encourages more informed decision-making at all levels, from government to communities to individuals. In a period marked by many changes, PRIOCHEM 2021 is an important moment for INCDCP – ICECHIM that continues to grow and adapt, remaining permanently motivated, focused and open to new ideas, making sure that Romanian research and academic institutions continue to be part of the global research elite.

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HYDROGELS BASED ON POLYSACCHARIDES GRAFTED FERULIC ACID: A BIOMIMETIC APPROACH

Ahdi HADRICH[1], Didier LE CERF[1], Virginie DULONG[1], Luc PICTON[1*]

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Keywords: hydrogels; biomimetic approach; artificial polysaccharides.

Abstract: Some cereal seeds present mucilage composed of polysaccharides bearing ferulic acid (FA) groups which are capable of reacting in the presence of an enzyme such as laccase to generate chemical hydrogels [1]. The main idea of this work, following a biomimetic approach, is to elaborate artifi-cial polysaccharides grafted with ferulic acid groups [2]. Various polysaccharides have been stud-ied: anionic ones (carboxymethylpullulane (CMP) as a model, hyaluronan (HA) for application) and neutral one (pullulan (P)). We report here the availability of the grafting, the evidence of crosslinking (figure below) leading to hydrogels in the presence of laccase (as a function of FA, polymer and laccase amount) and evidence of antioxidant properties of such derivatives [3].

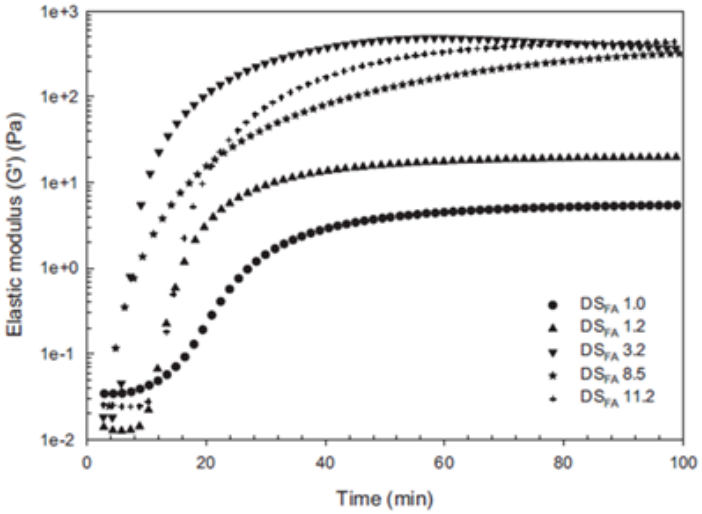

Fig. 5. G′ versus time for CMP-FA1.0 (black circle) CMP-FA1.2 (black triangle up) CMP-FA3.2 (black triangle down) CMP-FA8.5 (black star) CMP-FA11.2 (black plus) with laccase at 2 nkat, 20 g L^{-1} in polymer, 25 °C in citrate/phosphate buffer (0.1 mol L^{-1} pH 5.5).

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BIOINFORMATICS SUPPORTED LIQUID CHROMATOGRAPHY – MASS SPECTROMETRY FOR CHARACTERIZATION OF BACTERIAL METABOLITES

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Keywords: metabolomics; lipidomics; natural products.

Introduction: Metabolomics enables the comprehensive characterization of the set of low-molecular-weight compounds being starting, intermediate, or end products of metabolic transformations in the living organisms. Therefore metabolomics provides information about mechanisms of action of new potential drugs [1]. Metabolomic fingerprinting or footprinting supported by bioinformatics provide a powerful tool for a comprehensive description of perturbations observed within bacteria, indicating up- or down-regulated bacterial molecules, altered metabolic pathways [2]. In that sense metabolomics depicts the metabolic response of bacteria to stress induced by natural products.

Methods: Because this field is poorly explored, the new findings about the influence of plant based and medicinal plants derived compounds on the bacteria metabolism studied with LC-MS metabolomics will be presented.

Results: These research provide insights into novel molecular targets within bacteria, identify biomarkers of cellular stress and indicate how reorganization of cell envelope impact the bacteria survival under influence of inhibiting agents.

Conclusions: LC-MS metabolomics supported by bioinformatics is a powerful tool for determination of changes in bacterial metabolism.

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

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DEVELOPMENT OF SAFE NANOAGROCHEMICALS – THE NANOPOROUS ROUTE

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Keywords: agrochemicals, nanoformulation, nanoporous material, natural zeolites, diatomaceous earth

Introduction: Nanoagrochemicals have the advantages of enhanced bioavailability of active ingredients and targeted delivery. In the meantime, nanoparticles proposed as agrochemicals raise environmental concerns. The utilization of siliceous natural nanomaterials (SNNMs) is a solution for preparing agrochemicals nanoformulations with a low environmental impact. SNNMs such as natural zeolites of diatomaceous earth are *biorationale*, i.e., are generally recognized as safe (GRAS) due to their long utilization without significant side effects and are without endocrine-disrupting, neurotoxic or immunotoxic effects; [1]. We developed nanoformulated foliar fertilizers, wherein we used SNNMs as nanoporous carriers. The presentation aims to present the evidence related to the nanoporous nature of such nanoformulation and the results obtained after applying the nanoformulated foliar fertilizer on the performance of stone fruits trees, apricot, and peach.

Materials and methods: The SNNMs were activated by heat (natural zeolites) and acid treatment (diatomaceous earth). The activated SNNMs were characterized by FT-IR, SEM, TEM, determination of the active surfaces, and the cation exchange capacity (CEC). The activated SNNMs were used to manufacture NanoFert Z (with zeolites) and NanoFert D (with diatomaceous earth). The nanoformulated foliar fertilizers were applied in 2020 and 2021 to treat stone fruits from Research Station for Fruit Growing Constanța.

Results: The nanoporous structure of activated SNMMs was demonstrated by the physicochemical characterization. Figure 1 presents the transmission electron microscopic images of activated SNNMs, wherein nanopores could be observed. Application of SNNMs together with foliar fertilizer reduced leaves temperature up to 4°Cand improve photosynthetic performance. The yield of apricot and peach trees was increased by 12.82% - 16.36%. The quality of fruits produced by the treated sone fruit trees was enhanced, with a higher accumulation of polyphenols.

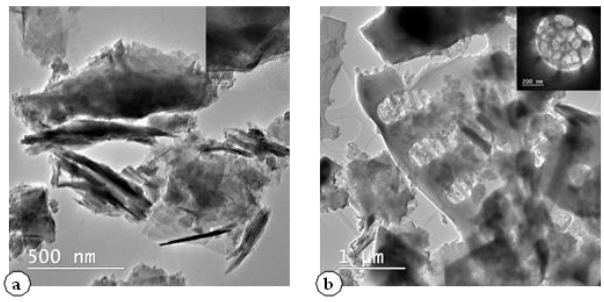

Fig. 1. Transmission electron microscopy images of activated SNNMs, (a) Rupea natural zeolites, (b) Pătârlagele diatomaceous earth. From ref. [2]

Conclusions: SNNMs act as bioactive carriers, slowly releasing nutrients from foliar fertilizers and improving fruit tree photosynthesis due to the particle film formation.

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

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POROUS MATERIALS AS PLATFORMS FOR THE DELIVERY OF POLYPHENOLS

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Keywords: mesoporous materials; drug delivery; polyphenols; dysbiosis.

Abstract: Drug delivery systems are intensively studied for a wide range of biomedical applications [1-3]. A special class of materials is related to the porous materials which, have the ability to host and release the biological active agents (BAA). The release of the biological active agents can be tuned according to the needs. Mesoporous Silica has a history of about 30 years and can be used for the release of a wide range of BAAs. The release is depending on the size of the pores and can be further tuned based on the surface functionalisation.

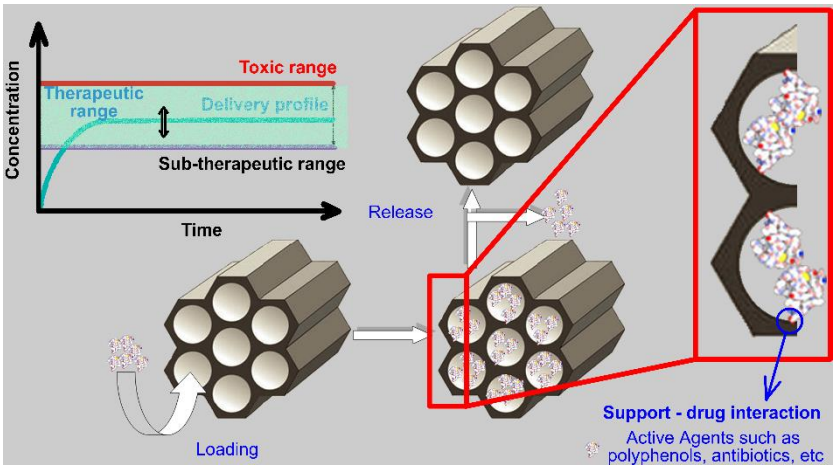

Figure 1. Mesoporous Silica-based drug delivery system for the treatment of dysbiosis

Starting from the advantages of the mesoporous silica supports, innovative drug delivery systems can be developed in order to obtain controlled, targeted drug delivery systems able to maintain the therapeutic needs of the BAAs (Fig 1). In this work, several examples of drug delivery systems based

on mesoporous silica and different polyphenols will be discussed highlighting the potential of their use in the treatment of different diseases and especially in the treatment of dysbiosis.

***Acknowledgements**: The authors gratefully acknowledge the support obtained by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI—UEFISCDI, project No. PN-III-P2-2.1-PED-2019-4018, contract 524PED/2020 within PNCDI III. Also, UPB is part of the COST action CA_20126: Network for research, innovation and product development on porous semiconductors and oxides.*

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ENGINEERING MATERIALS AND SENSORS FOR SUSTAINABLE ENVIRONMENTAL SYSTEMS

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Ensuring sustainability of our environment and food systems is critical in addressing environmental and food security challenges while achieving social, economic and environmental goals.

A key approach for advancing environmental sustainability is to develop affordable technologies and universal tools to help the public and communities learn more about their environment, test and monitor their water, air and food supplies. Portable and inexpensive sensors are increasingly important in providing rapid, real time and inexpensive measurements in the field.

A key issue in the development of these devices is selecting materials and creating suitable surface chemistry with recognition capabilities for the selective binding of target analytes for designing effective detection and remediation systems.

This presentation will discuss development, manufacturing, analytical characterization and deployment of portable sensors incorporating smart materials and receptor molecules for: i) monitoring active and functional ingredients in food, ii) assessing contamination in water and environmental systems, and iii) evaluating exposure to UV irradiation; and their possible implementation in the field.

The role of materials selection and implementation in environmental systems will be highlighted. These devices have a built-in detection mechanism, are portable and inexpensive and no specialized equipment is needed to perform analysis. Sensors are fabricated in large quantities from printable custom-made hydrogels or custom-designed paper and the low cost and ease of use are expected to advance large-scale food technologies, water and environmental monitoring applications.

These systems can provide important insight to preserve and avoid waste of natural resources and enhance environmental sustainability.

NANOBIOSENSORS FOR POINT-OF-CARE DIAGNOSTICS APPLICATIONS

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Keywords: nanobiosensors; paper-based biosensor.

Abstract: There is a high demand to develop innovative and cost-effective devices with interest for health care beside environment diagnostics, safety and security applications.

The development of such devices is strongly related to new materials and technologies being nanomaterials and nanotech-nology of special role.

We study how new nanomaterials such as nanoparticles, graphene, nano/micromotors can be integrated in simple sensors thanks to their advantageous properties. Beside plastic platforms physical, chemical and mechanical properties of cellulose in both micro and nanofiber-based networks combined with their abundance in nature or easy to prepare and control procedures are making these materials of great interest while looking for cost-efficient and green alternatives for device production technologies.

These devices should be REASSURED: Re-al-time connectivity, Ease of specimen collection, Affordable, Sensitive, Specific, User-friendly, Rapid, Robust, Equipment-free, Delivered to those who need it. How to design simple paper-based biosensor architectures? How to tune their analytical perfor-mance upon demand? How one can couple nanomaterials with paper and what is the benefit?

Which are the perspectives to link these simple platforms and detection technologies with mobile communication?

I will try to give responses to these questions through various interesting appli-cations related to protein, DNA and even contaminants detection all of extreme importance for diagnostics, nanotheranostics, environment control, safety and security.

LIPASE ENZYME FOR BIOMASS VALORIZATION

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Keywords: lipase; biocatalysis; biomass; renewable carbone.

Lipase enzymes are part of the hydrolases family acting on the carboxylic ester bonds. Physiologically, lipase catalysed the hydrolyses of triglyceride leading to di-/mono-glycerides, fatty acids and glycerol. Additionally, lipases can assist the (inter/trans)-esterification reactions in nonaqueous media. This versatile behaviour makes lipases one of the most useful enzyme in industrial area. The most significant applications of lipases have been mainly developed in the food, detergent, and pharmaceutical industries.

Actual industrial applications rely on the fossil resources for most of the industrial production. However, these natural sources are limited and their stock cannot be refilled in a short time. In addition, they are expensive and their exploitation has a negative impact on the environment. These are the main arguments taken under consideration to launch the new world strategy with biomass as renewable carbon source. So far, the biomass composition used as feedstock imposed at least three general platforms, such as sugar, terpenes and combustibles.

In this context, our research group explored the lignocellulose, turpentine, and oil as biomass samples with promising perspectives of renewable C sources. Lipase-based biocatalysis systems were adapted for biomass valorization leading to added-values products with high impact on food, cosmetics and pharmaceutical areas. Limonen/α-pinene/menthol derivatives, grafted lignin, silybin esters, glycerol carbonate and glycidol are few examples of the reaction products based on lipase biocatalysis developed in our lab. More details about these aspects demonstrating the high impact of lipase on the efficiency of the process biocatalysis especially for biomass as raw materials will be provided during the lecture.

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

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2. Keynote Lectures

CARBON MATERIALS FOR HYDROGEN STORAGE AND PRODUCTION

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Keywords: hydrogen storage; hydrogen production; catalyst; carbon; composites.

Introduction: As a catalyst support, activated carbon has many advantages, such as high surface area, tunable pore structure and surface chemistry, resistance to acidic or basic media, stability at high temperatures in inert or reduction atmosphere, as well as ability to recover the supported active metals [1].In order to improve the hydrogen sorption characteristics of magnesium a lot of investigations with the use of different additives (transition metals and their oxides, intermetallics, carbon materials) were performed. Depending of the nature of the additives the effects on the hydrogen sorption characteristics are different [2].
In this study nanoporous carbons with different textural and chemical surface characteristics were synthesized from different precursors. The obtained nanoporous carbons and metal loaded nanoporous carbons were characterized, and catalytic properties of metal loaded nanoporous carbons were tested in methanol decomposition to hydrogen. In addition, The absorption-desorption characteristics during prolonged cycling towards hydrogen of Mg-C composite are investigated.

Materials and methods: Synthetic carbons was prepared after treatment of the precursors with H_2SO_4 or HNO_3 at 200 ^oC until solidification. The solid product was subjected to further carbonization up to 600 ^oC; the activation of the obtained carbonizate was performed at 700-900^oC in the presence of water vapor, followed by thermal treatment in Ar atmosphere at 1000^oC.
The obtained nanoporous carbons and metal loaded samples were characterized by complex of various physicochemical methods, such as: low temperature physisorption of nitrogen, XRD, XPS, etc.

Results: The catalytic properties of metal loaded nanoporous carbons were tested in methanol decomposition to hydrogen. The dominant effect of activated carbon texture over the surface chemistry on the state and catalytic behavior of cobalt species was discussed.
The absorption-desorption characteristics during prolonged cycling towards hydrogen of Mg-C composite obtained by ball milling under Ar atmosphere are investigated. Mg-C composite reached about 7 wt% of hydrogen absorption capacity. The presence of nanoporous carbon influences positively on hydrogen absorption/desorption properties of magnesium, leading to enhanced rate of hydriding reaction and high absorption capacityduring prolonged cycling.

Conclusions: The catalytic properties of metal loaded nanoporous carbons were tested in methanol decomposition to hydrogen. Synthesized carbon materials are appropriate additive to magnesium based materials for hydrogen storage.

Acknowledgements: `
Authors kindly appreciate the funding by the Projects KP-06-29/2, KP-06-27/9 and Romanian-Bulgarian Project POMCAME.

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THE INVESTIGASIONS' IMPORTANCE IN CONSERVATION AND RESTORATION OF THE NATIONAL CULTURAL HERITAGE.

MOBILE CULTURAL HERITAGE AND HISTORICAL MONUMENTS

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Keywords: noninvasive and non-destructive analyzes, radiography, optical microscopy, interdisciplinarity

Abstract: National Cultural Heritage is the memorable synthesis of events and interactions within human society and, at the same time, the imprint left by human civilization in relation to the irrational and impersonal dimension of reality. The importance of this imprint is outlined not only by the role of landmark or source of history and civilization, but also by the fact that it has the power to support and strengthen society, crystallizing group values, local, national or global values.

By placing themselves at the same cultural landmarks, the members of a society are aware of partic-ipating in their own history, and protecting the values of their own history, the continuity of these values, is, or should be, a priority as high as the continuity of their own existence.

Thus, from the appearance of the first specialized institutions for the preservation and capitalization of cultural heritage to the development of auxiliary sciences in museology was a single step. The conservation and restoration of cultural assets in Romania has developed since 1975 from a limited number of Zonal Laboratories and reaching today almost every museum institution has a conservation and restoration department. The evolution of this field in the last 20 years is colossal, both from the point of view of the equipment, of the inventory that enters the laboratories, but also from the point of view of the professional training of the specialists.

More and more often the word interdisciplinarity and archaeometry is used in the field of conservation and restoration of the national cultural heritage. What is certain is that hyperspecialized and high-performance devices appear every two minutes, and the field of cultural heritage cannot keep up with funding. To this end, the interdisciplinarity of the team has led to colossal performances in terms of conservation, restoration and capitalization of the mobile national cultural heritage and historical monuments.

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RECOVERY OF WASTE INDUSTRIAL WATERS CONTAINING RED CONGO BY MULTIFUNCTIONALIZED MESOPOROUS SILICA NANOMATERIALS

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Keywords: platinum nanomaterials; functionalized mesoporous silica; Congo red; porphyrin derivatives.

Introduction: Colored wastewaters, containing toxic dyes such as: Congo red, methylene blue, malachite green, fuchsine B, bromothymol blue demand for dyes removal before of any other recovery treatment.

Comparing the efficiency of adsorbent materials used to remove dyes, functionalized silica derivatives, tailored to have specific surface areas exceeding 600 m^2/g, are among the best performing [1]. Particularly, for the removal of Congo red dye, silica and chitosan materials have also been shown in the literature to be effective adsorbents [2, 3].

Materials and methods: A set of mesoporous silica nanomaterials functionalized either with Pt-metalloporphyrin (***PtTAOPP-silica hybrid***), or with PtNPs (***PtNPs-silica hybrid***) or bis-functionalized with both the same porphyrin-base and PtNPs (***TAOPP-PtNPs)-silica hybrid***, were successfully used as adsorbent materials for methylene blue, malachite green, fuchsine B, bromothymol blue and Congo red [1,4].

Results: A novel example of monitoring (by UV-vis spectrometry) the capacity of the three impregnated-silica hybrid materials: ***PtTAOPP-silica hybrid***, ***PtNPs-silica hybrid*** and (***TAOPP-PtNPs)-silica hybrid*** in comparison with ***silica control***, for Congo red removal from wastewaters, is given in Figure 1.

From Figure 1 it is obvious that the intensity of the absorption intensity of the Congo red solution is significantly decreased, meaning that the most part of the dye was absorbed by the silica materials.

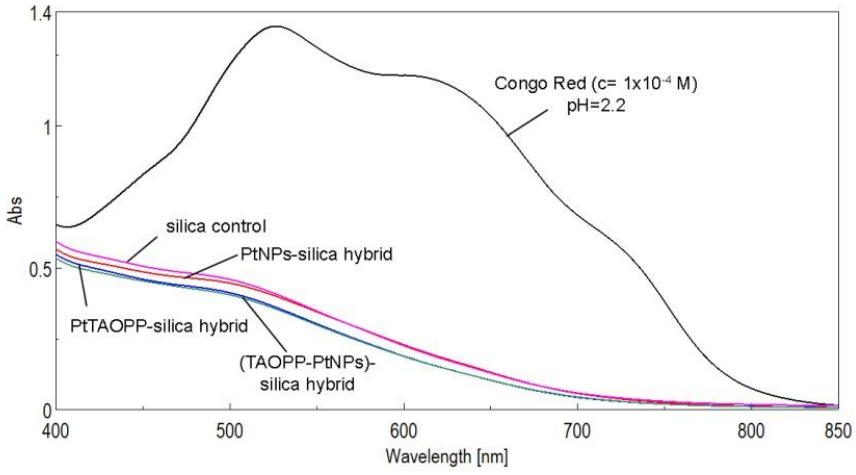

Figure 1. Overlapped UV-vis spectra of the remaining Red Congo concentration (initial conconcentration concentration **5 x 10^{-5} M Congo red**), after 160 min of contact between the Congo red solution and the functionalized silica hybrid materials. The solutions were centrifugated and filtrated.

After the Congo red was absorbed very interesting haystack aggregates, randomly distributed, were deposited on silica matrices, proving the absorption of the dye.

In the Figure 2 there are represented the atomic force microscopy (AFM) images of PtNPs-silica hybrid material after Congo red adsorption from waters containing an initial concentration of 5 x 10^{-5} M Congo red.

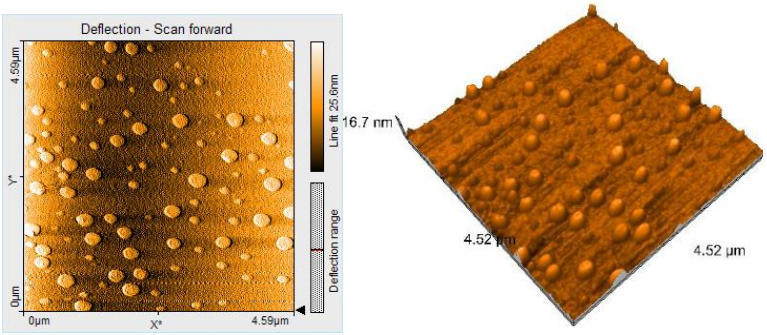

Figure 2. 2D (a) and 3D (b) AFM images of PtNPs-silica hybrid material after red Congo adsorbtion from waters containing 5 x 10^{-5} M Congo red

The results regarding the adsorption capacity of Congo red (for initial concentration of the dye: 5×10^{-5} M) by the tested silica materials, at a loading of 3.33g/L are:

- ***silica control***: q_e=8.25 mg\g; η= 78.13%
- ***PtTAOPP-silica hybrid***: q_e=8.43 mg\g; η= 79.84%
- ***(TAOPP-PtNPs)-silica hybrid***: q_e=8.73 mg\g; η= 82.75%
- ***PtNPs-silica hybrid***: q_e=8.02 mg\g; η= 76.03%

Conclusions: As easily can be concluded, all the functionalized silica materials have a good performance in removing red Congo dye, with the best result, a yield of 82%, registered for the bis-functionalized ***(TAOPP-PtNPs)-silica hybrid***.

Acknowledgements: *This research was funded by UEFISCDI-Romania, grant number 76-PCCDI/2018 belonging to PNIII-Future and Emerging Technologies and partially by Programme 3-2021 from the Institute of Chemistry "Coriolan Dragulescu".*

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BIOACCUMULATION POTENTIAL OF SELENIUM NANOPARTICLES

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Keywords: selenium, zerovalent nanoparticles, plant biofortification, metabolic regulator aquaculture

Introduction: Selenium is an essential poison with a very narrow physiological window [1]. In amino acids, selenium replaces sulfur. The proteins, including selenium amino acids, are more resistant to oxidation than proteins incorporating related sulfur amino acids [2]. Ionic selenium is more than 50 times more toxic than zerovalent selenium [3]. Zerovalent selenium tendency is to form hydrophobic nanoparticles in aqueous environments. Such hydrophobic nanoparticles are stabilized by amphiphilic biopolymers (e.g., chitosan, various protein), generating products that are considered effective agents for plant biofortification [3] or aquaculture metabolic regulation [4]. Such applications will be related to a high release in the environment of manufactured selenium nanoparticles. The hydrophobic nature of zerovalent selenium could enhance the bioaccumulation potential of the selenium nanoparticles released in the environment. This study aimed to evaluate the present knowledge related to the bioaccumulation of selenium nanoparticles

Materials and methods: An extensive bibliographic study was done to find and analyze the peer-reviewed papers referring to selenium nanoparticles bioaccumulation and biomagnification in sentinel organisms from the aquatic and soil food webs. The study was done in the main databases, Clarivate Web of Science, Scopus, CABI, PubMed. The comparison was made with the studies done related to the bioaccumulation of ionic selenium.

Results: Although several review papers discuss the bioaccumulation potential of selenium nanoparticles, only one experimental research article analyzed the accumulation of selenium nanoparticles red sea bream (*Pagrus major*). It is a lack of studies related to the effects of selenium nanoparticles on sentinel organisms from the soil food web – e.g., detritivores such as earthworms and functional guild of nematodes, such as fungal-feeding nematodes, bacterial-feeding nematode, plant-feeding nematodes and predators and omnivores. It is also a gape in knowledge related to bioaccumulation and biomagnification of selenium nanoparticles in organisms from the aquatic food web and related to the toxicity of selenium nanoparticles. There are plenty of data regarding the toxicity and bioaccumulation of selenium ionic species. It is necessary to determine the selenium nanoparticles toxicity for the aquatic environment primary producers (micro-algae), planktonic herbivores, other herbivores (Crustacea, Mollusca). A dose-response curve needs to be generated for each species bioassay and toxicity endpoints, including no observable effect concentration (NOEC), lowest observable effect concentration (LOEC), EC/LC10, and EC/LC50. Where possible, this data should be used to formulate a species sensitivity distribution (SSD) for the nanoparticles and help provide a holistic assessment of environmental risk for bioaccumulation and biomagnification.

Conclusions: There is a deep knowledge gap related to selenium nanoparticles toxicity, bioaccumulation, and biomagnification. This gap needs to be filled. Otherwise, the lack of knowledge related to selenium nanoparticle environmental behavior will hinder the potential application of selenium nanoparticles in agriculture and aquaculture.

Acknowledgments: *This research was funded by the NO Grants 2014-2021, under Project RO-NO-2019 540 STIM 4+, contract no. 14 / 2020.*

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BURNED CLAY CERAMICS USED IN WATER TREATMENT

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Keywords: ceramics; acid-base character; caustic module; water treatment;

This research is the result of an detailed study done on construction bricks and traditional ceramics of fired clay involved in water treatments, as last stage of filtration, after the active charcoal. Using the data obtained through the scanning electron microscope coupled with energy dispersive X-ray analysis and pH analyses, on the basis of the atomic composition and free concentration of hydronium ions, the normal caustic (Si/Al) and summative [(Si+Ti+FeIII+Cl)/(Al+Ca+Mg+Na+K)] modules were assessed. These data were correlated with the free acidity and, respectively, the capacity of absorption and ionic exchange of the Fe^{3+} and Al^{3+} ions [1-2].

The base-acidic activity of these groups from the structure of the fired-clay ceramics is due to the Si:Al stoichiometric ratio (known in practice as the caustic module, which varies from 1:1 to 4:1), but also to the position of the two coordination centers of the basic elementary cell [3-4].

The capacity for ionic exchange is attributed to the acidic structures Si(IV)–O^-H^+, Ti(IV)–O^-H^+, and Fe(III)–O^-H^+. The ceramics with high concentrations of Al(III), Ca(II), and Mg(II) have a character that varies from amphoteric to weakly basic, while those with Si(IV), Ti(IV), and Fe(III) vary from amphoteric to acidic.

As a conclusion, based on the caustic module of the ceramics with high capacity for ionic exchange, the materials presented good performances, even though are low cost, being waste materials or scraps from the technological flow of construction bricks/tiles or traditional ceramics.

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3. Oral Presentations

DESIGN OF NANOPLATFORMS FOR TARGETED DELIVERY OF IRINOTECAN

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Keywords: irinotecan, targeted action, mesoporous silica, natural polysaccharide

Introduction: Irinotecan is an antineoplastic used for the treatment of different types of cancer and solid tumors (rectal, colon, ovarian and glioblastoma) [1, 2]. However, its use is currently associated with serious side effects such as neutropenia, severe diarrhea that determines a significant dehydration and could potentially lead to death [2].An ideal drug delivery system for antitumoral agents needs to be designed to significantly improve the classical treatment, showing a protective action to prevent drug degradation, which is related to an increased drug concentration that enriches the tumoral sites. Moreover, the nanoparticles should be synthesized to ensure a selectivity for accumulation in tumoral cells to reduce side effects on healthy cells [3].
The aim of this study was to assess the influence of the support on the irinotecan release from developed systems, an investigation of how the carrier modification (folate moiety binding or ulvan deposition) can lead to a modulation of irinotecan release kinetics from proposed mesoporous silica-type carriers in correlation with their biological activity.

Materials and methods: The mesoporous supports and cytostatic agent-loaded supports were characterized by specific techniques: XRD, FT-IR spectroscopy, N_2 adsorption-desorption isotherms and thermal analysis. Cell viability of irinotecan loaded supports was tested on tumoral colon cells (Caco-2 and HT-29). The cell cycle analysis was performed using flow-cytometry (HT-29) for irinotecan alone or loaded on ulvan-silica supports in comparison with the corresponding nanoplatforms.

Results: A modulation of irinotecan release from proposed carriers was obtained, a slower release kinetics being observed from pristine SBA-15 carrier or modified with folate moiety (up to 40% in52h in PBS pH 5.7), while a faster release of cytostatic agent was obtained from silica-ulvan-type carriersfor which a complete release of antineoplastic agent was achieved in 8 h in PBS at a pH of 7.6. For irinotecan loaded silica-ulvan supports, a significant toxicity was noticed against tumoral cell line HT-29. Irinotecan loaded ulvan-silicananoplatforms influenced the cell-cycle (HT-29) at 250 µg/mL. It was observed that the cells are trapped in a higher proportion in the synthesis stage, therefore a reduction of cell growth is observed.

Conclusions: Iri@SBA-NH-folate system would be recommended for a targeted antitumoral action, with diminished side effects,whileif a complete delivery of the cytostatic agent in a shorter time is desired, silica-ulvan-type nanoplatform could be used for Irinotecan.

Acknowledgements: *This study was funded through Romanian UEFISCDI project no. 525PED/2020 (CYTOSIN).*

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POLYSACCHARIDE COATED MESOPOROUS SILICA FOR DRUG DELIVERY APPLICATIONS

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Keywords: mesoporous silica; polysaccharide; nanocomposite; targeted delivery.

Introduction: Currently, two widespread problems of therapeutic agents used in cancer therapy are the poor-water solubility and the side effects caused by their non-specific biodistribution.In this study, fucoidan-mesoporous silicananoplatforms are used foririnotecan encapsulation to improve its bioavailability [1].Fucoidan is a sulfated polysaccharide naturally occurring in brown algae [2].

Materials and methods: Mesoporous silica was synthesized through sol-gel method [3] and was further functionalized with positive charged organic moieties. Fucoidan was then adsorbed on the silica surface based on electrostatic interactions between organic groups bounded on silica surface and sulfate groups of fucoidan. Finally, the therapeutic agent was loaded through incipient wetness impregnation method. The resulted materials were investigated by thermogravimetric analysis, FT-IR spectroscopy, XRD analysis, N_2 adsorption/desorption isotherms, as well as scanning electron microscopy. The release profiles of irinotecan from silica-fucoidan-type nanocomposites were assessed in simulated body fluid, phosphate buffer solution pH=7.6.

Results: The quantity of fucoidan, which is retained on silica nanoparticles surface depends on the type of functional groups linked on silica. The presence of fucoidan influences the release profiles of irinotecan from silica-fucoidan nanocomposites.

Conclusions: Fucoidan-mesoporous silica nanocomposites represent a promising strategy to improve the targeting ability and bioavailability of therapeutic agents used for cancer treatment.

Acknowledgements:*This research was funded by the UEFISCDI (Romania) through the project no. 525PED/2020.*

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CHIRAL MAGNETIC AND LUMINESCENT MATERIALS BASED ON TRIDENTATE SCHIFF BASE LIGANDS

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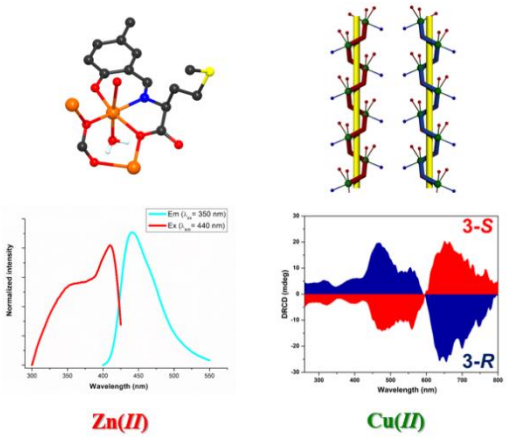
Keywords: chirality, luminescent materials, Schiff base ligands, magnetic coordination polymers.

Introduction: The most employed strategy for introducing the chiral information into a metal-ion based network consists of choosing of an enantiomerically pure ligand. In this respect, the usage of natural amino acids as chiral precursors is a simple and practical alternative. Moreover, the preservation of amino acid moieties within the resulting ligand can afford both an increased denticity and different kinds of hydrogen bonds that play a critical role in the self-assembly process.

Materials and methods: Following this idea, we present herein a chiral monodimensional Cu(II) and Zn(II) complexes based on L- or D-amino acid-containing tridentate Schiff ligand. The dehydrated form for copper(II), undergoes a single crystal to single crystal transformation to the dehydrated helical double chain, that generates significant changes in magnetic behaviour. [1] These complexes constructed from enantiopure Schiff-base ligands have been employed as metalloligands towards mercury(II) ions. [2]

Results: In this communication we present: (i) supramolecular architectures of simple organic chiral Schiff base, (ii) chiral 1-D ladder like coordination polymers constructed from these ligands, (iii) physical properties (fluorescence, CD spectra and magnetic behavior).



Conclusions: Drastic changes of the magnetic and optical properties were observed for all these solid phase transformations.

Acknowledgements: *This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, UEFISCDI, project number PN-III-P1-1.1-TE-2019-1345, within PNCDI III.*

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ANTIOXIDANT CAPACITY OF SOME EXTRACTS FROM ARONIA AND LONICERA FRUITS

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Key words. Antioxidant capacity, berries, flavonoids, phenolic compounds

Introduction: Literature studies have shown high levels of phenolic compounds in the fruits of *Aronia melanocarpa* (fam. *Rosaceae*, black chokeberry) and *Lonicera caerulea* L. (fam. *Caprifoliaceae*, Siberian blueberry). Aronia fruits contain high levels of flavonoids and have a significant antioxidant activity [1]. It has been observed that Lonicera fruits have many beneficial effects: anti-aging, anti-inflammatory, antimicrobial, anticancer, cardio- and neuroprotective activity, etc. [2]. In addition, it is known that all of these pathologies were strongly associated with free radicals formation and lipid peroxidation, also involved in many other diseases [1].

Materials and methods: This study has assessed the antioxidant capacity of ethanolic extracts from chokeberries and blueberries obtained by Soxhlet extraction, maceration, ultrasounds, and microwave-assisted extraction methods. First, the phenol compounds from extracts were analysed by HPLC [3]. Then, the antioxidant capacity was determined by the DPPH$^{\bullet}$ method, and the total phenol (TP) content was investigated using the Folin-Ciocalteu reagent (spectrophotometric methods) [4].

Results: The ranged of quantified extraction yields varied from 10.8 to 15.2 g semi-solid extract / 100 g fruit. The p-coumaric acid, caffeic acid, chlorogenic acid, rutin, and epicatechin were identified in the chromatographic method in all extracts. The scavenging capacity of DPPH$^{\bullet}$ was expressed as μg antioxidant/mL equivalents and varied between 2.07 ± 0.066 and 4.01 ± 0.069 for gallic acid, 4.25 ± 0.13 and 8.15 ± 0.14 for caffeic acid, 23.4 ± 0.63 and 41.6 ± 0.65 for quercetin, 22 ± 0.52 and 37.0 ± 0.54 rutin and 37.2 ± 1.1 and 68.3 ± 1.1 for morin. Ultrasounds assistant extraction was the most efficient method of extraction.
The analysed berries extracts have also a high antioxidant capacity, expressed in terms of flavonoid equivalents. The ultrasounds extraction was the most efficient method of extraction.

Conclusion: This study concludes that Aronia and Lonicera fruits show high antioxidants content, proved by chromatographic and spectrophotometric methods.

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MESOPOROUS SILICA SYSTEMS LOADED WITH POLYPHENOLS

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Keywords: mesoporous silica, p-coumaric acid, trans-ferulic acid, epicatechin, catechin.

Introduction: The work consists in obtaining mesoporous silica systems loaded with polyphenolic compounds (p-coumaric acid, trans-ferulic acid, epicatechin, catechin). Polyphenolic compounds are used as biologically active agents for the treatment of various diseases, these compounds having high antioxidant activity.

Materials and methods: As a carrier, two types of mesoporous silica have been proposed and obtained according to the classical templating method with cetyltrimethylammonium bromide - CTAB under alkaline conditions. Polyphenols (p-coumaric acid, trans-ferulic acid, epicatechin, catechin) were loaded under vacuum into the mesoporous silica.

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

Conclusions: In this study, mesoporous silica systems were obtained and further loaded with p-coumaric acid, trans-ferulic acid, epicatechin and catechin. The results highlight that the materials can be used as drug delivery systems the results in relevant environments (simulated gastric fluid - SGF and simulated intestinal fluid - SIF) being promising. The proposed loading methodology is suitable for loading these natural agents, mostly, inside the pores.

Acknowledgement: Authors recognize financial support from the UEFISCDI through PN-III-P2-2.1-PED-2019 project: "Evaluarea potentialului de exploatare a materialelor poroase in tratarea disbiozelor microbiotei" no. 524PED/2020.

THE POTENTIAL OF BIOPOLYESTERS AS PLASTICIZERS FOR POLYLACTIDE

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Keywords: polyesters, poly(lactic acid), blends, ductility

Introduction: It is estimated that fossil fuel resource will dwindle by the end of 2050 if the current utilization rate persists [1]. Consequently, the scientific community has searched for new polymer materials that can decrease the consumption of fossil plastics, with focus on biodegradable bioplastics. Poly(lactic acid) (PLA) is the frontrunner of bioplastics due to its excellent mechanical properties, compostability, biobased nature and a cost comparable to conventional polyolefins [2, 3]. Still, its inherent brittleness often hinders its utilization where ductility of the material is required. Therefore, in this study, we focus on solving this issue by synthesizing bio-based polyesters for tuning PLA's ductility. These materials were obtained from 1,4-butanediol (B) and sebacic acid (S) in various molar ratios using titanium (IV) butoxide (TBT) as a catalyst.

Materials and methods: Sebacic acid (S) (purity 99%), 1,4-butanediol (purity 99%) (B) and titanium (IV) butoxide (TBT) were used as received without further purifications. PLA was blended with the obtained bio-based polyesters via melt mixing. The obtained polyesters and PLA based blends were characterized by FT-IR, TGA, DSC, DMA, water contact angle, and tensile properties.

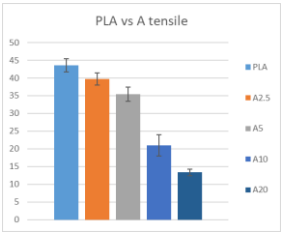

Figure 1. PLA tensile strength reduction by blending

Results: The introduction of the bio-based polyesters in the PLA matrix led to a monotonous decrease of the tensile strength, along with a considerable increase of elongation at break.

Conclusions: The proposed bio-based polyesters exhibited a good plasticizing effect on PLA thus broadening its applications.

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number 67TE/2020, within PNCDI III.*

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EFFECT OF NANOCELLULOSE TYPE ON THE PROPERTIES OF A BIO-BASED EPOXY SYSTEM

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Keywords: nanocellulose; epoxidized linseed oil; thermal properties

Introduction: With the continuous depletion of fossil oils and environmental concerns, there is an urgent need to develop polymeric materials from renewable resources [1, 2]. Epoxy resins are thermoset polymers that are recognized for their tunable properties (adhesiveness, tensile and electrical strength, stiffness, heat and chemical resistance) and for their various industrial and domestic applications. Still, the main drawback of epoxy resin is its brittleness. Thus, the addition of functional vegetable oils such as epoxidized linseed oil (ELO) can improve the toughness of epoxy resin while increasing the bio-based content of the final materials [1]. The goal of this work is to study the influence of composition, cross-linking conditions, and addition of reinforcing agents on the properties of a bio-based epoxy resin obtained from epoxidized linseed oil (ELO) and a commercial hardener. Nanocellulose from common sources (microcrystalline cellulose MC) and agro-industrial residues (plum seeds shells-SC) were used as fillers in the epoxy-systems.

Materials and methods: Epoxidized linseed oil (ELO, TRAQUISA, Spain), Epilox - Hardener H 10-30 (G) (NANOCHEM, Romania), microcrystalline cellulose (MC) (20 μm, Aldrich) and plum seed cellulose (SC) (laboratory obtained via acidic hydrolysis) were used as raw materials. A 2/1 weight ratio of ELO/G was used to obtain the cross-linked materials. Two types of cellulosic modifiers, MC and SC, were used to reinforce the epoxy systems. The resulted epoxy composite systems were characterized by means of FT-IR, TGA, DMA and water contact angle analysis.

Results: TGA analysis showed that the onset and maximum degradation temperatures were increased upon employing of an extra cross-linking step at 140°C or by addition of the cellulosic fillers (Fig. 1). Moreover, an increase of the storage modulus of the final epoxy systems was attained as a result of cellulosic fillers addition as seen in DMA results.

Conclusions: Addition of low weight percentage (0.5%) of cellulose modifiers (MC and SC) enhanced the thermal stability of the epoxy system and had a reinforcing effect by increasing the storage modulus of the final materials.

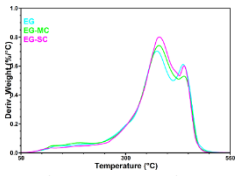

Figure 1. DTG of cellulose reinforced epoxy resins

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PED-2019-5002, no. 530/PED – EPOCEL, within PNCDI III.*

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IMPREGNATION OF 3D PRINTED ZnO-CNT BASED STRUCTURES WITH PHASE CHANGE MATERIALS FOR ENERGY STORAGE

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Keywords: nanocomposites; 3D printing; phase change material; energy storage; carbon nanotubes.

Introduction: Carbon nanotubes (CNT) is a semiconductor material which can be used in the energy storage field due to its high electrical conductivity. Combining CNT capacitance with a pseudocapacitive material such as zinc oxide a composite with improved structural and electrochemical features for the field of energy storage devices can be obtained. In order to assure an efficient thermal management of the composite material, phase change materials (PCM) can be used. PCM allow the storage and release of the thermal energy using high values of latent heat with an improved energy density transfer. The purpose of this study is to obtain via a robocasting technology ZnO-CNT based porous structures which will further be impregnated with PCM [1-3].

Materials and methods: ZnO-CNT nanocomposite powder synthesized by hydrothermal method is mixed with organic additives in order to obtain a printable paste. The composite pastes are processed using the 3D-BioPlotter Starter system. The CAD models were obtained using SolidWorks 2019. The designed square cuboids with dimensions of 10x10x5 mm had the printing parameters as follows strand thickness of 0.4 mm, distance between strands of 1.3 mm and the line-based pattern with a rotation angle between 2 consecutive layers of 0° and 90°. Using a solvothermal process at high pressure the 3D printed porous structures were impregnated in sodium nitrate which plays the role of the PCM. The morphology of ZnO-CNT 3D structures before and after impregnation was analyzed using scanning electron microscopy (SEM). In order to prove the thermal properties of the impregnated structures the DSC and DSC-TG analysis were performed on both impregnated and nonimpregnated samples.

Results: In this study the 3D printed ZnO-CNT structures were impregnated in sodium nitrate (figure 1). The SEM micrographs of the printed samples before and after impregnation were performed and it was noticed that the printed samples before impregnation respected the printing parameters, and the impregnated samples had the strand thickness increased which is a sign of the $NaNO_3$ presence. Using DSC and DSC-TG the presence of sodium nitrate was established and by performing successive cooling-heating cycles the thermal stability of the impregnated samples was proved.

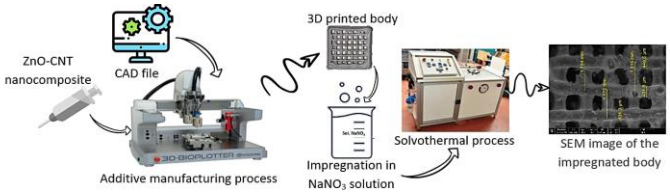

Figure 1. Ilustration of the 3D printing and impreganation with PCM processes.

Conclusions: CNT-ZnO 3D structure that respected the printing parameters were fabricated via a robocasting technique. The obtained 3D bodies were successfully impregnated in PCM and their thermal stability was confirmed by successive cooling-heating cycles.

Acknowledgements: The authors very much appreciate the support of Ioan Albert TUDOR for performing the investigation of 3D structures by thermal analyses and Paul STANCIU for performing solvothermal impregnation of 3D structures. This work was performed through the Core Program, carried out with the support of MCI, project no. PN19190101/2019-2022.

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KEY INTERMEDIATES FOR BUIDING THE ω-SIDE CHAIN OF PROSTAGLANDINS WITH A CONSTRAINED PENTALENOFURANE SCAFFOLD LINKED TO C-15 CARBON ATOM TO DIMINISH THE PG INACTIVATION

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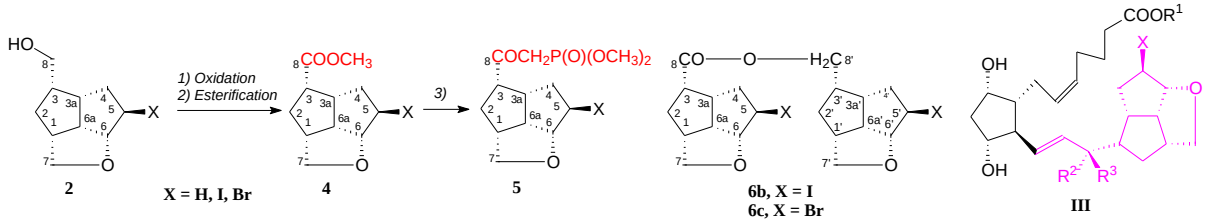
Keywords: halogeno-pentalenofurane scafold; pentalenofurane esters; penalenofurane-β-ketophosphonates; X-ray analysis

Introduction: The inactivation of prostaglandin (PG) and prostaglandin analogs (PGs) is realized by enzyme oxidation of the 15α-OH to the 15-keto group via the 15-PGDH pathway. To slow down this oxidation, some structural modifications have been done: the introduction of a 15-methyl group, a 16-OH,16-methyl group, two methyl groups at C_{16}, cyclopentyl and cyclohexyl scafolds, etc [1]. In this direction, we previously introduced bicyclo[3.3.0]octene or bicylo[3.3.0]octane fragments in the β-ketophosphonates [2,3]. Now we present the synthesis of new key β-ketophosphonates with a pentalenofurane scaffold linked to the keto group (Scheme 1).

Materials and methods: ***Synthesis of the compounds*** started from the pentalenofurane alcohols **2** by their oxidation to the acids **3**, esterification of the acids **3** to methyl esters **4** and the reaction of the esters **4** with lithium salt of dimethyl methanephosphonate at low temperature. The secondary compounds **6b** and **6c** were formed in small amounts in the oxidation reactions of **2b** and **2c**, and the NMR spectroscopy showed that their structure is that of an ester of the acid with the starting alcohol. Their molecular structures were confirmed by single crystal X-ray determination method for **6c** and XRPD powder method for **6b**.



Scheme 1. Synthesis of pentalenofurane _-ketophosphonates **5a**–**5c**; by-products (**6b** and **6c**) in the oxidation of alcohols 2 and PG analog III with a pentalenofurane scaffold linked to 15-C atom.

Results: Three key intermediate β-ketophosphonates **5** were synthesized, fully characterized, and used for obtaining PGs analogs of type **III**. The bulky constrained pentalenofurane scaffold in the ω-side chain is waited to slow down the inactivation of the PGs analogs by enzyme 15-PGDH pathway.

Conclusions: The synthesis of key β-ketophosphonates with a pentalenofurane scaffold linked to the keto group was realized in a sequence of three high yield reactions. Two by-products formed in the oxidation of alcohols **2** were characterized by NMR and confirmed by single crystal X-ray crystallography for **6c** and XRPD powder method for **6b**. The key intermediates **5** were used for obtaining the PG analogs III (Scheme 1).

Acknowledgements: *The funds were done by Orizont-2000, 45/1999/1.*

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EXTRACTION BY ULTRASOUNDS AND CHARACTERIZATION OF BIOACTIVE COMPOUNDS FROM *ZINGIBER OFFICINALE*

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Keywords: ginger, bioactive compounds, antioxidant activity, absorbance, ultrasonic extraction.

Introduction: Ginger *(Zingiber officinale)* is an herbaceous perennial plant which contains phenolic chemicals, primarily gingerol and shogaol [1], that are responsible for the many bioactivities of ginger, including antioxidant [2], anti-inflammatory, antibacterial and anticancer properties [3]. The usual process used for separation of active compounds include maceration and Soxhlet extraction. [4] The objective of this work is to extract the bioactive compounds of ginger, using a modern extraction method, ultrasonic assisted extraction, as well as the characterization of their structural properties and the antioxidant assay of the extracts.

Materials and methods: The organic ginger powder was added to a jacketed beaker cooling system, together with solvent, isopropyl alcohol, and stirred using an ultrasonic processor. Extraction tests were performed by variation of extraction time and also the load of ginger powder used, in order to determine the duration of the operation and the necessary quantity of ginger to obtain the highest amount of active ingredients in the extract. The obtained extracts were subjected to filtration. A sample was taken from the obtained solution to perform thin layer chromatography, using as a fixed phase a plastic sheet Silicagel F_{254} and a mixture of solvents as eluent (e.g. hexane:acetone). Antioxidant activity was determined using DPPH (1,1-difenil-2-picrilhidrazil) method.

Results: For the evaluation of the obtained extracts, UV-Vis absorbance measurements were performed. The plant residues left after the extractions were characterized by reflectance measurements and FTIR spectra. The efficiency of the extraction process according to various parameters was followed by the spectrophotometric characterization of the remaining plant residues. The increase in reflectance in the case of residues confirms that a considerable amount of substances has been extracted from the raw material. Coordinates in the CIELab system were used to explain the process of loss of color intensity and the process of oxidation of certain compounds in the residue. From the comparison of the IR spectra of the raw material and the residues, it results that the extractions were effective in incorporating a significant amount of useful organic substances from the plant. Antioxidant assay was determined by DPPH method with ascorbic acid and absorbance was measured at 520 nm.

Conclusions: Optimal parameters for the extraction of active compounds from ginger were established by the ultrasonic method which proved to be more efficient than the classical methods due to the shorter extraction time and the use of a smaller amount of solvent. The spectrometric analyzes performed confirm the isolation of the bioactive compounds in the extract. Their identification was made by thin layer chromatography.

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PED-2019-1471, within PNCDI III.*

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STABILITY OF BIOACTIVE EXTRACTS FROM *PORPHYRIDIUM PURPUREUM* MICROALGAE BIOMASS UNDER VARIOUS STRESS FACTORS

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Keywords: Porphyridium purpureum, bioactive extracts, stability, stress factors

Introduction: Nowadays, the interest for high-quality products of natural origin is increasing worldwide. Algae derived products have been recognized to have great potential as a rich source of bioactive compounds and their importance is growing rapidly. The bioactive compounds contained in algae extracts are: proteins, unsaturated fatty acids, antioxidants (polyphenols, vitamin E, vitamin C) and other pigments (phycobiliproteins, carotenoids and chlorophylls). Such bioactive compounds have antibacterial, anti-inflammatory, antiviral, antifungal and antioxidative properties, with numerous health benefits. Algal extracts are widely used as biostimulants, bioregulators, nutritional supplements, pharmaceutical, food and cosmetics colorants [1].
The present study investigates the stability of bioactive extracts obtained from *Porphyridium purpureum* microalgae biomass subjected to a series of stress factors generated by exposure to a light source for diferent time intervals and at different temperatures.

Materials and methods: Experiments were performed using *Porphyridium purpureum* microalgae strain from ICECHIM's strain collection, inoculated in its specific growth medium, ASW (artificial sea water). After cultivation, microalgae biomass was harvested, dried and grinded for more efficient processing. Extractions of bioactive compounds from *Porphyridium purpureum* powder were obtained using different solvents. For the phycobiliproteins extracts, a sodium phosphate buffer solution with a pH value of 6.8, was used, while for the chlorophylls and carotenoids extracts, the proposed solvents were acetone, methanol and ethanol. Various exposure times between 3 h and 40 h, at a light source with an intensity of 36.5 $\mu moli \cdot m^{-2}s \cdot^{-1}$ and temperatures between 30°C and 70°C were used.To observe and compare the stability of the extracts, the absorbances of the samples were measured spectrophotometrically at wavelenghts specific to the biocompound monitored, before and after applying the stress factors.

Results: It was observed, in the case of the chlorophylls and carotenoids extract, that the presence of a light source played a more significant role on the stability of biocompounds, with up to 90% degradation after 40h of exposure, no matter which extraction solvent was used, with chlorophyll a being the most abundant pigment and at the same time the most vulnerable to degradation as a result of light exposure. In the case of using temperature as a stress factor, it was observed that for a lower temperature, of about 40°C, the concentrations of both chlorophyll and phycobiliproteins extracts were reduced by a maximum of 20%, but when a higher temperature of 70°C was proposed for the phycobiliproteins extract, a few minutes of exposure to this stress factor were sufficient to reach almost complete degradation of biocompounds.

Conclusions: Studies were carried out for the obtained sample of solvent containing the bioactive compounds, in order to evaluate their stability in different stress conditions. Light stress proved to be a more important factor for the stability of chlorophylls, while high temperatures led to faster degradation of phycobiliproteins.

Acknowledgements: *"This work was supported by a grant of the Romanian Ministry of Education and Research, project number PN 19.23.01.01, and a grant of UEFISCDI, project number PN-III-P1-1.1-TE-2019-1842, within PNCDI III."*

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MODELLING THE SEED COATING PROCESS ON MUNG BEANS USING SODIUM ALGINATE EXTRACTED FROM *CYSTOSEIRA BARBATA*

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Keywords: seed coating; design of experiments; sodium alginate

Introduction: Efficient, sustainable and productive agriculture in the 21st century faces new challenges that will ultimately lead to the development of new materials and technologies in order to keep up with the ever-growing needs of a continuously growing world population, currently at 7.9 billion and estimated to reach its maximum in 2100 at about 11 billion. The characteristics of the perfect solution would require finding the right formula for increasing production, reducing the risk of crop diseases using biodegradable materials and is readily available around the world and which also does not lead to the accumulation of secondary compounds in the soil. Our approach is to use a commonly available compound extracted from brown seaweeds, sodium alginate, that has been shown to have plant-growth promoting effects and also has the property of forming mechanically strong films which are also biodegradable. The process used, bottom spray fluidized bed coating (Wurster process) [1], can achieve the desired result in mild conditions.

Materials and methods: The coating process is characterized using factorial experimental designs which describe the relative importance of chosen factors with a minimum of necessary runs. The most important factor is shown to be the flow of the liquid feed containing sodium alginate and concentration of glycerol. To characterize the dynamic process three response variables were determined for each run: final pressure in the unit, total time and the total mass of sodium alginate solution introduced in the system. The drying process was also characterized and modeled. A mass balance model for ideally shaped seeds was derived. The results were checked by SEM.

Results: An optimum combination of parameter values was obtained which ensures maximum seed coating efficiency. The drying of *Cystoseira barbata* alginate suggested that under the drying conditions used in this work, a mass transfer coefficient of 0.0023 m/s was obtained by regression. The proposed model suggested a reasonable value for the expected film thickness (28.6 μm) with values obtained by SEM (39.8 μm).

Conclusions: The seed coating process was optimized with respect to the proposed process parameters and a better understanding was developed with respect to the significant phenomena involved thus achieving a repeatable and practical setup. Sodium alginate seems to be a good solution for seed coating technology, with a potential dual function: as a coating agent and biostimulant.

Acknowledgements: This work was funded by the subsidiary contract no. 1230 / 02.07.2020 of project POC-A1-A1.2.3-G-2015-P_40-452-"Sequential processes of closing the side streams from bioeconomy and innovative (bio)products resulting from it" (SECVENT) 81/2016 funded by cohesion funds of the European Union.

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CARBON NANOMATERIALS FROM BIOMASS WASTES

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Keywords: carbon nanomaterials; hydrothermal carbonization; carbon adsorbents; biomass; wastes.

Introduction: Biomass represents sequestrated carbon from environment by plants through photosynthesis and nutrition. Burning biomass is a polluting process that releases into atmosphere greenhouse gases (CO_2, CO, NO_x) and it should be globally avoided. An environmentally friendly biomass conversion method, with plenty capitalization opportunities, is represented by the hermetic hydrothermal carbonization with super-heated sub-critical water [1,2]. Between 110-250°C, super-heated water acts like a mild acidic solvent and brakes hemicellulose structure by dehydro/carboxylation into alcohols, aldehydes, (poli)phenols, aminoacids, organic acids and other water-soluble molecules, while the remaining ligno-cellulosic solid is named hydrochar and has adsorbent properties. Over 250°C are favored the decarbonylation, denitrogenation and aromatization reactions, which lead to a nano(micro)porous biochar and carbon nanomaterials.

Materials and methods: Residual biomass of wheat straws was submitted to hydrothermal carbonization at temperatures between 140-260°C, autogenerated pressures between 20-80 atm and 1:5-1:10 biomass:water mass ratios. The obtained carbon nanomaterials were analytically characterized by transmission electron microscopy (TEM), Fourier Transform Infra-Red spectroscopy (FT-IR), X-Ray diffraction (XRD), nitrogen adsorption/desorption porosimetry, and thermogravimetric analysis (TGA).

Results: TEM images showed different shapes of carbon nanomaterials like nanospheres, nanowhiskers and carbon nanodots (Fig.1a). FT-IR spectroscopy evidenced adsorption bands of higher intensity for hydrogen bonds and functional groups with oxygen at lower reaction temperatures and pressures. XRD analysis showed specific diffraction patterns for the graphitic carbon structures obtained at higher temperatures. Nitrogen adsorption/desorption analysis evidenced a high N_2 adsorption at P/P0<0.1, which indicates the presence of many micropores (<2 nm) and also mesopores (2-50 nm) at 0.1<P/P0<0.5, with a total surface area of 10-15 m^2/g, 100 times higher than initial raw materials (Fig.1b). TGA evidenced a higher lignin-type carbon with increased reaction temperature.

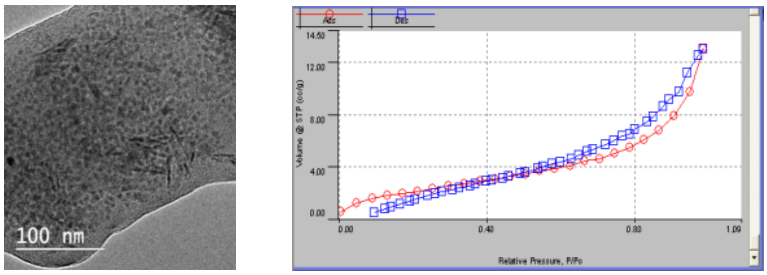

Figure 1. a) TEM image of carbon nanowhiskers and nanodots; b) N_2 adsorption/desorption isotherm.

Conclusions: Hydrothermal carbonization is a "green" and facile method of converting residual biomass into carbon nanomaterials with high porosity and graphite-like structure.

Acknowledgements: *This work was supported by the Government of Romania, Ministry of Research, Innovation and Digitalization Nucleu Programme in the frame of the Chem-Ergent project PN19.23.03.01 Contract no. 23N/2019.*

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APPLICATIONS OF DEEP EUTECTIC SOLVENTS FOR LIGNIN EXTRACTION

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Keywords: DES, BSG, lignin, extraction

Introduction: Deep eutectic solvents (DESs) represent a new class of compounds with properties similar to ionic liquids, that have a significantly lower boiling point compared to the boiling point of each component, as well as practical applications on extractions from lignocellulosic biomass. Since 2004 they have been studied in terms of their applicability in the biodegradation of biomass of different types, the field being in continuous development [1]. Several DESs were shown to be good solvents for lignin solubilization and extraction from lignocellulosic biomass [2].

Lignin is a natural, complex aromatic hetero-polymer resulting from the radical polymerization of guiacil (G) units derived from coniferyl alcohol, syringyl (S) derived from synapilic alcohol, p-hydroxyphenyl (H) resulting from the p-coumaril precursor [3]. Fragmentation or depolymerization of lignin leads to practical applications that allow the implementation of lignin in the food industry, as a precursor in the synthesis of some drugs, in engineering, as well as in genomics [4]. In this study we prepared, characterized and tested several DESs for lignin solubilization and extraction.

Materials and methods: High purity reagents (over 98%) purchased from Merck, Scharlau, Sigma Aldrich were used for the experimental analyzes. The FT-IR technique was applied to characterize DESs and lignocellulosic material. Other parameters, such as refractive indices, densities, pH, and surface tension were determined. UV-VIS spectrophotometric analyzes was used for determining the concentrations of extracted and solubilized lignin based on calibration curve for each DES. The application of DESs for processing of lignocellulosic biomass was carried out under certain mixing conditions, temperature, and time intervals.

Results: The solvents showed different refractive indices, densities, pH, and surface tension, which are influenced by the types of molecular interactions, hydrogen bonds, and the arrangement of molecules within the solvent. The ability to solubilize and/or extract lignin depended on the type of DES, water content and other parameters. The best DESs for lignin extraction were based on organic acids. Not all DESs that solubilized lignin were good candidates for lignin extraction.

Conclusions: Several DESs were characterized and subsequently applied in the process of extraction and solubilization of lignin from lignocellulosic biomass. Some DESs, especially those which include organic acids, are good candidates for lignin extraction.

Acknowledgements: *This work was supported by project POC-A1-A1.2.3-G-2015-P_40_352-SECVENT, contract funded by cohesion funds of the European Union, subsidiary project 1500/2020.*

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SOLVENTS' INFLUENCE ON *ZIZIPHUS FOLIUM* YIELD EXTRACTS

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Keywords: ziziphus, antioxidant, anticancer, plant extracts, solvents, DPPH

Introduction: Recent pharmacological results have shown that polysaccharides, flavonoids, triterpene and betulinic acids are the main active ingredients of the genus Ziziphus, contributing to its immunomodulatory and hematopoietic functions [1], antioxidant activities [2], anti-inflammatory, anticancer [3], as well as beneficial effects on the cardiovascular system [4].

Materials and methods: The extracts were obtained by continuous extraction with Soxhlet, maceration, ultrasound and microwave. In all cases, 5 g of thawed plant were extracted in ethanol 96%. The antioxidant effect was verified by DPPH● method. The reagents used were: DPPH ● (1,1-diphenyl-2-picrylhydrazyl) (Alpha Aesar), gallic acid, caffeic acid (Sigma), ethanol 96% and methanol abs (Chemical Co.).

Results: In the case of microwave method, we used four different solvents and the highest extraction yield was established for ethanol-water solution (v:v). The antioxidant capacity was determined by the spectrophotometric method with DPPH ●. The values of antioxidant capacity expressed in caffeic acid and gallic acid equivalents.

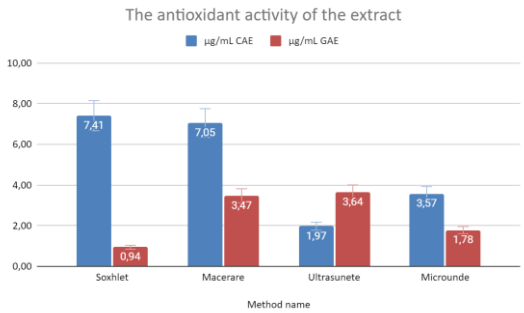

Figure 1. The antioxidant activity of the *Ziziphus folium* extract

Conclusions: The aim of the work was to find a non-toxic solvent used to obtain a good extraction efficiency of semi-solid plant products. The values of antioxidant capacity were found and expressed in caffeic acid and gallic acid equivalents. The antioxidant capacity of the extracts expressed in caffeic acid equivalents was higher than if it was expressed in gallic acid equivalents, regardless of the method.

Acknowledgements: *This work was supported by University of Bucharest, Faculty of Chemistry*

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FLOW CHEMISTRY FOR DEVELOPING PLANT BIOSTIMULANTS: DESIGNED GRAFTING OF HYDROXYCINNAMIC ACIDS TO CHITOSAN

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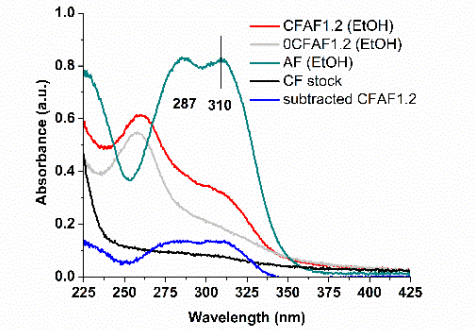
Keywords: plant biostimulants; flow chemistry; chitosan; ferulic acid; grafting.

Introduction: A plant biostimulant (PBs) is any substance or microorganism applied to plants and intended to enhance nutrition efficiency, abiotic stress tolerance, and/or crop quality traits, regardless of its nutrients content. The first generation of organic plant biostimulants were complex mixtures obtained by extracting the existing organic fertilizer/soil improvers. The second generation of plant biostimulants are products based on the selected active ingredient. One of these active ingredients is chitosan. One of the problems is that chitosan is not water-soluble and cannot be applied easily to plants. Chemical covalent grafting of hydroxycinnamic acids could solve this problem and improve plant biostimulant activity. We investigated the grafting approach by flow chemistry and compared the results of the flow system with the batch reaction.

Materials and methods: We made batch and in-flow grafting reactions based on the radical grafting methods. After the reaction, the conjugate was dialyzed for 3 days and lyophilized. Solubility was studied in water. The lyophilized grafted conjugates were characterized with FTIR, UV-Vis, TEM, DLS and analyzed for their antioxidant activities. We compared the reaction performed in batch with the ones performed in flow chemistry.

Results: We determined the qualitative grafting of ferulic acid of dialyzed and lyophilized powder solubilize in water. The presence of absorbance at 287 and 310 nm corresponding to ferulic acid was observed on the hybrid [1]. The antioxidant activities were maintained for the flow chemistry reactions when compared to batch. FTIR showed an appearing peak corresponding to amide II groups, confirming the grafting. TEM images and DLS revealed the formation of particles of dimensions of around a few hundred nm.



Conclusions: Grafting was successful, but we need a more rapid quantitative determination method. Flow chemistry decreased the reaction time 10 times when compared to batch. Parameters such as pressure and temperature are to be optimized further, together with other molar ratios.

Acknowledgments: *The research leading to these results has received funding from the NO Grants 2014-2021, under Project RO-NO-2019-540 STIM 4+, contract no. 14 / 2020. The authors thank dr. Bogdan Trică for his experimental support.*

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OPTIMIZED EXTRACTION OF GLYCOPROTEINS FROM *GANODERMA LUCIDUM*

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Keywords: glycoproteins; Ganoderma lucidum; factorial design.

Introduction: *Ganoderma* mushrooms are a valuable source of bioactive compounds [1]. One type of these ones are glycoproteins, which were demonstrated to be able to support symbiotic bacterial biofilm formation and dispersal of dysbiotic biofilm [2]. The aim of this study was to optimize the extraction of glycoproteins from *Ganoderma lucidum*, in order to use them in various applications, such as obtaining oral health products.

Materials and methods: A three factors-two levels optimization plan was used for glycoprotein extraction from *Ganoderma lucidum* powder. The chosen plan aims to evaluate the statistical significance of the interaction terms: three main effects (A, B, C), three secondary interaction effects (AxB, BxC, AxC) and a tertiary effect (AxBxC). Following ANOVA analysis, each effect is associated with a p value which is a measure of the correlation between effect and response variabilities. Total protein was determined using copper-based assay (Biuret) against a bovine serum albumin (BSA) standard curve [3]. The molecular weights of the proteins were analysed on sodium dodecyl sulphate - Polyacrylamide Gel Electrophoresis (SDS-PAGE). Total water-soluble carbohydrates were measured using phenol-sulfuric acid (PSA) assay against a glucose standard curve. The extracts were characterized using Fourier transform infrared spectroscopy (FTIR).

Results: The analysis of the experimental data pointed out to a correlation between the input and output variables, exhibiting a suitable ratio between the interaction terms, in order to increase the glycoprotein extraction yield. The SDS-PAGE profile shows a narrow distribution of molecular weights (MW), with several intense bands under 5 kDa. FTIR analysis evidenced the structural bonds vibrations caused by IR radiant energy absorption that are characteristic for monosaccharides, amidic and glycosidic bonds at specific frequencies / wavenumbers and a variation in the intensity and position of bands with the experimental parameters.

Conclusions: The data analysis provided an optimized process in order to obtain glycoproteins from *Ganoderma lucidum* which could later on be used for different 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. We also acknowledge financial support from the Ministry of Research and Innovation, Nucleu Programme, grant number P.N.19.23.01.01 Smart-Bi. We thank Dr. Bogdan Trică for helpful discussions in designing the optimization plan.*

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THE INFLUENCE OF STRIGOLACTONE ANALOG AND MIMETIC ON *TRAMETES VERSICOLOR*

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Keywords: strigolactones, SL analogs, signaling molecules.

Introduction: Strigolactones (SLs) are apocarotenoids, belong to carotenoid-derivative metabolites that includes other phytohormones, signaling molecules, and volatile compounds [1]. The appearance of strigolactones can promote the development of fungi and the establishment of symbiosis (a "cry for help") [2]. In order to study the SLs effect on biological processes, model compounds were designed and prepared. These SL analogs should have a simpler structure, but almost the same bioactivity as natural SLs [3]. In this study we tested the bioactivity of a strigolactone analog and a new mimetic on structural development of *Trametes versicolor*. We also tried to identify the influence of these SLs on phosphatase synthesis.

Materials and methods: For cultivation methods we used PDA medium following the standard procedure which include preparation, inoculation and an incubation at 28°C. After 5 days we observed the colony apperance of *Trametes versicolor*. We inoculate other plates with the selected strain on different media which contain different solutions of SLs incorporated in agar medium. After 3 days, the developed fungal colonies were observed. The observations were focused on the diameter and on the number of hyphae. Statistical analysis was applied on the data using SPSS. Phosphatase activity was made to determine the potential of *Trametes versicolor* to solubilize TCP on PVK agar supplemented with different concentrations of SLs.

Results: The responses of tested fungal strain to compound SL mimic 5 are relatively similar to the response of GR24. For both controls (water and acetone agar), the formation of lateral branches was the same as the treatments. The presence of these compounds in the culture media appears to inhibit a little the growth of *T. versicolor*. The phosphate solubilization of *T. versicolor* had no activity either in treatments nor in control after 3 days of incubation.

Conclusions: Our results suggested that the SL mimic compound have the same effect as GR24, having no effect on the structural development of the fungul strain. The selected strain was not capable of mobilizing TCP in PVK agar after 3 days of incubation.

Acknowledgements: *The research leading to these results has received funding from the NO Grants 2014-2021, under Project RO-NO-2019 540 STIM 4+, contract no. 14/ 2020.*

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MESOPOROUS SILICA-BASED PHASE CHANGE MATERIALS FOR THERMAL ENERGY STORAGE

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Keywords: Mesoporous silica; phase change materials; thermal energy storage; metal nanoparticles.

Introduction: Phase change materials (PCMs) can store latent heat by undergoing a solid-liquid phase transition at constant temperature. These types of materials have large enthalpies of fusion, but, their molar volume changes significantly during the phase transition, leading to a decrease in their thermal properties and leakage.[1] This problem can be solved by encapsulating the material in a porous matrix. In this study, metallic nanoparticles are employed as the phase change material, while the porous matrix is mesoporous silica. Metals are known for their high density and therefore they exhibit high volumetric heat storage. The mesoporous silica matrix has several suitable properties such as high pore volume, tunable surface properties and pore size and high thermal and chemical stability.[2]

Materials and methods: Mesoporous silica was synthesized trough the sol-gel method, while the composite PCMs were obtained by incipient wetness impregnation method, followed by aqueous chemical reduction using sodium borohydride.

Results: Phase change materials containing metal nanoparticles were successfully obtained at 50 – 70% wt. metal loading.Both the melting point and the heat of fusion of the metal phase were reduced with respect to bulk, suggesting that the encapsulated PCM is subjected to nanoconfinement effect.All thematerials show good thermal reliability after 50 heating – cooling cycles, as evidenced by the DSC analyses.

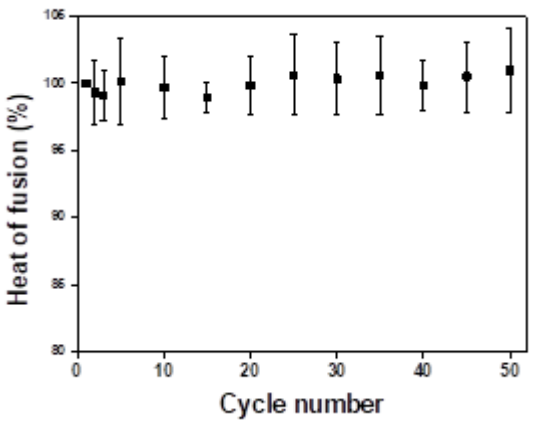

Figure 1. Thermal reliability of the 60% wt. metal nanoparticles / mesocellular foam silica composite

Conclusions: Novelmetal-silica composites were synthesized and characterized. The samples can be used as phase change materials for thermal energy storage, while maintaining good thermal reliability.

Acknowledgements: *This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS-UEFISCDI, project number PN-III-P1-1.1-TE-2019-1456, TE No. 166/2020, within PNCDI III.*

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A COMPUTATIONAL STUDY TO IDENTIFY SOME POTENTIAL INHIBITORS OF SARS-COV-2 MAIN PROTEASE FROM BIOLOGICAL ACTIVE QUINOLONES

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Keywords: SARS-CoV-2; drug design; molecular docking; antimicrobial quinolones; antitumoral quinolones

Introduction: The coronavirus pandemic known as COVID-19 is caused by severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2). This is a highly pathogenic human coronavirus (CoV) first reported in Wuhan, China [1]. So far there is no specific treatment available for COVID-19 [2]. The discovery of new antiviral agents is extremely important. For the development of the anti-SARS-CoV-2 drugs, the fastest way is to find potential molecules from the marketed drugs by molecular docking studies [3].

Materials and methods: A computational study to identify some potential inhibitors of sars-cov-2 main protease from antibacterial and antitumoral quinolones has been realized. Molecular docking studies have been performed to identify and visualize the most likely interaction of the ligand with the protein/enzyme receptor. The docking score and hydrogen bonds formed with the amino acids from of the group interaction atoms are used to predict the binding modes, the binding affinity, and the orientation of the docked ligands in the active site of the protein/enzyme receptor. The docking study have been carried out with some quinolones against the SARS-CoV-2 main protease (PD ID: 5R7Z).

Results: The docking study have been carried out with eight 1-ethyl-quinolone compounds with antimicrobial activity and with four 1-benzyl-quinolone compounds with antitumoral activity against the SARS-CoV-2 main protease (PD ID: 5R7Z). The study has been realized relating to two fluoroquinolone compounds known in medical therapeutics: ciprofloxacin and moxifloxacin.

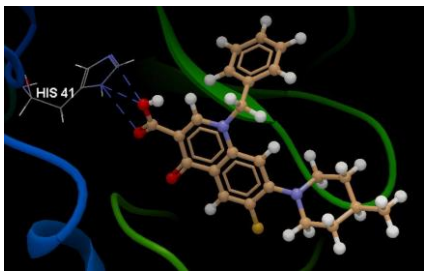

Fig. 1 Docking pose of the 6FPQ11 ligand interacting with amino acid residues (Score -66.38; RMSD 0.02)

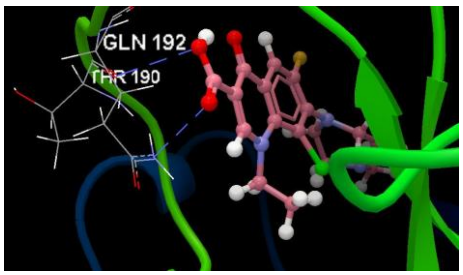

Fig. 1 Docking pose of theFPQ51 ligand interacting with amino acid residues (Score -56.28; RMSD 0.62)

Conclusions: The docking studies reveals that all compounds presented good docking score. The best score docking was obtained for 1-benzyl-quinolone compounds. 6FPQ11compound presents the great docking score (Fig.1). From the 1-ethyl-quinolone compounds, FPQ51 compound has the better docking score (Fig.2) comparative with ciprofloxacin (Score: -54.29; RMSD 0.59 Å) and with moxifloxacin (Score: -51.53; RMSD 0.50 Å).

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

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NANOSTRUCTURED CARBON ADSORBENTS FOR WATER DEPOLLUTION

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Keywords: carbon nanomaterials; adsorbents; hydrothermal carbonization; water depollution.

Introduction: Carbon materials, especially nanostructured ones, have well-known adsorbent properties due to their ability to establish covalent bonds, hydrogen bonds, hydrophobic, electrostatic, and π-π interactions [1]. A sustainable and low-energy method to obtain carbon nanomaterials is by hydrothermal carbonization of residual biomass with super-heated sub-critical water under auto-generated pressure [2]. Depending on the reaction temperature, solid:water ratio and reaction time, carbon nanostructures of different shapes and with various functional groups can be obtained.

Materials and methods: Grinded corn stalks were used as biomass raw material for hydrothermal carbonization in temperature mild conditions (≤250°C), when a type of char rich in N- and O-functional groups is obtained, particularly named hydrochar. Methylorange (MO) was used as organic dye pollutant representative due to its wide application in textile, leather, pulp and paper industries. The morphological structure and adsorbent properties of the obtained nanostructured carbon materials were analytically investigated by Fourier Transform Infra-Red spectroscopy (FT-IR), X-Ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption/desorption porosimetry, X-Ray fluorescence (XRF), and UV-Vis spectroscopy.

Results: TEM images evidenced spherical carbon nanostructures (Fig.1a), while nitrogen adsorption showed an increased porosity with the reaction temperature and time. FT-IR spectroscopy evidenced particular N- and O-functional groups in the nanostructured carbon materials, and also specific functional groups of MO dye (Fig.1b). XRD analyses confirmed the presence of MO in the carbon adsorbents, while XRF strengthen the presence of MO by correlation with the S content.

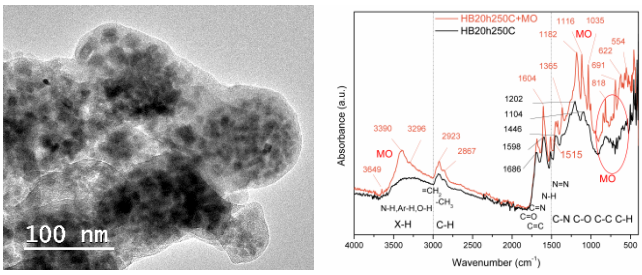

Figure 1. a) TEM image of nanoporous carbon materials; b) FT-IR spectra of carbon adsorbents before adsorption(black) and after adsorption of MO (red).

Conclusions: Nanostructured carbon adsorbents can be obtained by hydrothermal carbonization of residual biomass. The adsorbent properties depend both on the porosity and functional groups.

Acknowledgements: *This work was supported by the Government of Romania, Ministry of Research, Innovation and Digitalization Nucleu Programme in the frame of the Chem-Ergent project PN19.23.03.01 Contract no. 23N/2019.*

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PROPERTIES OF POLYSILOXANE/NANOSILICA NANODIELECTRICS FOR ENERGY STORAGE APPLICATION

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Keywords: nanocomposites; dielectric properties; DMA.

Introduction: Nanodielectrics are polymer composites with inorganic nanoparticles showing interesting dielectric properties. Nanodielectrics with high dielectric permittivity and great breakdown strength are characterized by a high energy density, which recommend them for energy storage and energy conversion devices [1]. These characteristics must be accompanied by lightweight, low-cost and easy processing for being attractive for this application field.

Most of the studies were focused so far on polyvinylidene fluoride (PVdF) nanocomposites with different ceramic nanoparticles, such as barium titanate. However, ferroelectric polymers like PVdF may cause large polarization hysteresis and high dielectric loss under high electric fields [2]. This may lead to premature failure of the devices. Therefore, nonferroelectric polymers gained increased significance provided that their dielectric properties are improved. In this study, we report the preparation procedure, along with dielectric, thermal and mechanical properties of polysiloxane based nanocomposites containing nanosilica. An environmentally friendly mixing process without solvents was used to obtain the nanocomposites.

Materials and methods: A commercial polysiloxane was mixed for 10 min at room temperature with different concentrations (5%, 15% and 25%) of nanosilica particles (15-20 nm) using a Brabender mixing device. After homogenization, the mixtures were thermally crosslinked in a laboratory press. The unfilled polymer (E0) and the nanocomposites (E5, E15 and E25) were characterized by dielectric spectroscopy, thermo-gravimetric analysis, tensile tests and dynamic mechanical analysis. The real part of the relative permittivity (ε_r') and the loss tangent (tan δ) were determined at room temperature over a wide frequency range (10^{-2} - 10^6 Hz).

Results: A continuous increase of the Young's and storage moduli with the increase of nanosilica concentration was observed. In addition, an increase of the real permittivity of nanocomposites with the concentration of nanosilica, especially in the low frequency range, was noticed (Figure 1).

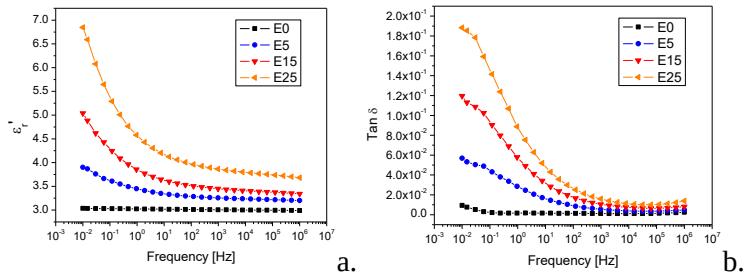

Fig.1. Dependence of ε_r' (a) and tan δ (b) versus frequency for nanocomposites with different nanosilica content.

Conclusions: The new nanodielectrics show good thermal and mechanical properties and high dielectric permittivity being promising for the design of energy storage devices.

Acknowledgements: *This work was supported by a grant of the Romanian Ministry of Research, Innovation and Digitization, CNCS–UEFISCDI, project number PN-III-P2-2.1-PED-2019-4687, contract no. 398PED/2020, NaDUMAS.*

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EXPERIMENTAL MODEL FOR HIGH-THROUGHPUT SCREENING OF MICROALGAE STRAINS USEFUL FOR CO_2 FIXATION

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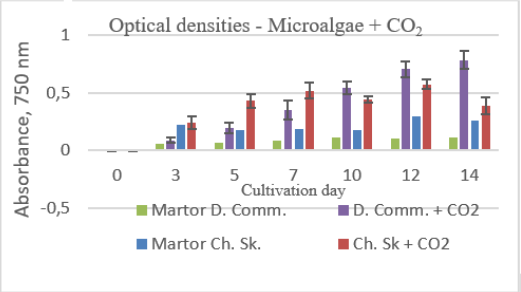
Keywords: CO_2, microalgae, experimental model, high throughput screening.

Introduction: In this study, we developed an experimental model for microalgae cultivation and CO_2 fixation. We used three different species of microalgae and several cultivation media. The industrial gas emissions contain significant proportion of CO_2, 3-30% [1]. Addition of the extra-CO_2 to microalgae culture initially boost their development, but further acidification process limits microalgae development [2].

Materials and methods: In this study, three strains of microalgae were cultivated: *Chlorella sorokiniana* NIVA-CHL 176, *Desmodesmus communis* NIVA-CHL 7 and *Raphidocelis subcapitata* ATCC22662, with three different cultivation media, BG11 [3], BBM and, respectively, Z8. The experimental model used for cultivation of the microalgae was developed by using GLS80 glass reactor and LED stripe for illumination. The nitrogen containing 7% CO_2 was discontinuously added (90 minutes/day), in order to avoid acidification of the cultivation medium [4], at 25°C, 200 RPM and approximately 10 µE. Microalgae growing was monitored by: optical density, turbidity, chlorophyll content, biomass, pH, cell number.



Results: The best cultivation protocol was selected after the initial experiments. *C. sorokiniana* NIVA-CHL 176 was raised in BG11 medium and *D. communis* NIVA CHL-7 in Z8 medium. *R. subcapitata ATCC22662* had around half of the other two microalgae raising rate, and the experiments were discontinued. Subsequent to CO_2 bubbling, the pH dropped with one unit after the first 7 days (from pH 6 to 5), from day 7 to day 10 the values were constant (pH=4), and 4 more days, the pH increased (to 6 and 6.5, depending on the microalgae). The control culture had constant pH – 8. Based on optical density, the growth rate of the studied microorganisms was monitored. *D. communis* had the best results, 8 times higher growth rate than the control and *C. sorokiniana* 2 times higher growth rate compared to the control, non-supplemented with CO_2.

Conclusions: Higher rate of CO_2 brings significantly increase in the growth rates, but pH monitoring is needed. Our experimental model is efficient for the high-throughput screening of the microalgae strains useful for CO_2 fixation.

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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EVALUATION OF PVA-BASED CRYOGELS IN THE CLEANING PROCESS OF CONTEMPORARY ACRYLIC PAINTINGS

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Keywords: cryogel, acrylic paintings, cultural heritage, conservation, cleaning

Introduction: History can be defined as the study of people who have lived in the past. From one generation to another, people transmit values and knowledge through art. The more efficient the processes of evaluation, cleaning, restoration of cultural heritage, the more efficient the communication between generations.

Over time, the painting undergoes numerous oxidation processes, by exposure to light or various contaminants from the environment, which causes loss of visibility through the formation of unwanted layers [1]. Today's study aims to evaluate some recipes for cryogels in the process of cleaning acrylic paints.

Materials and methods: Samples preparation consisted in application of pigments in two steps on a black paper with thickness 0,2 mm, using ordinary brushes.

Aging process was simulated when the paintings samples was introduced at climate chamber KK150 for 3 days at T=50 ºC and RH=15% with 4h/day. An artificial soil with the composition described in [3] was applied on the paintings in order to partially simulate the natural soiling of the paintings exposed to pollutants, dust or smoke. For cryogel synthesis was used 10 g polyvinyl alcohol (PVA) dissolved in 100 mL H_2O through magnetic stirring for 2 h at 800 rpm and 85 ºC.

After this step the content was transferred in a Petri dish and keep at room`s temperature to get colder. The subsequent freezing-thawing cycles consisted in placing the samples on the freezer for 20 h at a temperature of -20 ºC then thaw for 4 h at room`s temperature [4].

For the removal of the hydrophobic layer, a microemulsion O/W based on toluene, water, Triton X-100, and n-butanol was used. The microemulsion can be uploaded in cryogel through 2 methods: before starting the first FT cycle or through immersion in microemulsion for 24 h after the last FT cycle.

Results: To remove the excess of microemulsion, the gel is placed for a few minutes in a sheet of filter paper. The gel application on the substrate was done with tweezers, at every 2 minutes, when the position of gel is changed. Color analysis was made with a chromameter Konica Minolta CR-410 and with a hyperspectral camera GreenEye Vis-NIR in the initial state, after the soiling process, after the application of the first stage of treatment and respectively after few seconds.

The differences of the values between the chromatic parameters of the initial and the final state must be as small as possible.

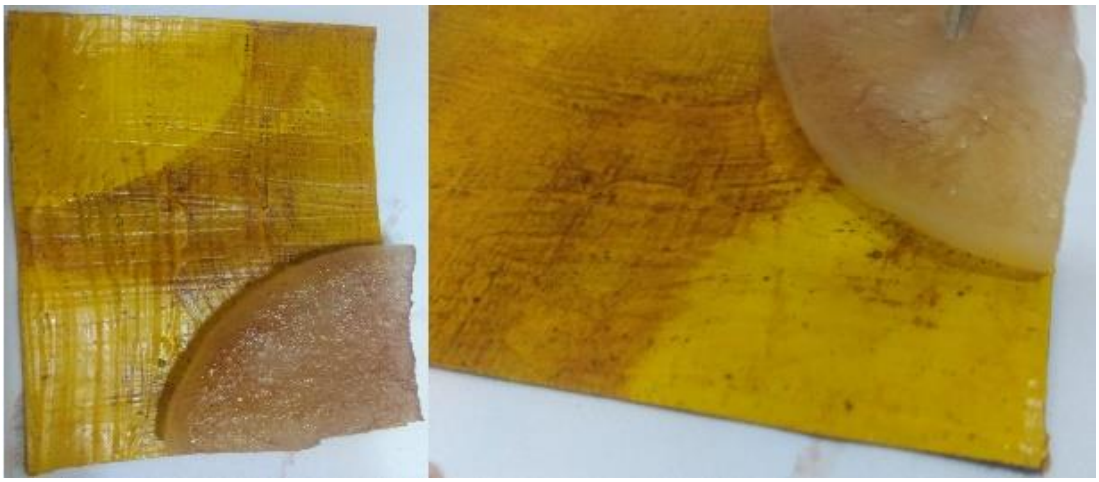

Figure 1. The application of first treatment

Conclusions: The layer of dirt was removed and the acrylic pigment it`s not absorbed by cryogel. The evaluation of cleaning capacity was quantified through optical microscopy, colorimetry and imaging spectral data.

Acknowledgements*: This paper was supported by the Romanian Ministry of Research and Innovation, Project 51PCCDI/2018 within PNIII and PN 19.23.03.01.11 within the NUCLEU program.*

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MESOPOROUS CE-SBA15 CATALYSTS FOR ALGAL BIOMASS PYROLYSIS

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Keywords: pyrolysis, mesoporous catalysts, algal biomass, bio-oil.

Introduction: Algae have been suggested for use as a biomass-energy resource for fuel production. Biomass or bio-energy has been recognised as a renewableenergy source that can be used to replace fossil fuels, with the added bonus that the crops, plants or trees can absorb $CO_2$from the atmosphere, reducing the greenhouse effect.Various thermochemical techniques can be utilized withalgae to generate fuel in different forms, for example, pyrolysis wich is induced by heating the biomass at an anoxic condition and a temperature of approximately 500^0C[1]. The products obtained after pyrolysis are bio-oil,bio-char and gaseous components, with potentially used in fossil fuel industries. Bio-char with carbon content over 50%, has a highly porous structure, and the addition of bio-char to soil could improve water retention and increase the surface area of the soil, increasing the efficiency of nutrient use [2].

In this paper two mesoporous Ce-SBA15 catalysts based on the soft-templating method weresynthesized and used for algal biomass pyrolysis. In the synthesis mesoporous silicas were applied as pore structure templates. Differentiation of the synthesis conditions was type of copolymer, Pluroic P123 or Pluronic P9400, obtaining materials with different structure. The physicochemical properties of the mesoporous materials were characterized by using various techniques: adsorption/desorption of nitrogen, XRD, transmission electron microscopy (TEM)and thermal analysis. In order to verify their applicability for algal biomass pyrolysis complex reactions measurements were performed.

Materials and methods: Ce-SBA15 catalysts were prepared by soft-templating method using amphiphilic P123 triblock copolymer and Pluronic P9400 as templates and tetraethyl orthosilicate as the silica source according to the method reported by P. Hongmanorom et colab.[3]

Catalytic pyrolysis was performed in a laboratory-scale stationary tubular reactor.

Results: The components of the bio-oil from the pyrolysis reaction were analysed by gas chromatography.GC-MS Triple Quad from Agilent Technology was used to analyse the oil components. The identification of the peaks is matching of the mass spectra with the NIST standard library from the instrument. Themain groups of aromatic hydrocarbons, heterocyclic, phenol,amine, amide, indole, alkane and nitrile were identified in the bio-oil. The length of the carbon chain in the bio-oil was in the range of C7-C17.

Conclusions: The pyrolysis process of algal biomass was performed at the temperature of 450^0C in a stationary tubular reactor.The main compounds from the GC-MS analysisof the bio-oil are heptadecane, toluene, ethylbenzene and indole. The hydrocarbon groups were found to be in a range of heavy naphthas, kerosene and diesel.

Acknowledgements: *This work was supported by a grant of the Romanian Ministry of Education and Research, project number PN 19.23.01.01*

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EVALUATION OF THE CATALYTIC DEGRADATION CAPACITY OF GREEN SYNTHESIZED SILVER NANOPARTICLES ON BIS-AZOIC DYES

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Keywords: catalytic degradation, silver nanoparticles, green synthesis, bis-azoic dyes.

Introduction: Silver nanoparticles (AgNPs), widely recognized for their antimicrobial and antioxidant capacity, can be prepared following both conventional and unconventional routes and have a multitude of applications in numerous scientific domains including catalytic degradation of dyes that result from the textile industry [1, 2]. The present research paper describes the one-pot eco-friendly synthesis of silver nanoparticles from different plants (Celadine, Magnolia, Red deadnettle, Dwarf everlast, etc.) and their potential application in the catalytic degradation of bis - azoic dyes (Direct Orange 26, Direct Brown 2 and Direct Black 38).

Materials and methods: Aqueous extracts, prepared using the above-mentioned plants at room temperature, for 24 h were further used for the green synthesis of AgNPs at room temperature, at 30^0 C and at 50^0C. In order to confirm the formation of the AgNPs, UV-Vis, FTIR, DLS and SEM spectra were recorded. The antioxidant activity of the green synthesized AgNPs was determined using the DPPH method and their potential use in the degradation of the bis - azoic dyes was investigated.

Results: The formation of eco-friendly AgNPs was monitored by recording UV-Vis spectra at different time intervals and revealed peaks at 438 nm (AgNPs-Celadine), 442 nm (AgNPs-Magnolia) and 450 nm (AgNPs-Red deadnettle). FTIR determinations revealed the major functional groups present in the structure of the AgNPs (e.g.: C=C, C=O, C-H, etc.). The catalytic degradation of the bis-azoic dyes showed that the highest decrease of the maximum absorption intensity was observed in the case of Celadine – AgNPs (Table 1);

Sample	Reaction time				
	0 min	15 min	30 min	1 h	ΔA
DO 26 (sol 50 mg/L)	1.786	-	-	-	-
DO+AgNPs-Celadine	1.496	1.456	1.440	1.411	22.34
DO+AgNPs-Magnolia	1.500	1.458	1.392	1.347	28.33
DO+AgNPs-Red deadnettle	1.697	1.674	1.670	1.658	8.79
DO+AgNPs- Celadine +reductive agent (RA)	1.151	1.212	1.170	1.125	43.35
DO+AgNPs- Magnolia +RA	1.187	1.188	1.124	1.072	46.02
DO+AgNPs- Red deadnettle +RA	1.297	1.291	1.208	1.146	45.02

Conclusions: This paper describes the green synthesis of AgNPs from different plants and their physical – chemical characterization using UV-Vis, FTIR, DLS and SEM. Also, the preliminary studies carried out to investigate their potential use in the degradation of some azoic dyes revealed that in the studied reductive degradation, the highest values for ΔA were found for Direct Brown 2.

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

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4. Poster Presentations

LUMINESCENT LANTHANIDES MATERIALS BASED ON PHENANTHROLINE DERIVATIVES

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Keywords: phenanthroline based ligands, luminescent materials, lanthanides complexes.

Introduction: Lately, lanthanides have been of great interest due to their luminescent properties, such as long lifetimes, large Stokes shifts, and narrow emission bands in the visible region [1]. Lanthanide based materials can be used as light emitting diodes, amplifiers for optical communications and optical storage [2].

Materials and methods: In this work, we synthesized a new series of complexes using as ligands phenanthroline derivatives. For the first family of lanthanides based compounds we used as antenna ligand 4,7-Diphenyl-1,10-phenanthroline (Bphen) and for the other one, Pyrazino[2,3-f][1,10]phenanthroline (Pyrphen). The general structures are: $[Ln^{III}(Bphen)_2(NO_3)_3]$ (Ln^{III} = Eu, Tb, Nd, Er, Yb, Tm) and $[Ln^{III}(Pyrphen)_2(NO_3)_3]$ (Ln^{III} = Eu, Tb). The third lanthanide complexe of Eu(III)isbased on 1,10-phenanthroline-5,6-dione ligand.

Results: The new complexes were characterized by X-ray diffraction (single-crystal and powder), IR and UV-Vis measurements.

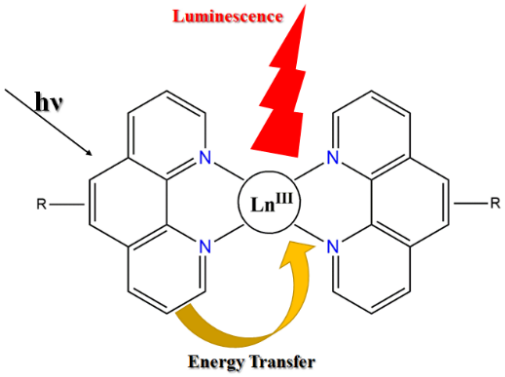

Fig. 1: Schematic representation of the obtained complexes and the antenna effect.

Conclusions: The luminescent spectra for the compounds show specific emission for the lanthanide ions.

Acknowledgements: *Thisworkwassupported by a grant of the Romanian National Authority for ScientificResearchandInnovation, UEFISCDI, projectnumberPN-III-P1-1.1-TE-2019-1345, within PNCDI III.*

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HYBRID MATERIALS BASED ON MULTI-WALLED CARBON NANOTUBES AND TiO_2 NANOPARTICLES WITH ANTIMICROBIAL PROPERTIES

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Keywords: hybrid materials; decorated nanotubes; nanoparticles; antimicrobial properties

Introduction: Worldwide, one of the most significant threats to human health problems remains the antibiotic resistance. In the last several years, bacteria have evolved in order to survive antimicrobial treatments by effectively developing resistance mechanisms [1]. It has been shown that nanoparticles and nanotubes have outstanding antimicrobial activity due to the increased contact area with bacteria [2]. The aim of this study was to design and characterize hybrid materials composed by multi-walled carbon nanotubes (MWCNTs) decorated with TiO_2 nanoparticles, in order to obtain an efficient nanosystem with improved antimicrobial activity by a fast and low-cost method.

Materials and methods: The carbon nanotubes used in this study were obtained by chemical synthesis [3] and used as template for TiO_2 nanoparticles formation. The nanocomposites (MWCNTs_TiO_2) were obtained by TiO_2 *in situ* attachment on the surface of MWCNTs, by using a titanium (IV) isopropoxide precursor. The obtained hybrid nanomaterials were further characterized by Raman Spectroscopy Analysis, X-ray Diffraction Analysis (XRD) and Transmission Electron Microscopy (TEM). The antimicrobial activity of MWCNTs_TiO_2 was investigated against two Gram-positive (*S. aureus*, *B. subtilis*), two Gram-negative (*P. aeruginosa*, *E. coli*) and one yeast (*C. albicans*) to cover the most important model opportunistic pathogens.

Results: TEM micrographs revealed that the MWCNTs have a diameter between 9 - 50 nm and a length of 600 nm and TiO_2 nanoparticles with a diameter of about 15 nm were successful deposited on the nanotubes surface. Qualitative testing of antimicrobial activity demonstrated that MWCNT_TiO_2 were able to inhibit growth for all tested strains, mostly in the case of the Gram-negative bacteria (*E. coli* and *P. aeruginosa*). Quantitative tests showed that the obtained nanocomposites have more pronounced antimicrobial effects on Gram-negative bacteria compared to the yeast or Gram-positive bacteria. This can be explained with the particularities of the cellular wall of each type of bacteria, Gram-negative bacteria have a thin peptidoglycan layer and an outer lipid membrane, which make the bacteria easier to inhibit and leads to a faster destructibility of the cell membrane.

Conclusions: The decoration of MWCNTs with TiO_2 nanoparticles has been successful carry out, spherical nanoparticles with a diameter about 15 nm being attached to the nanotubes surface. The obtained nanocomposites presented more pronounced antimicrobial activity on Gram-negative bacteria. The obtained results sustained that the synthetized nanocomposites can be considered as competitive candidates for the development of efficient antimicrobial systems.

Acknowledgements: *This work was supported by a grant of the Romanian Ministery of Research and Innovation, CCCDI – UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0476/51PCCDI/2018, within PNCDI III and PN.19.23.03.01 contract no. 23N/2019 within the Nucleu Program.*

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IBUPROFEN AND HYALURONICACID-LOADED CHITOSAN: PEG COATINGS FOR WOUND HEALING PROMOTION

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Keywords: Ibuprofen, Hyaluronic acid, wound healing, immunomodulation, rat animal model

Introduction: Wound healing is a dynamic and complex process involving biochemical and physiological phenomena such as inflammation, proliferation, and remodeling [1**].** Several formulations have been investigated as a drug carrier for local delivery of compounds that are able to activate immune cells to enhance wound healing [2]. From a clinical point of view, topical application is attractive for full-thickness wound, due to reducing adverse effects on other organs.Here, we developed a new patch formulation containing Chitosan and PEG coatings (CS: PEG), loaded with Ibuprofen (IBUP) and Hyaluronic acid (HA), compounds with anti-inflammatory, antioxidant and wound healing modulation properties.The physical-chemical characteristics and *in vitro* biocompatibility of CS:PEG:IBUP:HA was investigated. In addition to *in vitro* studies, a rat model was used to evaluate its potential effect to accelerate cutaneous would healing.

Materials and methods: The effect of CS:PEG:IBUP:HA on the viability of THP-1 differentiated macrophages was assesed by MTS (Promega) colorimetric assay. The anti-inflammatory potential was investigated using an experimental model of inflammation, macrophages stimulated with bacterial endotoxins (LPS) and the level of pro-inflammatory cytokines determined by ELISA method. For *in vivo* study, CD-SD rats were devided into two groups according to the wound treatment: first group received CS:PEG:IPUB:HA coated patches and second group received untrated patches. Samples of wounds/ scars were collected on the 7th and 14th postoperative days and evaluated histological and immunohistochemically.

Results: No cytotoxic effect was found whencells were treated with CS:PEG:IBUP:HA.The *in vitro* assay confirmed that the formulation containing IBUP and HA reduced LPS-induced inflammation by suppressing the of IL-6 pro-inflammatory cytokine production.When the results were evaluated immunohistochemically, there was a significant increase in collagen synthesis, a better and faster re-epithelization observed in the IBUP-HA containing coatings applied to animal group compared to control group. Clinical and histological results showed that topical application of CS:PEG:IBUP:HA patches also stimulate the re-epithelization process.

Conclusions: These findings suggested that the topical application of CS:PEG:IBUP:HA can promote the cutaneous wound healing process and represents a promising candidate for skin tissue therapy.

Acknowledgements: *This project was supported by UEFISCDI funding, grant number PN-III-P1-1.2-PCCDI-2017-0728, acronym TERAMED.*

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FORMULATION OF PULLULAN ACETATE NANOPARTICLES LOADED WITH 5-FLUOROURACIL

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Keywords: nanoparticles, pullulan, 5-fluorouracil, cancer.

Introduction: The aim of this study was to obtain and evaluate pullulan acetate-based nanoparticles loaded with an anticancer agent, 5-fluorouracil (5-FU). 5-FU is a first-line chemotherapeutic agent employed in the treatment of various types of cancer such as: gastric, pancreatic and esophageal cancer, breast cancer, head and neck cancer, cervical cancer, kidney cancer and so on. However, 5-FU has a short biological half-life, non-selective distribution, variable oral bioavailability and toxicity, which limits its therapeutic applicability. A way to overcome these limitations is loading 5-FU in nanoparticles [1-3].

Materials and methods: Pullulan was produced through a fermentation process by *Aureobasidium pullulans* strain and was further chemically modified with dimethylformamide, pyridine and acetic anhydride to obtain pullulan acetate. The 5-FU-loaded pullulan acetate nanoparticles were obtained by various methods: nanoprecipitation method, modified nanoprecipitation method and double emulsion method. Nanoparticles were characterized in terms of entrapment efficiency, size and polydispersity index using spectrophotometric and dynamic light scattering techniques.

Results: The 5-FU-loaded pullulan acetate nanoparticles were successfully produced by the three methods: nanoprecipitation method, modified nanoprecipitation method and double emulsion method. All samples showed satisfactory size and polydispesity index.

Conclusions: This study shows that pullulan and its derivatives have a great potential for the production of nanoparticles with application in biomedical field, including for the delivery of anticancer agents, as 5-fluorouracil.

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

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CHARACTERIZATION AND *IN VITRO* BIOLOGICAL EVALUATION OF NOVEL OBTAINED pNIPAM-BASED COATINGS

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Keywords: pNIPAM, MAPLE, coating, cell viability, cell morphology

Introduction: The successful application of materials in the medical field is related to the the processing methods used to produce composite coatings with good control on the thickness and stability in harsh environment. Due to its characteristics poly(N-isopropylacrylamide, pNIPAM) is widely used to produce substrates for medical application [1, 2]. In this context, the aim of our study was to use different techniques and to choose the flexible method for a controlled depostion of pNIPAM-based coatings in terms of biocompatibility, to assure an efficient antitumoral drug delivery system (i.e. pNIPAM-Butyl acrilate copolymer pNIPAM-BA). The effect of surfaces obtained by different techniques was evaluated *in vitro*, on both normal and tumoral cell lines.

Materials and methods: pNIPAM-BA based coatings were obtained using matrix assisted pulsed laser evaporation (MAPLE) and spin coating methods. The influence of solvents and laser parameters were evaluated. MAPLE allows to enhanced sensitivity, antitumor and antibacterial potential of the thin film substrates by tailoring deposition parameters such as thin film composition, laser fluence and the target system. Spin coating allows a facile single element coating. *In vitro* experiments were performed with human normal HEK 293T and murine melanoma B16-F1 cells. Viability and proliferation of cells grown on different surfaces were evaluated after 24 and 48 h using MTS (CellTiter96® Aqueous Non-Radioactive Cell Proliferation, Promega) assay. Cell adhesion and morphology were investigated by Scanning Electron Microscopy (SEM) technique to assess the biocompatibility of obtained pNIPAM-based coatings.

Results: pNIPAM-BA substrates were obtained by MAPLE and spin coating and were analyzed by Atomic Force Microscopy, SEM and contact angle measurements, demonstrating the dependence of the coating morphology on the deposition method and the solvent used, and in the case of MAPLE, of the laser fluence. Cell viability and proliferation were found to be dependent on both cell line and deposition method of polymeric coatings. Thus, no cytotoxic effect was observed for normal cell line at 24 and 48 h, with a moderate proliferation rate for spin coating deposition method. Unlike normal cells, murine melanoma cells did not retain the proliferation capacity for almost all the tested coatings. Cell adhesion and morphological investigations revealed an adaptation of cell behavior to the type of surface.

Conclusions: The pNIPAM-BA coatings obtained by spin coating showed smooth and hydrophilic surfaces, while in the case of MAPLE method, the surface morphology was dependent on both solvent and laser fluence, keeping the hydrophilic characteristics. Biological assays performed *in vitro* evidenced morphological and proliferation changes conditioned by cell line and type of coatings preparation.

Acknowledgements: *This project was supported by UEFISCDI funding, grant number PN-III-P2-2.1-529PED-2020, acronym BioSMARTplat.*

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SPION NANOPARTICLES *IN VITRO* AND *IN VIVO* TESTING FOR ANTIMELANOMA DRUG RELEASE INTO TUMORS

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Keywords: melanoma cells, syngeneic melanoma mouse model, drug delivery, IHC, RT-qPCR

Introduction: We synthesized superparamagnetic iron oxide nanoparticles (SPION) by a co-precipitation method [1]for localized therapy of melanoma tumors. This approach would diminish the systemic toxicity of currently applied chemotherapeutic drugs by limiting their distribution to vital organs in the body through blood circulation [2]. As proof-of-concept for *in vitro* and *in vivo* testing of SPIONs, we used doxorubicin (Dox) as a model drug, which can be traced in cells and tumors due to its fluorescence emitting properties.This was attached to the metal core *via* a citrate linker. We used B16F10 cells and the C57BL/6 inbred SPFsyngeneic mouse model for all experiments.

Materials and methods: Nanoparticles were morphologically (TEM and HRSEM), structurally (XRD) and compositionally (XPS, FT-IR andMössbauer spectroscopy)characterized. Additionally, their size and Zeta potential were assessed by DLS.Dox loading capacity, Dox equivalent dose and Dox release during the hyperthermia tests were determined. The IC50values of SPION-citrate-Dox and of free Dox were determined by MTS assay (Promega). Magnetic properties of the SPION nanoparticles were analyzed by vibrating-sample magnetometry (VSM).The percentage cells to uptake the proposed NP-drug formulationand the consequent cell apoptosis werequantitatively assessed by conventional (FACSVerse, BD) and imaging flow cytometry (FlowSight, Luminex). PBS suspensions of SPION-citrate-Dox were injected into pre-formed tumors biweekly in parallel with drug only and NP only controls and tumor volume monitored. At the end of treatment, tumors were removed from the animals and subjected to histology, immunohistochemistry and Real-time RT-qPCR analyses. Organs were collected for biodistribution analysis using histological Prussian blue staining. Analysis of key proliferation and apoptosis markers was assessed by immunohistochemistry (IHC) and automatic scanning of tissue sections (TissueFAXSiPlus, TissueGnostics). Dox resistant cell lines were produced by exposing B16F10 to escalating doses of drug. Gene expression analysis was assessed in these cells in parallel with treated tumors from mice by Real-time RT-qPCR (RotorGene 6000, Corbett).

Results: The proposed SPION-citrate-Dox formulation was successfully internalized by melanoma cells, which inducedcellapoptosis. Tumor volume decreased in mice treated with drug-containing nanoparticles as opposed to nanoparticles alone treated mice.

Conclusions: Citrate functionalized SPIONs can be further developed as a promising vehicle for local treatment of melanoma tumors using hyperthermia.

Acknowledgements: *This project was supported by UEFISCDI funding, grant number PN-III-P1-1.2-PCCDI-2017-0728, acronym TERAMED and grant number PN-III-P2-P2.1-PED-2019-3292, acronym EMA-HYPERMAT*

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SYNTHESIS OF SILVER NANOPARTICLES EMBEDDED IN MICRO-HYDROGEL PARTICLES BY ELECTRON BEAM IRRADIATION

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Keywords: hydrogel, silver nanoparticles, graphene oxide, polypyrrole.

Introduction: The present study focuses on synthesizing the silver nanoparticles - hybrid micro-gel with antibacterial properties. The micro-gel matrix is based on biocompatible polymer poly(vinyl)alcohol additivated with antibacterial compounds [1,2]: graphene oxide and silver salt. The polymer composite was synthesized by irradiation with an electron beam at 10, 25, 50 Gy to form silver nanoparticles.

Materials and methods: The morphostructural characteristics of hybrid micro-gel are investigated by UV-Vis and FTIR Spectroscopy, Differential Scanning Calorimetry (DSC), and Scanning Electron Microscopy (SEM).

Results: The crystalline fraction is between 0.427 and 0.235. The crystalline fraction is anticorrelated with the dose. By contrast, the glass transition temperature is correlated with the received dose.
The samples additivated with pyrrole/iron salt (codified 1 and 2) have no visible UV-Vis peak for silver, opposite to the samples additivated with pyrrole (codified with 3and 4), which present a clear peak for silver nanoparticles between 416 and 419 nm.
Qualitative testing of the antimicrobial effect of the analyzed samples, in the presence of resazurin, showed that the polymeric composites have a bactericidal effect on the bacterial strains used (Escherichia coli ATCC 25922 and Staphylococcus aureus ATCC 9737), most likely due to the synergism of the bactericidal effect of graphene oxide and silver nanoparticles**.**

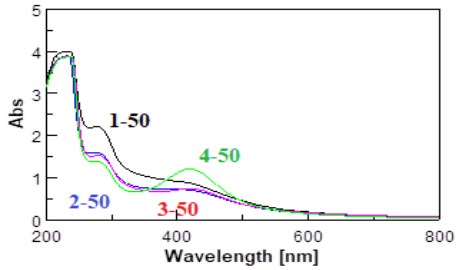

Figure 1 UV-Vis samples irradiated at 50 KGy.

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Conclusions: Antimicrobial effect of silver nanoparticles - hybrid micro-gel synthesized by e-beam is anticorrelated with the dose, making it suitable as antibacterial gels in wound dress application.

Acknowledgements: *The work was supported by the projects from position no. 2 of the JINR Order 322/21.05.2018 and position 3 of the JINR Order 365/11.05.2021. The irradiation facilities were supported from the project 149N / 2019s.*

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SYNTHESIS, CHARACTERIZATION AND BIOCOMPATIBILITY OF ANISOTROPIC SILVER NANOPARTICLES

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Keywords: silver nanoparticles, anisotropic nanoparticles, biological properties.

Introduction: The properties of nanoparticles are strongly related to their size, shape and surface functionalization. The dependence of properties with size and surface characteristics was widely investigated in the last decades, while the influence of the shape is still a subject of interest, due to the progress of synthesis. Also, the biological properties (antibacterial, antitumoral, etc.) are strongly dependent of the shape of silver nanoparticles [1-3].

Materials and methods: Silver nanoplates (Ag NPLs) were synthesized using a simple wet chemical method of reduction of Ag precursor and directing the growth of particles. The reaction was conducted in the presence of two polymers - polyvinyl pyrolidone (PVP) and Chitosan - as reagents used to prevent aggregation and to reduce the size of the obtained particles. The size and size distribution of Ag NPLs were determined by Dynamic Light Scattering (DLS). The morphology of the obtained nanoparticles was evaluated by transmission electron microscopy (TEM). UV-VIS spectra were recorded on Ag NPs dispersions as final products and also on the reaction system during the synthesis of silver nanoplates, in order to observe the evolution of the real-time spectra. Also, the effect of the Ag NPLs, compared to quasi spherical nanoparticles, on the viability of neuron cultures was investigated.

Results: Silver nanoplates were prepared in the presence of the nontoxic compound sodium citrate as reduction reagent and of H_2O_2 as chemical etching agent. By tuning the concentration of the polymer stabilizers, particles with dimensions between 20 and 70 nm were obtained, with significant stability and narrow size distribution. The UV-VIS spectra exhibited specific strong absorption in the visible region, depending on the size of nanoplates. A comparison between the effect of Ag nanoplates and spherical Ag nanoparticles on the viability of neuron cultures was also performed.

Conclusions: The proposed method is suitable to produce anisotropic Ag particles with enhanced stability and good biologic properties, without using of harmful reagents. Moreover, the Ag NPLs stabilized with PVP and Chitosan showed a relatively good biocompatibility related to the neuron cells viability when compared to the unprotected ones.

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PED-2019-4657, contract 318 PED / 2020, within PNCDI III.*

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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITIES OF SOME SCHIFF BASES WITH NON-LINEAR OPTICAL APPLICATIONS

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Keywords: organic synthesis, Schiff bases, antimicrobial, nonlinear optical properties.

Introduction: Schiff bases or imine compounds are considered as a very remarkable category of organic compounds because of their π-delocalized structure and because of their pharmacological properties. Thus, the delocalization of the π-electrons, define the classic structures with optical response due to large hyperpolarizabilities which result from a "push-pull" system. Also, imine compounds have been revealed to be promising leads for the design of more competent antimicrobial agents [1-3].

Materials and methods: Organic commercial and synthetic materials were used for the synthesis of the heterocyclic compounds. All compounds were characterized with physicochemical techniques (elemental analysis, ^{1}H, ^{13}C, FTIR and UV-Vis spectroscopy) [4]. The SHG capability of samples was measured by using an experimental set-up [1,5].

Results: A series of Schiff bases containing heterocyclic compounds (pyrazoles, pyrimidines, benzimidazoles, benzothiazole, etc) was synthesized and characterized. The nonlinear optical (NLO) response of some Schiff bases is investigated by the static hyperpolarizability coefficients (β), calculated using the semi-empirical quantum chemistry algorithms (MOPAC software). All compounds were evaluated by qualitative and quantitative methods against a panel of selected bacterial and fungal strains [6,7].

Conclusions: It was found that relationship between donor/acceptor moieties, the dihedral angles around the azo bridge (-N=N-) transmitter group, the pass length as well as the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), strongly influenced the NLO response.

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CCCDI - UEFISCDI, project number PN-III-P2-2.1-PED-2019-3009, within PNCDI III.*

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SYNTHESIS AND NONLINEAR OPTICAL STUDIES OF N-CONTAINING HETEROCYCLIC COMPOUNDS

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

Introduction: The organic compounds which contain a "push-pull" system, that means a couple donor (D) – acceptor (A) connected to a system which contributes to the delocalization of the π-electrons, define the classic structures with optical response due to large hyperpolarizabilities. These arise from a combination of strong electron donor groups (e.g., $–NR_2$, –OR) and strong electron withdrawing groups (e.g., $–NO_2$, –CN), positioned at opposite ends of a conjugated system [1,2] (Fig. 1).

Figure 1. Scheme of one organic compound with a "push-pull" system

Materials and methods: Organic commercial and synthetic materials were used for the synthesis of the heterocyclic compounds. All compounds were characterized with physicochemical techniques (elemental analysis, ^1H, ^{13}C, FTIR and UV-Vis spectroscopy). The SHG capability of samples was measured by using an experimental set-up [1,3].

Results: A series of N-containing heterocyclic compounds (benzimidazoles, benzothiazole pyrazolones, octahydroacridines) was synthesized and characterized [4-9]. The SHG (second harmonic generation) value was determined for each compound. The molecular polarizability (α), first order hyperpolarizabilities (β_{tot}), dipole (μ_{tot}) and quadrupole (Q) moments, were calculated using DFT (density functional theory) method.

Conclusions: Our results highlight that the nonlinear optical (NLO) response of such small, twisted or flat molecules, mainly depends on the dihedral angles of aromatic and heteroaromatic rings toward the transmitter group. We also found that the electronical and structural peculiarities, of these compounds to be favorable for ultra-fast response times, i.e., femto-seconds applications, as confirmed by our previous publications [2,5].

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization CCCDI - UEFISCDI, project number PN-III-P2-2.1-PED-2019-3009, within PNCDI III*

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PRELIMINARY STUDIES ON SILICA NANOPARTICLES PREPARATION AS TRANSPORT VECTORS FOR CURCUMIN

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Keywords: silica nanoparticles, curcumin, nanocarrier, biomedical applications

Introduction: Mesoporous silica nanoparticles (MSN) have been nowadays the centre of studies in different scientific areas. One of the most promising domains for the MSN applications is nanomedicine. They have gained significant advantages over other types of nanoparticles used as transport vectors for drugs, such as adaptable structure depending on the synthesis conditions, biocompatibility, high specific surface area and a large pore volume [1]. In this study we used three different surfactants and various silica co-precursors in order to create silica nanoparticles able to encapsulate curcumin and to use them as potentially transport vectors.

Materials and methods: During the synthesis, three different surfactant Tween 80 (RB and RD series), Triton X (RA series), and Sodium bis(2-ethylhexyl)sulfosuccinate (RC series) were evaluated as templates for the preparation of the mesoporous silica particles. In order to have a fine control over MSNs size, we also used different silica co-precursors: octadecyl-triethoxisilane (ODTES), octyl-triethoysilane (OTES), phenyl-triethoysilane (PhTES), tetraethyl-ortosilicate (TEOS), and vinyl-triethoxysilane (VTES). After synthesis, the excess of surfactant was removed through a dialysis purification process, using a membrane with MWCO of 6-8 kDa.

Results: FT-IR, DLS and SEM analyses were performed on the obtained transport vectors in order to study their structure, size and morphological aspects. From the FT-IR spectra of RB series (fig. 1) it was observed that the predominant peaks were generated by the surfactants. The Dynamic Light Scattering (DLS) measurements (fig. 2) revealed that the control samples (marked with "1"), showed bimodal distributions, which correspond to the main population of silica particles, but also to a secondary population of small micelles, formed by the excess of surfactant. With the addition of different co-precursors to the sol-gel system (such as TEOS for the samples marked with "2"), the average size of the silica particles increased, while the peak corresponding to the empty surfactant micelles diminished. It was also observed that by addition of VTES or PhTES in the composition, the resulted particles have comparable sizes for the both samples. However, their average size varies with the type of surfactant.

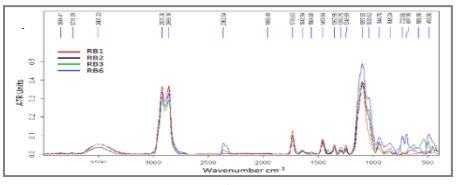

Figure 1. FT-IR spectra of RB series

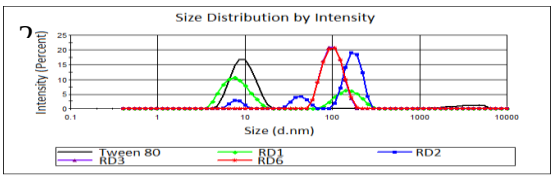

Figure 2. DLS results of RD series

Conclusions: Following these results, we selected for further investigations the compositions of RB (with ODTES) and RD series (with OTES), both produced in the presence of Tween 80, as being the most stable, with uniform and reproducible dimensions. In addition, we took into account that Tween 80 is a surfactant more suitable for biomedical applications. Thus, these sets of samples have the highest potential to be tested as curcumin transport vectors for biomedical applications.

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PED-2019-4657, contract 318 PED / 2020, within PNCDI III.*

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CALCIUM CARBONATE ENRICHED-CHITOSAN PREPARED FROM SHRIMP SHELL WASTE

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Keywords: chitin, chitosan, chemical deacetylation

Introduction: Chitosan is a natural, nontoxic, biocompatible, biodegradable and, water- insoluble polymer, obtained by deacetylation of chitin. Chitosan finds a wide range of applications, that may be summarized as follows: medicine, pharmaceutics, cosmetics, agriculture, and food, where it has various characteristics such as antibacterial, antifungal, antimicrobial, antitumor, anticoagulant, antioxidant, and effects on immunity and wound healing. Chitin is a semi-crystalline homo-polymer, representing the main component of the exoskeleton of crustaceans, invertebrates, insects, arthropods, mollusks and arachnids, but also a component of the cell wall of some species of fungi, being the second most widespread after cellulose [1, 2]. The first step involved in the extraction of chitin involves washing and grinding of crustacean shells (most commonly shrimp). The next stage consists of demineralizing the water to remove minerals, particularly calcium carbonate. Deproteinization is aimed at removing a significant number of proteins from the structure. The obtained chitin is deacetylated before being converted to chitosan. The final stage in the procedure consists of washing and drying of the final product [3-4].
The main objective of this research is to obtain calcium carbonate enriched- chitosan starting from raw shrimp waste. A comparison with commercial chitosan and chitosan obtained from commercial chitin was also performed.

Materials and methods: The first research direction refers to attempts of producing chitosan from commercial chitin by means of a deacetylation process. The second research direction deals with chitin extraction from shrimp shell waste through a deproteinization process. Subsequently, on this particular obtaining process, chitin undergoes deacetylation, to obtain chitosan.

Results: In order to fulfill the main objective, consisting of obtaining chitosan from shrimp shell waste, modern characterization techniques were used to determine the Degree of Deacetylation (DD, by pH titration), the textural properties (BET), the structure and composition (by X-Ray Diffraction-XRD and Fourier-Transform Infrared Spectroscopy- FTIR) and viscosity (by Rheometric Analysis).

Conclusions: This study is the first step towards developing an innovative technology for the obtaining of an enriched type of chitosan from shrimp waste shells. By-passing the process of demineralization, leads to a raw chitosan with high content of calcium carbonate, which is further useful to increase the mechanical strength of thereof.

Acknowledgements: *The authors would like to thank the EU, JPI Oceans and the Romanian National Authority for Scientific Research and Innovation UEFISCDI for funding, in the frame of the collaborative international consortium (BIOSHELL, contract no. 157/2020) financed under the ERANET Cofund Bluebio 2019*

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CHITOSAN-BASED BACTERICIDAL INTERPENETRATED HYDROGELS

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Keywords: hydrogels, bactericide, chitosan, interpenetrated network, quaternary ammonium salts

Introduction: Bactericidal interpenetrated hydrogels are known to be an interesting topic in the latest years due to their unique properties with potential applications in wound healing devices [1], controlled release of drugs or the release or retain of nutrients from soil [2]. Therefore, there have been numerous reports focused on the improvement of the design and synthesis for the ideal interpenetrated material with bactericidal properties. Consequently, the goal of the current study is to obtain a series of new polymer networks with interpenetrated structure using commercial chitosan (CC)/ chitosan synthesized from commercial chitin (CCH) and vinyl benzyl-trimethylammonium chloride (VBTAC), a quaternary ammonium salt used for its excellent bactericidal properties [3,4]. The new hydrogels were physico-chemically characterized by infrared spectroscopy (FTIR) for determining the composition and by thermo-gravimetric analysis (TGA/DTG) for studying the thermal behavior. Also, the swelling degree (SD%) and the potential bactericidal effect of the hydrogels were investigated in order to determine the influence of the type of chitosan used in the interpenetrated network.

Materials and methods: The interpenetrated hydrogels were synthesized by radical polymerization using CC/ CCH, VBTAC monomer, variable concentrations of N,N'-methylenebisacrylamide (MBA) as crosslinking agent and a radical initiator. Acetic acid and distilled water were used to prepare the chitosan solutions.

Results: The obtained results showed that the type of chitosan influenced the swelling degree for each hydrogel. In the case of hydrogels with less MBA, differences between the values of the maximum SD% were observed. This showed that a higher concentration of crosslinker lead to much more rigid polymer networks, which prevented the absorption of larger amounts of water. The FTIR and TGA/DTG analysis indicated the presence of chitosan, indicated by characteristic peaks in the infrared spectra and characteristic degradation stages in thermal analysis, respectively. Bactericidal tests reflected the potential of the synthesized materials, especially the hydrogel based on CCH, to destroy both coliforms and clostridia in high proportions.

Conclusions: This study describes the successful synthesis of interpenetrated hydrogels by radical polymerization based on commercial chitosan, chitosan synthesized from commercial chitin and quaternary ammonium salts. The physico-chemically characterization of the new materials indicated the presence of the compounds of interest, showing no degradation in the chemical structures. The bactericidal investigation confirmed the potential of the materials in removing coliforms and clostridia from effluent waste waters, particularly for materials based on chitosan synthesized in the laboratory.

Acknowledgements: *The authors would like to thank the EU, JPI Oceans and the Romanian National Authority for Scientific Research and Innovation UEFISCDI for funding, in the frame of the collaborative international consortium (BIOSHELL, contract no. 157/2020) financed under the ERA-NET Cofund Bluebio 2019 Call.*

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SYNTHESIS AND CHARACTERIZATION OF CHITOSAN-STABILIZED SELENIUM NANOPARTICLES

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Keywords: Selenium nanoparticles; medium molecular weight chitosan; antioxidant activity

Introduction: Due to its physiological, metabolic, and pharmacological actions, selenium is considered an essential micronutrient in human nutrition. Red selenium nanoparticles (Se NPs) have been shown to have excellent bioavailability, antioxidant activity, and low toxicity, making them an alternative to inorganic and organic forms of selenium [1]. Se NPs gained attention in agriculture as plant protectants against plant pathogens and insects, plant biostimulant/plant growth promoters, and crop biofortification ingredients [2]. Chitosan (CS) is the only positively charged (semi)natural polysaccharide extracted from arthropods, insects, and fungi. Chitosan, which is used as a carrier for various drugs because of its low toxicity, was also tested for SeNPs encapsulation and stabilization [3]. The main aim of this study was to obtain and characterize SeNPs capped by chitosan with medium molecular weight (CS-SeNPs).

Materials and methods: SeNPs were obtained by chemical reduction of sodium selenite with ascorbic acid added dropwise. Chitosan was used as a stabilizer agent for Se NPs. A solution of 1% medium molecular weight chitosan (in 4% acetic acid) was added dropwise to the system and stirred for 30 min at 1000 rpm to prevent the aggregation of the synthesized particles**.** CS-Se NPs were characterized with SEM, TEM-EDX, DLS, and XRD. The antioxidant activity of the nanoparticles was determined by the DPPH method.

Results: The formation of SeNPs was confirmed by the color of the mixture turning a deep red. The HR-TEM and SEM (Fig. 1) images reveal the homogeneity of the sample and the distribution of the uniform spherical Se NPs. The average particle size of CS-SeNPs was 100 and 270 nm, as determined by TEM, UV-VIS, and DLS, respectively. The XRD analysis showed the amorphous CS-SeNPs formation. EDX confirmed Se as the mean element in CS-SeNPs.

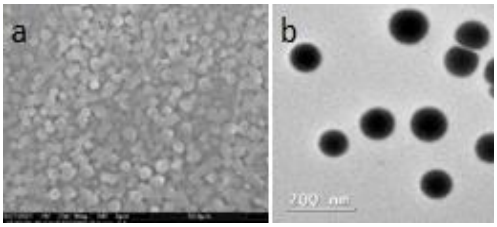

Figure 1. SEM (a) and TEM (b) images of CS-SeNPs

The antioxidant activity of CS-SeNPs was found to be 13.35 µM equivalent Trolox/ml.

Conclusions: Our study obtained medium molecular weight chitosan-stabilized selenium nanoparticles with high antioxidant activity and high stability, which could be used for agricultural applications.

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

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NOVEL COMPOSITE HYDROGELS BASED ON NATURAL COMPONENTSAND AKERMANITE ENRICHED WITH ICARIIN FOR OSTEOCHONDRAL HEALING

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Keywords: composites, gelatin, akermanite, icariin, osteochondral defects.

Introduction: Osteochondral regeneration becomes a big challenge due to the different composition of cartilage and subchondral bone and different biochemical, biomechanical and biological properties. For this reason, a biomimetic scaffold is necessary to provide different biological signals needed to allow the osteochondral regeneration [1]. This study aimed to design novel biodegradable cross-linked composite hydrogels based on gelatin, polysaccharidic components **(**chondroitin-4-sulphate and hyaluronic acid), mixed with akermanite and enriched with small bioactive molecule (icariin). Akermanite was used as a better alternative to conventional ceramics, due to its bone-like apatite formation ability and good bioactivity [2]. Icariin (Ica) flavonoid (from traditonal Chinese medicine *Epimedium* herb) was used as substitute for growth factors to enhance cell proliferation, chondrogenic and osteogenic differentiation [3].

Materials and methods: Variants of biodegradable cross-linked composite hydrogel based on gelatin, polysaccharidic components (chondroitin-4-sulphate and hyaluronic acid), in two ratios of 2:0.8:0.2 and 2:0.08:0.02 (w/w/w) were developed and mixed with akermanite, in a ratio of 2:1 (w/w). Subsequently, both composite hydrogel variants were cross-linked with (N, N-(3-dimethylaminopropyl)-N-ethyl carbodiimide (EDC) and enriched with small bioactive molecule (icariin). The obtained cross-linked composite hydrogel variants enriched with Ica were characterized related to the enzymatic biodegradation (type I collagenase), the swelling capacity, the degree of cross-linking (TNBS assay) and morphology (SEM). Their cytocompatibility was evaluated by analyses of cell viability and cellular cycle (flow cytometry), cell proliferation (Neutral Red assay) and cell adhesion to composite hydrogels (SEM) using NCTC clone L929 cell line.

Results: The final results have showed that both cross-linked composite hydrogel variants enriched with Ica presented optimal physicochemical and structural properties to be used as scaffold for osteochondral healing. Our data did not reveal any toxicity of composite hydrogels in NCTC cell line within the tested range of concentrations (10 – 50 mg/mL). Also, cells were capable to spreading and proliferating on the surface of composite hydrogels.

Conclusions: The designed biodegradable cross-linked composites enriched with Ica are recommended for further studies as natural temporary scaffolds, which can allow both cartilage and subchondral regeneration with implications in the management of osteochondral healing.

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PED-2019-1714, within PNCDI III.*

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HOMO AND HETEROCLUSTERS OF MN(II/III) AND CO(II/III) CONTAINING AMINOALCOHOLS AND CARBOXYLATE ANIONS

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Keywords: metal clusters, carboxylate ligands, heterometallic complexes.

Introduction: Magnetic clusters, meaning molecular assemblies consisting of a finite number of coupled paramagnetic centers, are currently receiving much attention in several active fields of research such as magnetism or biochemistry. [1]
Of particular interest were Co/Mn hetero-clusters due to the important and interesting applications that these metallic compounds present: catalysis, molecular magnetism, mimicking of active sites in biological systems.

Materials and methods: New Co/Mn hetero-clusters were synthesized using cobalt perchlorate ($(Co(ClO_4)_2 \cdot 6H_2O)$, manganese perchlorate ($(Mn(ClO_4)_2 \cdot 6H_2O)$, triethanolamine ($H_3$tea), pivalic acid (Hpiv) and triethylamine (Et_3N) for deprotonation obtaining $[Co^{II}_2Mn^{II}_2Mn^{III}_2$ $(Htea)_4(piv)_6(Hpiv)_2] \cdot 8H_2O$ and the same salts, but changing the amino-alcohol with N-tertbutyldiethanolamine and using sodium acetate for $[Co^{II}_3Mn^{II}_2Mn^{III}_2(N\text{-tbdea})_4(AcO)_4(OH)_2(H_2O)_2] \cdot 2ClO_4 \cdot H_2O$.

Results: Single crystals of the two new metallic clusters were obtained and measured on single X-ray diffractometer.

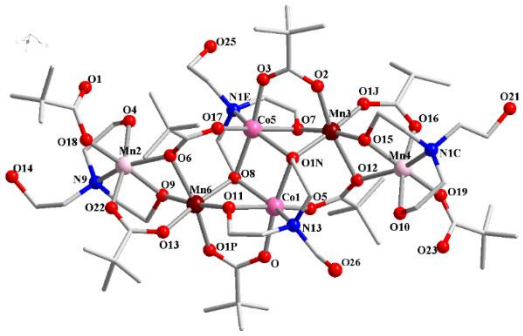

Fig.1 Structure unit in $[Co^{II}_2Mn^{II}_2Mn^{III}_2$ $(Htea)_4(piv)_6(Hpiv)_2] \cdot 8H_2O$

Conclusions: The crystal structure of the compounds confirm the presence of the Cobalt(II,III) and Manganese(II,III) metal ions, based on interatomic distances and stereochemical preference of these cations.

Acknowledgements: *This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, UEFISCDI, project number PN-III-P1-1.1-TE-2019-1345, within PNCDI III..*

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NANOCOMPOSITE HYDROGELS BASED ON POLY(*N*-VINYL PYRROLIDONE)

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Keywords: hydrogels; poly(N-vinyl pyrrolidone); reinforcing agent; nanocomposite; nano-clay.

Introduction: Poly(*N*-vinyl pyrrolidone) (PNVP) is one of the most studied and recognized polymer for pharmaceutical industry and medicine purposes due to its unique combination of highly important properties such as nontoxicity, biocompatibility with human tissue, chemical stability, good solubility in water and other solvents.

Most of the PNVP based hydrogels are characterized by low mechanical properties when handled in swollen state. For this purpose, several methods have been reported to increase the mechanical properties of these gels. Among them, the one reported of Haraguchi[1] consisting in introducing an inorganic clay as reinforcing agent into the *N*-substituted acrylamide aqueous solution led to a polymer-clay nanocomposite hydrogel with improved mechanical toughness. Based on this study, Okay and Opperman[2] developed polyacrylamide nanocomposite hydrogels by using a mono vinyl monomer, acrylamide, and Laponite RDS as reinforcing agent.

Materials and methods: For this purpose, several methods have been reported in literature by Wang[3] et all., the present work deals with the preparation and detailed structural characterization of nanocomposite hydrogels based on amidic N-vinyl pyrrolidone (NVP) monomer, with or without *N*,*N*-methylenbis(acrylamide) (MBA) as chemical crosslinker and different concentrations of Laponite XLG as reinforcing agent. The hydrogels were synthesized by radical polymerization of the monomers using 2,2-azobisisobutyronitrile (AIBN) as the initiator.

Results: We evaluated, within this work, the structure of PNVP based nanocomposites by using FT-IR, their morphology through SEM-EDX and the influence of different amounts of Laponite XLG on the final properties, by performing rheological measurements and swelling studies.

Conclusions: The nanocomposite hydrogels were successfully obtained and characterized by different methods. The Laponite XLG used as reinforcing agent significantly contributed to the improvement of the mechanical properties of the nanocomposite hydrogels.

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SILVER (I) COMPLEXES WITH A LUMINESCENT TRIPODAL LIGAND

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Keywords : silver complexes, Schiff bases, fluorene derivatives, luminescence

Introduction: The tripodal ligands, as an extension of the podand concept to three dimensions, represent a category of molecules able to encapsulate more fully their guest. The tripodal ligands can act as receptors for different chemical species: transition metal ions,[1] lanthanide ions,[2] anions, [3] or cations and anions in the same time.[4] The thermodynamic stability of the host–guest complexes makes from the tripodal ligands good candidates for biomedical applications as sequestering agents.

Materials and methods: A series of mononuclear Ag(I) complexes was obtained using various silver (I) salts and the tripodal ligand derived from 2-fluorenecarboxaldehyde and tris(2-aminoethyl)amine. All the complexes were structurally characterized by X-ray diffraction on single crystal.

Results: In these complexes, the Ag(I) ions are tetracoordinated with a distorted tetrahedral stereochemistry (Figure 1). The silver ions are located outside of the tetrahedron formed by the four nitrogen atoms (three imino and one amino nitrogen atoms). Coordination of the silver ions is quenching the luminescence of the free ligand.

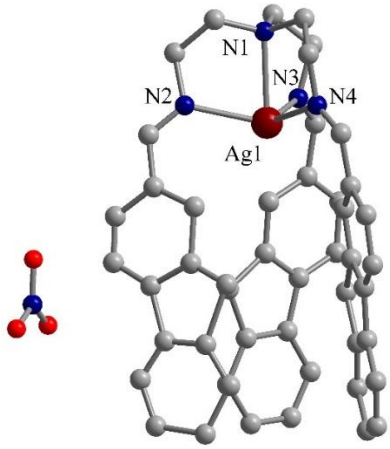

Figure 1. Crystal structure of the complex [Ag(L)](NO_3)

Conclusions: The tripodal Schiff base ligands derived from 2-fluorenecarboxaldehyde and tris(2-aminoethyl)amine are efficient chelators for the silver ions and the changes in the optical properties induced by coordination can be used for the detection of these metal ions.

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FUNCTIONALIZED β-CYCLODEXTRIN FOR SMART DRUG DELIVERY APPLICATION

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Keywords: β-cyclodextrin; drug delivery; cancer therapy.

Introduction: In recent years, an emphasis has been established on advanced cancer drug delivery, in order to improve the efficiency of the cancer therapy [1]. Cyclodextrin (CD) is a cyclic oligosaccharide formed by 6, 7, or 8 glucose units by α-1,4 glycosidic bonds, which are called α, β, γ-cyclodextrin respectively [2]. Due to its hollow truncated morphology with a hydrophobic inside and hydrophilic outside, CD has been studied in numerous drug delivery systems [3-5]. In the present study, the modification of β-CD with 3-(Aminopropyl)triethoxysilane (APTES) was investigated.

Materials and methods: For this study were used β-Cyclodextrin (β-CD) purchased from Fluka, 3-(Aminopropyl)triethoxysilane (APTES) from Sigma Aldrich, NaOH from Roth, dimethylforamide (DMF) from Acros Organics, acetone from Chimreactiv. Firstly, NaOH, APTES, and DMF was solubilized by magnetic stirring for 1 h at 40° C. After solubilization, β-CD was added and allowed to react for 2h, at 40°C, under magnetic stirring. The functionalized β-CD was precipitated in acetone, and in the end washed and filtered. The sample was dried at room temperature and investigated by NMR.

Results: The ^{1}H NMR was employed to further demonstrate the molecular structure of β-CD. The obtained NMR spectra of β-CD shows the presence of characteristic proton peaks.

Conclusions: The chemical structure of functionalized β-CD was studied, in order to look for possible biomedical applications, such as smart drug delivery systems.

Acknowledgements: *This work was supported by a grant from the Ministry of Research, Innovation and Digitization, CNCS/CCCDI–UEFISCDI, project number PN-III-P4-ID-PCE-2020-1154, Hemodialysis combined with stimuli-responsive drug delivery – a new generation of polymeric membranes for advanced biomedical applications within PNCDI III.*

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IN VITRO AND *IN VIVO* TESTING OF GROWTH FACTORS COATED TITANIUM IMPLANTS

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Keywords: mesenchymal stem cells, endothelial cells, rat bone implant, immunohistochemistry, RT-qPCR

Introduction: The long-term stability of an orthopedic implant can only be ensured by biological integration, which is facilitated by increased tissue vascularization [1]. In our previous work, we proposed a new bioactive surface of titanium implants with a synergetic PEG biopolymer-based composition for gradual delivery of growth factors (FGF2, VEGF, and BMP4) during bone healing [2]. All proposed coatings have shown biocompatibility when tested in human mesenchymal stem cells (hMSCs) and endothelial cells (EA-hy926) monocultures. The coating containing all growth factors showed accelerated healing in a rat diaphyseal *in vivo* tibial defect model. Here, we tested all material combinations in hMSC-EA-hy926 co-cultures and we used a different approach to test the efficacy of the FGF2-VEGF-BMP4 hierarchical coating in Wistar rats for implants applied to less vascularized areas, without prior wounding.

Materials and methods: The percentage of hMSC grown on each type of coating was assessed by flow cytometry (FACSVerse, BD). Osteogenic differentiation efficiency was assessed by alkaline phosphatase staining using NBT-BCIP as a substrate. For *in vivo* analysis, a bone defect was created in rats at the femur-tibio-patellar joint where titanium implants were inserted intercondylar. The animals were monitored clinically (weight, temperature, health), haematologically and biochemically. Bones were surgically removed from the animals and subjected to histology, immunohistochemistry and Real-time RT-qPCR analyses.

Results: A 5:1 hMSC-EA-hy926 cell ratio was determined optimal for enhanced osteogenic differentiation *in vitro*. Upon growing of the cells onto FGF2 and VEGF growth factors coated titanium disks, ~1/5 of the cells were represented by hMSCs, while this fraction increased to ~1/3 when BMP4 was used alone or added to the combination. These were all able to support osteogenic differentiation. We focused our *in vivo* study on Ti-FGF2-VEGF-BMP4, which we expected to enhance implant integration. The results of the histological examination showed that titanium implants treated with growth factors and inducers of osteogenesis contribute to a faster bone regeneration, and the local effects are favorable. Our results evidenced the expression of bone markers (ALP, osteocalcin) at the implantation site.

Conclusions: Dip-coated FGF2-VEGF-BMP4 containing polymer matrix can be further developed as a promising coating for enhanced titanium bone implant osteointegration.

Acknowledgements: *This project was supported by UEFISCDI funding, grant number PN-III-P1-1.2-PCCDI-2017-0728, acronym TERAMED.*

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NEW HYDROGEL FORMULATIONS BASED ON NATURAL AND SYNTHETIC POLYMERS FOR SKIN REGENERATION

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Keywords: gelatin, methylcellulose, cytotoxicity, wound healing

Introduction: The skin, which represents about 16% of the total body mass, acts as a protective barrier against external microbial factors [1]. Therefore, damaged tissues, especially burns, require rapid local coverage to avoid infections and ensure the protective barrier function of the skin [2]. The aim of this study was to design and characterize new hydrogel formulations, based on natural and synthetic polymers, biodegradable and cytocompatible, to serve as temporary dressings with regenerative properties for skin wound healing.

Materials and methods: The proposed experimental variants of hydrogels are based on mixtures of gelatin (Gel), sodium alginate (Alg), polyvinyl alcohol (PVA), methylcellulose (MC1500), in different weight ratios: Gel-Alg (1:0.75, g/g), Gel-Alg-PVA (1:0.27:0.18, g/g/g) and Gel-Alg-MC1500 (1:0.26:0.35, g/g/g). The physicochemical and biochemical characterization was performed in terms of swelling degree, biodegradation in physiological conditions (pH 7.4, 37^{o}C) and in the presence of collagenase (mimicking the inflamed wounded milieu), viscosity and syneresis, while their ultrastructure was investigated by SEM analysis [3]. The L929 murine fibroblast culture was used to assess the *in vitro* cytocompatibility of the hydrogels, after 24 h and 48 h of cultivation, using quantitative MTT and LDH assays [4]. Cell morphology was observed in treated cultures by light microscopy after Giemsa staining.

Results: The physicochemical and biochemical analyses indicated that the novel variants of polymeric hydrogels had swelling capacity due to Alg presence, adjustable viscosity and controlled biodegradation over time, in both physiological and inflamed conditions. Two mixture variants were outlined: Gel-Alg-PVA with reduced porosity and low biodegradability in time and Gel-Alg-MC1500 with increased porosity and higher biodegradation in time, even in the physiological environment. SEM morphology observations showed a dense and microporous structure of the hydrogels, with pores of irregular shape and size, which could ensure skin protection against external microbial agents, while maintaining the required degree of humidity and the oxygen exchange with the external environment. *In vitro* quantitative tests indicated a high degree of cytocompatibility for all tested hydrogels, with percentages of cell viability higher than 90%. Cell morphology observations revealed that, in the presence of hydrogel samples, L929 murine fibroblasts maintained their normal phenotype and the cell density was similar to that of the negative control (untreated cells).

Conclusions: Overall, our findings indicated the hydrogels containing synthetic polymers (Gel-Alg-PVA, Gel-Alg-MC1500) had adequate physicochemical, biochemical and biological properties to be further tested as biomaterials for skin tissue engineering applications.

Acknowledgements: *This work was supported by National Programme Nucleu, Project No. 25N/2019–19270102*

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COMPLEX STUDY OF PASTES OBTAINED FROM BIOECONOMY SIDE STREAMS FOR 3D PRINTING

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Keywords: rheology, mechanical properties, food fabrication, personalized food

Introduction: 3D printing technology, also called additive manufacturing, is an emerging processing method to create stereoscopic objects. . This technology is defined as fabrication of objects by the way of material deposition to build a three dimensional shape.[1] Additive 3D printing method technologies can be listed as inkjet technology, material extrusion, light polymerization, powder bed fusion, binder jetting, lamination, and direct energy deposition.

Materials and methods: The materials are deposited layer by layer using a nozzle under the command of 3D printer. Lately, there has been acceleration in sales of 3D food printers. 3D printing technology makes it possible to mix different ingredients and customize personalized recipe according to the textural and nutrition requirements.[1] The advantage of this technology is that it can be used as a printing material for homemade pastes, but printing technique has its own scope and limitations.[2] There was developed a function to relate the key parameters for 3D printing as nozzle diameter, movement, speed, and extrusion rate. [3]

Natively printable materials such as hydrogels, cake frostings, cheeses, and chocolate are materials that can adapt to the needs of printing. [2] These mixtures could compliment all judged parameters, including viscosity, consistency, and the ability to keep shape post-deposition.

Results: The purpose of the work is to use various food constituents obtained from bioeconomy side streams like protein, carbohydrate, or fat to make a material supply for 3D printing.

Conclusions: The components, when used in any concentration above the gelatinization point help in extrusion and improve retention of food structure after printing. The rheology of the obtained pastes and the stability of the compositions were studied. Food materials were filled into a plastic syringe and then inserted into a metal nozzle for printing. Printing accuracy was evaluated by correlating with nozzle diameter and print object height as well as the evolution of the object over time.

Acknowledgements: *This work was supported by project POC-A1-A1.2.3-G-2015-P_40_352-SECVENT, My_SMIS 105684, "Sequential processes of closing the side streams from bioeconomy and innovative (bio)products resulting from it, subsidiary project 1488/2020 3D-4Fish. The SECVENT project was co-funded by European Regional Development Fund (ERDF), The Competitiveness Operational Programme (POC), Axis 1.*

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SETTING AND RECOVERY OF SHAPE MEMORY FOR NEW SMART MATERIALS BASED ON RENEWABLE POLYMERS

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Keywords: smart materials, shape memory, setting, recovery

Introduction: The smart materials are types which respond to external stimuli by changing their shape/volume/ color /material physical properties (glass transition, deformation recovery speed, Young's modulus, stiffness etc.). In order to achieve such materials a complex program must be followed in which the stage of simple or multiple memory setting and its recovery has an essential matter because the subsequent material performance is conditioned by the accuracy with which these two phases were conceived and realized [1, 2].

Aim: Designing and validation of an experimental program for multiple memory setting and shape recovery of new compounds based on renewable polymers aimed [3] to function as smart materials.

Materials and methods: Samples achieved of polylactic acid compounds (PLA) - thermoplastic polyurethane (TPU) selected compounded were used. The program for multiple memory and recovery was done using a DMA Q800 from TA Instruments and contained the following 3 cycles of deformation under load at a selected temperature (60^{o}C) - cooling to 0^{o}C: device settling, cycle 1 (increase the temperature to 60^{o}C and keeping under 6 N load for 3 min., recording the clamp movement during keeping under load, temperature drop to 0 ^{o}C, isotherm for 3 min.), cycle 2 increase the temperature to 60^{o}C and keeping under 6 N load for 3 min., recording the clamp movement during keeping under load, temperature drop to 0 ^{o}C for 3 min.), cycle 3 (increase the temperature to 60^{o}C and keeping under 6 N load for 3 min., recording the clamp movement during keeping under load, temperature drop to 0 ^{o}C for 3 min.). The clamp movement during the 3 cycles was recorded by DMA Universal Analysis soft.

Results: The obtained results showed that the selected materials have a different behavior at the 3 cycles of under load deformation – deformation recovery and this behavior is perfectly explainable according to the chemical and morphological structure of the melt compounded polymers. The reproducibility tests performed for the selected compounds confirmed the information from the first experiment.

Conclusions: The ability of PLA-TPU compounds designed as smart materials to support multi memory setting and recovery procedures can be estimated by registering the displacement of the mobile clamp of DMA device during performing a special designed program with 3 cycles of loading of heated samples (60^{o}C)-unloading cooled (0^{o}C) samples. These results were used in preliminary smart polymeric material selections.

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number* PN.19.23.03.02.01.12

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TRIPLE SHAPE MEMORY OF NEW MATERIALS BASED ON RENEWABLE POLYMERS DESIGNED FOR 4D PRINTING

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Keywords: smart materials, triple shape memory, renewable polymers

Introduction: Smart materials with shape memory have the ability to recover their original shape, after plastic or quasi-plastic deformation, under the action of certain external stimuli such as: heating / cooling (thermo-sensitive), light (photo-sensitive), chemical substances (chemical-sensitive), mechanical stress (mechanical-sensitive), electrical stress (electro-sensitive) [1,2,3] etc. Therefore, on a macro scale, the polymeric materials which present shape memory exit in two forms: a temporary and a permanent one. Due to heating, deformation, cooling etc. a material in a temporary form reaches a permanent one under to the action of an external stimulus.

Aim: Achieving by melt compounding of smart polymeric materials with shape memory from polylactic acid (PLA) and thermoplastic polyurethane (TPU).

Materials and methods: New PLA-based compounds were achieved, using a classical Brabender procedure by modification of various grades of PLA with various grade of TPU. The proof of the ability to withstand one or more cycles of setting - recovery memory was performed according to the own method described in another paper.

Results: The obtained results showed a big difference between the behavior of various compounds in the 3 cycles setting- recovery memory test. If the TPU contains the same type of rigid blocks that, when melted, entangle with the PLA macromolecules, then, after cooling, results smart polymeric materials which support only a single memory setting - recovery cycle. If it consists of several types of rigid blocks, after compounding with PLA, the resulted materials support several cycles of setting – recovery memory. The further characterization of the selected compounds will bring additional information related to the way in which the memory effect can be controlled with the help of TPU morphology. The TPU morphology depends on the interactions between the -NH- and -CO- groups, so that depending on the chemical structure, the intensity of the resulted van der Waals bonds to be of high, intermediate or very low intensity. In these conditions TPU can show multiple phase transitions and so by proper choice of their chemical structure, after compounding with selected PLA to be possible the practical realization of compounds with multiple shape memory.

Conclusions: The ability of PLA-TPU compounds designed as smart materials to support multi memory setting and recovery procedures can be estimated by registering the displacement of the mobile clamp of DMA device during performing a special designed program with 3 cycles of loading of heated samples (60^{o}C)-unloading cooled (0^{o}C) samples. These results were used in preliminary smart polymeric material selections.

Fig.1 New compounds with memory recovery properties

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number* PN.19.23.03.02.01.12

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COMPOSITION, ANTIOXIDANT AND ANTIFUNGAL PROPERTIES OF LAVENDER FLORAL WATERS

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Keywords: lavender hydrosols, by-products, polyphenols, antioxidant activity, antifungal.

Introduction: During essential oil preparation from aromatic plants, floral waters or hydrosols or hydrolates are obtained as by-products presenting inhibitory effects on phytopathogenic fungi growth, while avoiding the main problem of soil accumulation observed for currently used fungicides [1, 2]. Lamiaceae family is widely distributed around the world and large growing fields of Lavandula sp. can be found in Romania. The aim of this study was to obtain a hydrosol of lavender and to evaluate its composition in correlation with the antioxidant and antifungal properties, in order to develop an alternative natural product to commercial fungicides.

Materials and methods: Floral water was obtained from aerial parts of *L. Angustifolia* subjected to reflux for 2 h, as by-product of essential oil preparation, and stored in the dark, at 4 °C. Gas chromatography-mass spectrometry (GC-MS) and high performance liquid chromatography (HPLC) analyses were performed to evaluate the composition in bioactive compounds. The antioxidant activity of lavender hydrosol was investigated by 2,2-diphenyl-1-picrylhydrazyl (DPPH) [3] and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) [4] assays, in comparison to butylated hydroxytoluene (BHT). Different concentrations were added in the culture media of the plant pathogenic fungus *Rhizoctonia solani* and the fungal growth was monitored at a wavelength of 600 nm, at predetermined periods of time using a SpectroStar Nano microplate reader. The untreated culture served as negative control, while bifonazole, a known antifungal agent was used as positive control.

Results: The process of lavender hydrosol extraction had a yield of 18% (w/w). The obtained lavender hydrosol presented quantifiable volatile oils and polyphenolic compounds, as showed by GC-MS and HPLC analyses, respectively. GC-MS showed the prevalence of linalool and small amounts of lavandulol, β-caryophyllene and trans-ocymene. HPLC showed the presence of caffeic and ferulic acids as main phenolic acids and astragalin, luteolin and isoquercetin as main flavonoids. The antioxidant activity of lavender hydrosol was higher than that of BHT, a known synthetic antioxidant, as showed by DPPH and ABTS assays. *In vitro* cell culture results showed that the obtained lavender hydrosol had fungistatic effect in the range of tested concentrations.

Conclusions: All these results indicated that this natural by-product could be valorized to develop novel natural formulas with antioxidant and antifungal activity for preventing plant diseases, providing several advantages, such as fast decomposing in the enviroment and no toxicity, thus being optimal for applications in ecologically sustainable agriculture.

Acknowledgement: *This work was supported by a grant of the Romanian Ministry of Education and Research, CCCDI-UEFISCDI, project no. PN-III-P2-2.1-PED-2019-3561, within PNCDI III.*

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NEXT-GENERATION OF BEE FEED BY BIOMIMETIC FORMULATION OF HYDROCINNAMIC ACID

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Keywords: honeybees, hydrocinnamic acids, prebiotic activity

Introduction: Honeybees, *Apis mellifera*, play an important role in the global ecology and economy. Honeybees produce various products (honey, pollen, royal jelly, beeswax, propolis) used for human wellness. Also, these insects are essential as pollinators of crops [1].
One major problem the honeybees face is the nutritional imbalance related to habitat loss and abuse of agrochemicals. The nutritional imbalance happens when bees are limited in harvesting nutrients from natural sources or in the case of excessive settlement of honey by humans. In this case, beekeepers should come to the aid of bees with an additional supply of nutrients. The bee feed substitutes used by beekeepers are those based on sugar, such as inverted sugar syrup, starch syrup, or high fructose corn syrup (HFCS), which do not provide essential nutrients for honeybees [2].

The main aim of this research was the use of hydroxycinnamic acids (i.e., ferulic acid) specific to plant cell walls, including pollen grains, as a nutraceutical supplement for bees. The role of these hydroxycinnamic acids (HCA) is to directly activate the defense system in bees and stimulate the development of fructophilic lactobacilli [3]. This combined activation enhances the defense and detoxification systems at the level of each bee and at the level of the whole colony.

Materials and methods: Three different concentrations of ferulic acid (AF) were mixed with isoglucoses syrup. The antioxidant activity (AOA) of the samples was assayed using five spectrophotometric methods: radical scavenging activity (ABTS and DPPH) and reducing antioxidant power (CUPRAC, FRAP, and PFRAP). The prebiotic activity of the samples was evaluated on a strain of *Lactobacillus plantarum* DSM 1055 and *Lactococcus lactis* DSM 20729.

Results: AOA of syrup enriched in HCA showed an exponential increase, directly related to HCA concentrations by all colorimetric methods analyzed. Our product showed higher prebiotic activity with almost 19 % at the concentration of 0.125 mg/g of AF after 72 H of incubation in the case of *L. plantarum*, compared with simple isoglucose syrup. In the case of *L. lactis*, the value of prebiotic activity was around 10 % after 72 H of incubation.

Conclusions: Our preliminary results showed that isoglucoses syrup enhanced with HCA indicated that it can be used as nutraceuticals supplements for bees feed due to its AOA and prebiotics activity. We need to continue the study with other strains of lactobacillus isolated from bees gut microbiota.

Acknowledgments: *This work was supported by project POC-A1-A1.2.3-G-2015- P_40-352 – SECVENT 81/2016, "Sequential processes of closing the side streams from bioeconomy and innovative (bio)products resulting from it," funded by cohesion funds of the European Union. Subsidiary project 5544/2020 Meli-STIM.*

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MOLECULAR DESIGN OF FUNCTIONAL INGREDIENTS STARTING FROM NATURAL BIOACTIVE COMPOUNDS

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Keywords: gallic acid, chlorogenic acid, functional food ingredients

Introduction: In the last few years, a new concept of functional foods has been developed, leading to the diversification of food production. Thus, not only basic nutrients are provided, but also products for good health and longevity. Phenolic acid derivatives are major bioactive compounds widely found in the vegetal world. Attempts to give them an added-value as functional food ingredients with beneficial health applications are recently discussed in literature data [1,2]. Thus, studies on gallic acid (3,4,5-trihydroxybenzoic acid) found in rice, corn or wheat [3] indicate its possible effects in reduced obesity and ameliorated related complications [4]. In this research, an extensively computational approach using dedicated software tools for predicting bioactivity and pharmaceutical properties are conducted on phenolic acids derivatives such as gallic and chlorogenic acids, aiming to highlight their potential use as functional ingredients in yoghurt type dietary products.

Materials and methods: The geometry of investigated structures was optimized in a multi-step procedure by molecular mechanics force fields, resulting the lower energy conformers as shown in Figure 1 a, b. Properties are calculated using ωB97X-D level of theory [5]. Bioactivity scores towards protein-coupled receptor (GPCR) ligand, ion channel modulators, kinase inhibitors, nuclear receptor ligands, protease inhibitors and other enzyme targets are predicted using *Molinspiration* online platform.

Results: Molecular properties and features of studied phytocompounds are obtained: area, volume, polar surface area, ovality, polarizability, dipole moment, water-octanol partition coefficient, energies of frontier molecular orbitals, descriptors related with the flexibility and electrophilic/nucleophilic sites.

Figure 1. a). Gallic acid 3D optimized structure b). Chlorogenic acid 3D optimized structure

Conclusions: Evaluation of relevant physical and chemical descriptors for hydrophilic-lipophilic balance suggests preliminary data to design furthermore functional ingredients with nutraceutical value.

Acknowledgements: *This research work was funded by the Romanian National Authority for Scientific Research ANCS, Competitiveness Operational Programme COP-A1-A1.2.3-G-2015, Project title "Innovative technologies for new, natural health products", ID P_40_406, SMIS 105542, Contract D02/23.03.2021*

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IN VITRO ANTIOXIDANT ACTIVITY DETERMINATION OF A MICROENCAPSULATED SYNERGIC POLYPHENOLS POLYSACCHARIDE MIXTURE

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Keywords: antioxidant activity, microencapsulation, synergic mixture, simulated digestion

Introduction: The aim of this work was to obtain a mixture of polyphenols and polysaccharides, extracted from forest fruit pomace (a side stream of forest fruit juice production) and chia seeds with a synergic antioxidant activity that will be further encapsulated and used in a fortified protein bar.
We also intended to demonstrate the *in vitro* antioxidant effect, including in cell cultures, of the synergistic mixture encapsulated and subjected to a simulated digestion process.
Materials and methods: Forest fruit pomace is the main source for polyphenols (PPH) and chia seeds for polysaccharides (PSH). PPH extraction was made in 70% ethanol, at room temperature, 48 h with agitation and PSH extraction was made by Soxhlet method. Antioxidant activity of PSH and PPH combinations with synergic effect was determined using 3 different methods ABTS, DPPH and CUPRAC. The PPH and PSH combinations with the higher synergic antioxidant activity were encapsulated using whey protein and inulin as matrix. Microencapsulated synergic polyphenols –polysaccharide mixture was analized by HITACHi SU 1500 Scanning Electron Microscope (SEM) operated at 15 kV (samples were fixed with glutharaldehyde, dihidrated in succesive ethanol concentrations and contrasted with osmium tetraoxide). The microencapsulated mixtures were also subjected to a simulation of gastrointestinal digestion *in vitro.* After digestion, the cells (primary human colonic tumor cells - Caco-2) viability, respectively the estimation of the cellular antioxidant capacity of the samples, was measured by Neutral Red assay, with or without induced oxidative stress. [1-3]
Results: In the forest fruit pomace the polyphenol content (PPH) was 304 mg gallic acid/g dw. The polysaccharide content in chia seeds (PSH) was 135 mg glucose/g dw. The antioxidant activity of forest fruit pomace was determined by 3 methods (ABTS - 1.32 mM TE/mg dw.; DPPH - IC_{50} 456.17 µg/ml; CUPRAC - 4.96 mM TE/mg dw.) For chia seeds polysaccharides the results were: ABTS - 0.038 mM TE/mg dw., DPPH - IC_{50} 5000.6 µg/ml, CUPRAC - 1.96 mM TE/mg dw. The PPH and PSH combinations had a higher synergic antioxidant activity especially in the ratio of 2:1 and 5:1. By scanning electron microscope analyse we observed microcapsules presence on the outer layer of the matrices obtained by freeze drying. The average size of microcapsules was in a range of 5-10 microns. *In vitro*, we observed that Caco-2 cells, pre-treated with encapsulated synergic mixture of PPH and PSH that was subjected to simulated digestion, had a viability up to 20% higher compared to the control treated only with H_2O_2, so the studied mixture had antioxidant protective effect on cells against the oxidative agent.
Conclusions: We observed that the synergic mixture of the PPH and PSH, with proved antioxidant activity, maintain this activity after encapsulation. The antioxidant capacity of microencapsulated mixture makes it suitable for being introduced in new formula of functional food.

Acknowledgements: *This work was supported by a grant of the Romanian Ministry of Education and Research, CCCDI - UEFISCDI, project number PN-III-P2-2.1-PED-2019-3805, within PNCDI III.*

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ORGANOMETALLIC COMPOUNDS AND METAL COMPLEXES IN CANCER THERAPY

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Keywords: metal complexes, drug delivery systems, cancer therapy

Introduction: Globally, colon cancer is a major cause of deaths, being the fourth most common type of cancer. The most common therapeutic choice in the early stages of colon cancer is surgical resection, but in some stages of the disease adjuvant chemotherapy is recommended, being essential for the proper treatment of this pathology. [1]Complex combinations based on metals play an important role in the treatment of cancer because of their cytotoxic properties against cancer cells. An organometallic compound used clinically that plays an important role in the treatment of patients with colon cancer is oxaliplatin.

Materials and methods: Following studies, chlorine-based derivatives of Au (I) -phosphate showed comparable values to cisplatin on HT-29 (colon cancer) cell lines. Studies continued to determine absorption at the cellular level showing that most lipophilic compounds, showing a higher absorption of colon cancer cells, results with which they could be correlated with high antiproliferative activity. [2]Copper-based complex combinations were studied, thus observing the inhibitory effect in the nanomolar range on the Colo 205 and Colo 320 colon cancer cell lines. Some complexes showed increased toxicity to cancer cells compared to the cell lines of type MRC-5. The antiproliferative activity of these complex combinations is significantly low in normal cell lines, thus increasing selectivity towards neoplastic cells was observed. Complex combinations based on Cu (I) show 5 times higher cytotoxic effect against LoVo MDR cell lines compared to oxaliplatin, thus showing the ability to overcome oxaliplatin resistance. [3]

Results: Nanostructured drug delivery systems allow the incorporation of metal-based drugs, thus limiting some of the most common shortcomings such as low selectivity, low solubility and permeability, high toxicity that limits dosage and the emergence of resistance at the cellular level. [4]

Conclusions: The drug delivery systems are able to carry the drug and to release it according to its requested dose even in a targeted manner, thus improving the therapeutic activity and limiting systemic toxicity.

Acknowledgements: *The present work was possible due to the EU-Funding Grant POSCCE-A2O2.2.1-2013-1, Project no. 638/12.03.2014, Code SMIS-CSNR 48652.*

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COMPARATIVE STUDIES CONCERNING BIOACTIVE PEPTIDES OBTAINED FROM FISH BY-PRODUCTS

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Keywords: : fish collagen, peptides, enzymatic hydrolysis, properties, biocompatibility

Introduction: Fish byproducts (bone, scale, or skin) contain a wide range of nutritional components, especially proteins and lipids, the most important of all being collagen. The hydrolysate of collagen from this source, obtained by enzymatic method with papain, is rich in bioactive peptides.The aim of this work was to obtain and characterize peptides obtained by enzymatic hydrolysis from fish byproducts.

Materials and methods: Collagen was obtained by enzymatic methods with pepsin. Peptides were obtained from extracted collagen by enzymatic hyrolysis with papain and were separated by tangential ultrafiltration (using ÄKTA flux cross flow filtration system). This method allowed the separation of low molecular weight peptides (1-30 kDa) from those with high molecular weight (> 50 kDa). Bovine collagen hydrolyzate was used as a control. For the peptide samples we determined: protein content (by Biuret method), antioxidant capacity (by DPPH and ABTS methods), protein hydrolysis degree (using 2,4,6-trinitrobenzenesulfonic acid-TNBS reagent [1]), the inhibitory potential of angiotensin converting enzyme (ACE) [2] and the cytotoxicity in NCTC fibroblast cell line (clone L929) according to the international standard SR EN ISO 10993-5, by MTT assay. SDS-Page electrophoresis was used to asses the presence of peptides in the mass range 1 – 100 kDa [3].

Results: The results obtained for the hydrolysis degree as well as for the ultrafiltrated peptides were confirmed by the electrophoresis profile. Biochemical determinations (the antioxidant capacity, the ACE inhibition potential) and the cytotoxicity of tested peptides, with MW lower than 50 kDa, demonstrated their bioactivity. The results of MTT assay demonstrated that obtained peptides did not affect the cell viability in the range of concentration 50-1000 µg/mL, except bovin collagen sample which is slightly cytotoxic at 1000 µg/mL concentration.

Conclusions: Our results showed that the collagen peptides obtained after fish collagen hydrolysis with papain had antioxidant and antihypertensive activity, and the treatment of NCTC fibroblast cells with these peptides did not affect the cell viability. These results suggest that peptides obtained by enzymatic hydrolysis from fresh water fishes by-products collagen can be used in food supplements or cosmetic products.

Acknowledgements:*This research was financially supported by the project* PN-III-CERC-CO-PTE-2-2019 *3PTE (COLSTIM)2020-2022*

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OBTAINING PROTEIN HYDROLYSATES FROM HEMP SEEDS

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Keywords: hemp, enzymes, hydrolysis

Introduction: Hemp (*Cannabis sativa ssp. sativa*) is a widespread textile plant whose seeds, obtained after the commercial utilization of fiber, contain 20-25% protein, which is rich in all the amino acids necessary to maintain good health. Hemp seeds protein has a very good bioavailability and digestibility, contains hypoallergenic peptides whose absorption is improved by the fiber complex and has a subtle aromatic profile, being a balanced food source for human nutrition. The current trend is to relaunch this underexploited plant to obtain seeds protein with benefits in various diseases which have been medically proven. The aim of this paper was to perform the enzymatic hydrolysis of hemp seeds protein to obtain bioactive peptides.

Materials and methods: Hemp seeds protein was used as a substrate for testing the following enzymes: Papain, Alcalase 2,4L, Pepsin and Pancreatin. The hydrolysis efficiency was evaluated for each enzyme by modifying the following parameters: enzyme/substrate ratio, pH, temperature and reaction time.
Enzymatic hydrolysis of hemp seed proteins was performed according to the methods described by [1] and [2], with minor modifications. Hemp seed protein (5% w / v protein weight) was dispersed in distilled water, at room temperature and homogenized at 10,000 rpm for 2 minutes. The temperature and pH of suspensions were adjusted to the values of each enzyme to ensure an optimum activity. The suspensions were gently agitated on a stirrer. The substrate/enzyme ratio was calculated from the amount of protein in the sample. During digestion, the pH values were kept constant by the addition of 2M NaOH or 1M HCl. After inactivation of the enzymes (90° C for 15 minutes) the protein hydrolysates were neutralized and centrifuged at 5400xg, 20 minutes, at 4° C, to remove undigested proteins. The supernatant containing a mixture of amino acids, oligopeptides and polypeptides was recovered, dried and stored at -20° C for further analysis.

Results: The specific degree of hydrolysis for each enzyme in descending order was: papain> pepsin> alcalase> pancreatin. The enzymes which achieved a higher degree of hydrolysis were papain, after 1h (2.25%), and pepsin after 2h (1.87%). Hydrolysis with alcalase reached the degree of hydrolysis of 1.12% after 2 hours, being faster than that with pancreatin, which recorded 1% after 3 hours. After the initial phase of increasing hydrolysis, the rate of hydrolysis decreases as time increases, entering a stationary phase.

Conclusions: Currently, interest for protein hydrolysates containing bioactive peptides is growing due to their potential to be used in the formulation of functional foods. For the production of bioactive peptides, hemp must also be considered, a cheap and sustainable undervalued plant, whose seeds protein is of high quality.

Acknowledgements: *This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P3-3.5-EUK-2017-02-0035, within PNCDI III and project number PN 19.23.01.01.*

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EXPLORING THE POTENTIAL OF BENEFICIAL *PAECILOMYCES* TO IMPROVE PLANT GROWTH

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Key words: ***Paecilomyces lilacinus; biostimulants; keratinolytic fungi; keratin waste.***

Introduction: For sustainable agriculture, an attempt has been made to reduce the consumption of fertilizers and agrochemicals, replacing them with biostimulants as viable alternatives. Biostimulant compounds can be obtained by hydrolysis of proteins derived from plant or animal material. Also, some microorganisms are used to obtain biostimulants which can increase crop yield and quality by helping the assimilation of nutrients [1-2]. The protein hydrolysates (PH) from microbial cultures represent a particular category of biostimulants, being an abundant protein or amino acid source for new upcycling processes targeting potential use in agriculture. In present paper, we have tried to highlight the ability of *Paecilomyces lilacinus* isolate to convert keratin waste into a mixture of sulphur and nitrogen, which can be used to stimulate plant growth and increase crop output [3].

Materials and methods: Several experiments were carried out, namely: strain characterisation (siderophores production, phosphorus and zinc solubilisation, secreting of hydrolytic enzymes); and the biocontrol capacity of the fungal strain against phytopathogens [4]. The qualitative tests were carried out in Petri plates on solid media with specific composition.

Results: The solubilization capacity of phosphorus and zinc expressed by our *Paecilomyces* refers to the property of transforming insoluble forms of phosphorus and zinc into forms accessible to plants. These properties could improve the absorption of phosphate and zinc by plants, helping their growth and development. Also, *Paecilomyces lilacinus* had the ability to produce hydrolytic enzymes (cellulase, keratinase, chitinase) responsible for degradation of pathogens cell walls. *Paecilomyces lilacinus* exhibited the highest antifungal activity against the *Cladosporium* sp. isolate (inhibition of 66.31%), followed by *Sclerotinia sclerotiorum* (inhibition of 50.23%) and *Rhizoctonia solani* (52.53%)**.** The lowest activity was found against our soil isolate, *Alternaria alternata* and *Botrytis allii.*

Conclusions: The present study showed the capacity of *Paecilomyces lilacinus* to solubilize essential micronutrients, to produce hydrolytic enzymes involved in the inhibition of pathogens. These characteristics recommend the strain as a good biostimulating agent and further investigations in greenhouse and field conditions are required.

Acknowledgements: *This research was financially supported by project PN 19.23.01.01.*

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MICROBES IN SALINE ENVIRONMENTS AND THEIR POTENTIAL APPLICATIONS IN SUSTAINABLE AGRICULTURE

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Keywords: halophiles, halotolerant, microorganisms, sustainable agriculture, saline environments.

Introduction: This review paper aims to summarize aspects related to the biotechnological potential of halophile and halotolerant microbes in sustainable management of agricultural practices. During the past years, different microorganisms were isolated from saline environments (including in Romania) and characterized for new species discovery and their potential use in industrial applications.

Materials and methods: This paper involved a brief literature review conducted using various open-access scientific databases following keywords such halophilic bacteria/bioinoculants, saline soils, halotolerants' ecology, novel halophiles, plant growth-promoting halophiles, salinity stress, salt-tolerant microbes etc.

Results: Presently, 33% of the global arable land (952.2 million ha) is affected by salinity and an annual growth rate of 7% for salt stress-affected soils is estimated (50% of agricultural areas will be affected by 2050). Saline soils in Europe represent 17.30%, while little is known about the biodiversity and ecology of halophilic microorganisms and their effects on agricultural processes. [1,2] In recent decades, the scientific community has been given more attention to saline and hypersaline environments, due to these unique ecosystems as new sources of microbial species capable to synthesize biotechnological products (i.e. hydrolytic enzymes or polymers, with industrial, agricultural, and environmental protection applications). Saline stress affects agricultural production, but alternative methods to sustainably manage saline and sodium soils, like those that involve the use of halophilic and halotolerant microorganisms, could be successfully applied. [3,4]

Conclusions: Some of the most frequently isolated microorganisms from saline environments in Romania (saline lakes – Techirghiol. Telega, Ursu, Balta Albă, Amara, Movila Miresei, Baia Roșie and Baia Verde) belong to the genera *Haloarcula*, *Haloferax*, *Halorubrum*, *Halobacterium*, *Halomonas*; order *Actinomycetales* (*Rhodococcus ovatensis*), *Euryarchaeota*, genus *Idiomarina*, *Salinibacter* sp., *Bacillus sp*. All of these have the ability to synthesize extremoenzymes (amylase, lipase, cellulase, pectinase, caseinase, gelatinase, inulinase), polyhydroxybutyrate (PHB), carotenoid pigments, melanin, or other bioproducts with applications in phytoremediation/bioremediation or plant growth stimulation (phytohormones - indoleacetic acids, gibberellic acids, and cytokines; siderophores; biocontrol agents, biofertilizers, biostimulators), contributing to the solubilization and plant absorption of nutrients (phosphorus, potassium, zinc) and/or triggering plant protection mechanisms against phytopathogens. [2, 3, 4, 5]

Acknowledgements: *This research work was carried out with the support of National Institute for Chemical-Pharmaceutical Research & Development, ICCF-Bucharest.*

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QUALITY INDICES OF FATS AS DESCRIPTORS FOR DAIRY PRODUCTS ADULTERATION WITH OILS AND FATS OF NON-DAIRY ORIGIN

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Keywords: cheese; adulteration, ^{1}H-NMR; vegetable oils; saponification value, iodine value

Introduction: Cheese and dairy products are some of the most expensive food products, hence it may be exposed to fraudulent procedures (replacement with cheaper fats/oils). [1,2] Some of the most intensively used technical quality indices of oils – saponification value (SV) and iodine value (IV) – may constitute useful descriptors for the authentication of the dairy products and the detection of the fraudulent practices. [3,4]
The present work aims at presenting the iodine and saponification values of dairy and non-dairy fats and oils (such as sunflower, soybean, rapeseed, lard, beef/sheep tallow, chicken fat) as determined from the ^{1}H-NMR data and to showcase the use of the obtained results in detecting the adulteration of dairy products by addition of non-dairy oils and fats.

Materials and methods: Oils and fats were extracted from dairy products, oilseeds, and animal tissues according to conventional methods. SV and IV were computed from the ^{1}H-NMR spectra.

Results: SV of cow dairy fats ranges from 239.13–245.32 mg KOH/g fat, owing to the important amount of short (C4, C6) and medium(C8-C12) chain fatty acids. Non-dairy fats have considerably lower SV (~190 mg KOH/g fat), being mainly constituted of C18 (C18:0, C18:1, C18:2, C18:3) and C16:0 species.

Conclusions: SV and IV may constitute indicators for adulteration of dairy products with oils and fats of non-dairy origin.

Acknowledgements: *This work has been funded through international grant AUF-ECO_SRI_2021_FRAUDmage_2144-2638, "Méthode rapide basée sur la spectroscopie de ^{1}H-RMN pour déceler les fromages adultérés par addition de graisses végétales (FRAUDmage)", financed by Agence Universitaire de la Francophonie (AUF) and co-funded by the University POLITEHNICA of Bucharest (Bucharest, Romania), the Technical University of Moldova (Chişinău, Republic of Moldova) and the University of Food Technologies (Plovdiv, Bulgaria).*

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METHODS OF OBTAINING EXTRACTS FROM *HEDERA HELIX* L. LEAVES AND EVALUATION OF THE TOTAL SAPONINS CONTENT

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Keywords: Hedera helix L. leaves extract, HPLC-MS/MS, total saponin content.

Introduction: *Hedera helix* L. is known for its therapeutic properties, such as analgesic, anti-inflammatory, expectorant activity. It is currently known that the characteristic therapeutic effects of ivy extracts are induced by phytocompunds, such as: saponins (hederagenin, α and β-hederin, hederacoside B and C), phytosterols (sitosterol, stigmasterol, campesterol), flavonoids, falcarinol, falcarinone, scopoline, chlorogenic acid, caffeic acid, elexin, phytoestrogens [1].

The purpose of our study was to evaluate the total saponin content of *Hedera helix* L. leaves extracts obtained by both conventional, and unconventional methods.

Materials and methods: The commercial fresh leaves of *Hedera helix* L. were purchased from Hofigal SA, Romania in April 2016. The following reagents used for testing were α-hederin, hederagenin, and hederacoside C at purity ≥ 98% (HPLC), DMSO (dimethyl sulfoxide) were purchased from Sigma Aldrich.

Results: The chemical composition of the obtained extracts was analyzed by MS / MS HPLC, and the total saponin content was evaluated by the Hiai method [2] adapted by Wang [3].

Conclusions: Our study indicated an optimal method for obtaining *Hedera helix* L. leaves extract with an enriched saponin content.

Acknowledgements: *The study was financing by the Project 381PED/2020.*

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ANTIOXIDANT AND ANTIINFLAMMATORY POTENTIAL OF *POPULUS NIGRA* L. BUDS

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Keywords: poplar buds, nitric oxide, antioxidant.

Introduction: *Populus nigra* L. (black poplar) (Salicaceae) is a deciduous tree widespread in Europe, Asia, Africa, North America and found in meadows, wet depressions, streams, forests, in the plains and low hills. The vegetal product has been described mainly to contain phenolic compounds, terpenoids, flavones, flavanones and more than 48 phytocompounds in the essential oils [1]. Antioxidant and antiinflammatory effects of poplar buds are widely known. This study aims at confirming these actions for a poplar selective extract.

Materials and methods: Preparation of extract: the vegetal material was extracted twice under reflux with 50% and 20% ethyl alcohol and further the extractive solutions were subjected to a liquid-liquid extraction with n-butyl alcohol. The combined butanolic solutions were evaporated to dryness (P fraction). Total polyphenolcarboxylic acids and flavones were spectrofotometrically quantifed [2]. For determination of total antioxidant activity the method of Prieto [3] was used and nitric oxide (NO) production in endothelial cells was evaluated by the Griess colorimetric method [4]

Results: Fraction P proves to have a strong antioxidant capacity with 5.57mM ascorbic acid equivalent at 10mg / ml (Fig. 1). A line of human endothelial cells (HUVEC) was chosen to perform the experiment because several phases of the inflammatory process take place in the endothelium and, in addition, nitric oxide has an important role in modulating endothelial tone. NO level in the cells treated with TNF-α is lowered by treatment with P fraction (Fig. 2).

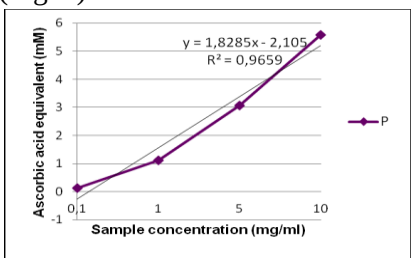

Fig. 1. The total antioxidant capacity of the P fraction highlighted by the phosphomolybdenic acid method

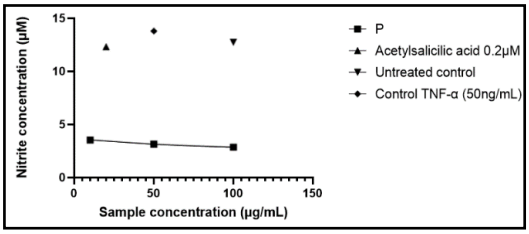

Fig. 2 The effect of L-fraction administration on NO production in endothelial cells under basal conditions and after TNF-α stimulation

Conclusions: The study confirmed the antioxidant and anti-inflammatory potential of a selective fraction isolated from poplar buds.

Acknowledgements: *This research was supported by UEFISCDI in the frame of the project PED 563/2020.*

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SETUP OF ASLT PARAMETERES FOR EVALUATION OF THE SHELF-LIFE FOR THE NEW DRY SNACK FOOD PRODUCT

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Keywords: ASLT, physico-chemical process, microbiological growth, dry snack.

Introduction: A challenge in the development process for the new products is represented by the stability study and the determination of the shelf-life of the products that will be launch on the market. Often, these important characteristics, for the success on the market, are needed without having the necessary time available for a real-life study. The purpose of this research was to study the physico-chemical and microbiological processes of degradation in order to set the Accelerated Shelf-Life Testing (ASLT) parameters for a new dry snack food product development.

Materials and methods: The experimental samples of dry snack food formulations were stored in certain conditions of temperature, humidity and light (accelerated degradation process) on the total period of 30 days. After the final period of storage to evaluate stability over time the product was subject to a physical-chemical analysis to determine the following parameters: moisture content and activity of water. Microbiological analysis regarding Total Plate Count (TPC) was performed also on the stored samples in order to highlight the microbiological growth.

Results: After performing the analysis, the intervals for the degradation process parameters were established: temperature (35°C, 45°C, 55°C), humidity (65%, 75%, 85%), and light (on/off). These data will be used later for the development of the accelerated aging model to evaluate the shelf life for a new dry snack food product**.** The water activity (a_w) must be below the value of 0.6, the moisture content between 6% and 10% and for microbiological analysis TPC below 10^4.

Conclusions: The greatest influence in the depreciation of the product was the temperature, which led to physico-chemical and microbiological changes. Given the light and the vapor barrier provided by the product packaging, the other depreciation factors (humidity, light) did not have a significant influence on the depreciation of the product.

Acknowledgements: *This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P3-3.5-EUK-2017-02-0035, within PNCDI III.*

BIOCATALYTIC ACYLATION OF MENTHOL WITH FATTY ACIDS IN DEEP EUTECTIC SOLVENT AS REACTION ENVIRONMENT

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Keywords: lipase; biocatalysis; menthol; deep-eutectic solvent.

Introduction: For decades, the administration of transdermal drugs has been accepted as a possible route of noninvasive administration, with advantages of prolonged therapeutic action, low side effect, easy use and better patient compliance. With all however, the major limitation of the transdermal drug delivery system is the skin itself. Terpenes can provide advantages over these enhancers due to their natural origin. A protective feature of terpenes is hydrophobicity (water repellent characteristic), which allows them to easily pass through the membrane of invading cells. When crossing a cell membranes, these compounds can increase the fluidity of the membrane, so that the cell no longer has ability to maintain a balanced internal environment.In this context, we developed a biocatalytic method for the fatty acid mathyl esters (FAME) transesterification with menthol in deep-eutectic solvent (DES) medium. From literary, the fatty acid menthol esters have an accepted hydrophobicity to be able to diffuses easily through the cell membrane. Lipase enzymes were proposed as biocatalyst of the transesterification process. Additionally, the use of DES combining menthol and fatty acids exhibited a proper reaction anvironment for an efficient transesterification process.

Materials and methods: The deep eutectic solvent (DES) contains (-) - menthol: fatty acid (3: 1, v/v). The mixture was homogenized in thermoshaker for 24 h, 250 rpm, at temperature of 40˚C. Biocatalytic tests for the transesterification reaction of fatty acid esters with menthol were performed according to a typical procedure, as follows: in 1.5 ml Eppendorf tube, DES (menthol: fatty acid = 3: 1 (v / v)), lipase (1 mg or 10 mg / ml distilled H2O) and fatty acid methyl ester (methyl laurate, methyl palmitate, methyl oleate) were mixed together. The final mixture were vortexed for 10 minutes, and incubated for 24h, under 1000 rpm stirring and at 40 ˚C temperature. After reaction, the samples were centrifuged for 15 min at 1500 rpm; the supernatant was filtered (0.2 μm porosity) directly in the HPLC. Sample analysis has been performed based on HPLC-DAD/RID method

Results: Transesterification of FAME with L-menthol catalysed by lipase enzyme has been performed. The reagents were mixed previously in order to provide a DES environment for the reaction. Enzymatic screening of lipases from different biological sources has been performed in order to establish the enzyme with high catalytic activity for the transesterification process. The experimental study demonstreated that the tested lipase hadn't catalytic activity for the esterification process. So that, the DES content unreacted in the set up chemical context. The optimization process has been considered. Different FAME were used demonstreating the the carbon chain of the fatty acid residue influenced the biocatalytic process. Also, both component of DES will affect the performance of the transesterification of FAME with menthol.
As an exemple, lipozyme RM 1M novozyme biocatalyst exhibited maximum ester convertion of 93% for DES1. Different conversion values were recorded in different DES environments for Lypozyme RM Novozyme. RM Novo prefered C12 type structures against the C16 and C18 type structures. At the same time, RM Novo preffered to catalyse the transesterification of FAME with saturated chains (methyl laurate) compared to those unsaturated (methyl oleate). Novozyme 435 novozymes exhibited catalytic affinity for methyl laurate. The maximum conversion value for Novo was reached in DES 1, amounting to 96%.

Conclusions: Biocatalytic method for the transesterification of FAME with menthol has been developed. The process was set up in DES environment. Maximum conversion of 53% has been achieved for optimum experimental conditions. The developed proceess is a promissing alternative for the efficient derivatization of FAME/menthol in order to improve their organoleptic properties.

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

EXTRACTION OF GERMINATED SEEDS BY CONVENTIONAL AND MODERN METHODS

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Keywords: germinated seeds, extract, alfalfa

Introduction: The germination process of whole seeds activates and multiplies composition of amino acids, antioxidants, vitamins, proteins, enzymes, sugars and decreases phytate and protease inhibitors concentrations. Also, germination contributes to: improved digestibility of plant proteins; conversion of carbohydrates to simpler forms for easy assimilation; bioavailability of minerals; freeing up minerals for absorption; increase of beneficial enzymes. The aim of this paper was to perform the extraction of alfalfa germinated seeds using conventional and modern methods for the purpose of physical-chemical characterization.

Materials and methods: The **e**xtraction of germinated seeds was done by several methods, namely conventional (hydro-alcoholic and autoclave extraction) and modern (ultrasound-assisted extraction). For each method have been set the following parameters: solvent/substrate ratio, temperature and reaction time.
Hydro-alcoholic extraction was performed according to the method described by Piantino et al. (2008) with minor modifications [1]. Parameters followed were ethanol:water ratio 70:30 v/v, reaction time 24h, at room temperature and stirred at 150 rpm.
Autoclave extraction was performed according to the method described by Maurizio D'Auria (2021) using parameters temperature (121°C), pressure (1 bar) and reaction time (15 min) [2].
Ultrasound-assisted extraction carried out according to the method described by Ahmad and Shehta (2020) with modifications [3]. Parameters followed were: 70% ethanol, substrat:solvent ratio 1:10, reaction time 10, 20, 30 min, at room temperature in an ultrasonic bath.

Results: The proximate chemical composition analysis for each extract was performed, which refers to water content, total nitrogen, crude protein, carbohydrates, ash and macro and micro elements, using standard methods. Following the comparative analysis of the preliminary results obtained for the 4 extracts, the modern method ultrasound-assisted extraction was selected. The mean percentage of chemical compounds was: moisture (at 105°C) 78.2 ± 0.48%, crude protein 23 ± 1%, ash (at 550°C) 3.09 ± 0.004%.

Conclusions: The preliminary chemical analysis of the extracts was the basis for the selection of the extraction method. Conventional methods need long time for extraction and use solvents at high costs. The interest for using modern methods for extraction of germinated seeds is growing due to reduced reaction time and solvent volume and accuracy of results.

Acknowledgements: *This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P3-3.5-EUK-2019-0169, within PNCDI III and project number PN 19.23.01.01.*

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CANNABIS SATIVA : A POSSIBLE SOLUTION TO INFECTIONS WITHDRUG RESISTANT GERMS?

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Keywords: antimicrobial activity, drug/multidrug resistant pathogens, Cannabis sativa/hemp

Introduction: Antimicrobial resistance (AMR) has been killing yearly about 1 million people and the estimation for 2050 increase to 10 million. The increasing trend of AMR determined the scientific community to ask WHO for a global priority pathogens list (PPL) of antibiotic-resistant bacteria in humans, ment to guide properly their research, for new antibiotics or alternative therapies to this global public health threat. This paper brings the spectrum of antimicrobial activity of *Cannabis Sativa* L/ hemp, in the attention of the specialists in the field of alternative therapies and prevention, to fight infections in general, and those with drug-resistant germs, in particular.

Materials and methods: One hundred fifty published works, relating to studies conducted since 1950, on the antimicrobial activity of *Cannabis sativa* extracts were reviewed, to highlight aspects of such an activity.

Results: The plant extracts showed antibacterial activity on Gram-positive and Gram-negative bacteria, including multi/drug resistant ones, as well as anti-fungal activity. The antimicrobial activity was found mainly due to several secondary metabolites of the plant, belonging to the phytocannabinoids family. Some *Cannabis sativa* terpens, showed to be synergistic or to potentiate the action of the above phytocannabinoids, in natural cannabis, full-spectrum and broad-spectrum, products. The following types of extracts showed antimicrobial activity: leaves - in aqueous, ethanol, acetone, methanole, n-hexane extracts; stem and leaves-in aqueous ethanolic extract; seed's oil- in n-hexane and methanol extracts; whole bud- in hexane, dichloromethane, ethyl acetate, ethanol, aqueous ethanol and aqueous extracts; whole plant- in acetone, petroleum ether and methanol, hydro-alcoholic extracts.

Conclusions: Various *Cannabis sativa* extracts proved antibacterial and antifungal activity, through their content in major phytocannabinoids and terpens. The plant extracts showed antibacterial activity even against multi drug/drug resistant pathogens, of which at least *Staphylococcus aureus* methicillin - resistant belongs to the WHO PPL. More studies, mostly clinical studies are required, to consolidate this antimicrobial profile of *Cannabis sativa*, in order the plant derived products become viable therapeutic alternatives.

SAPONIFICATION INDEX OF FATS AND OILS AS DETERMINED THROUGH ^{1}H-NMR SPECTROSCOPY

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Keywords: saponification index; ^{1}H-NMR; glycerol tributyrate; binary mixtures

Introduction: The saponification index (SI) is a useful tool for the evaluation of the chain length of fatty acids in oils and fats and is determined in the standard protocol [1] by reflux saponification of the sample with excess alcoholic KOH solution, followed by HCl titration of the excess KOH. Although simple as a technique, the conventional method requires time, harmful chemicals, and is susceptible to errors. On the other hand, ^{1}H-NMR spectroscopy can provide data for the computation of the SI, owing to resonances associated to specific protons in the fatty acyl chains. [2,3]
The present work aims at presenting a convenient algorithm for the computation of the saponification index from the ^{1}H-NMR data.

Materials and methods: Binary mixtures of glycerol tributyrate and vegetable oils in various ratios were prepared, to ensure a broad variation of the saponification index values. The mixtures were dissolved in $CDCl_3$ prior to spectral acquisition.

Results: Mean triglyceride molecular weight was computed based on ^{1}H-NMR data, eventually leading to the chemometric equation describing the SI.

Conclusions: The saponification index can be accurately determined from ^{1}H-NMR data, the method being fast, facile, without compromising the sample (oil samples can be recovered after evaporation of $CDCl_3$).

Acknowledgements: *This work has been funded through international grant AUF-ECO_SRI_2021_FRAUDmage_2144-2638, "Méthode rapide basée sur la spectroscopie de ^{1}H-RMN pour déceler les fromages adultérés par addition de graisses végétales (FRAUDmage)", financed by Agence Universitaire de la Francophonie (AUF) and co-funded by the University POLITEHNICA of Bucharest (Bucharest, Romania), the Technical University of Moldova (Chişinău, Republic of Moldova) and the University of Food Technologies (Plovdiv, Bulgaria).*

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EMULSIFYING EFFECT OF FULVIC ACIDS FROM SHILAJIT

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Keywords: shilajit, fulvic acids, emulsions, thyme essential oil, biostimulants

Introduction: Shilajit, also known in the north of India as salajit, shilajatu, mimie, or mummiyo is a blackish-brown powder or an exudate from high mountain rocks, especially in the Himalayans mountains between India and Nepal [1]. Shilajit is composed mainly of humic substances, including fulvic acids, that account for around 60% to 80% of the total nutraceutical compound [2]. The components are divided operationally in humins, humic acids, and fulvic acids according to their solubility in water at different pH levels. Fulvic acids are soluble in water under different pH conditions, because of its low molecular weight (around 2 kDa) [3]. The aim of this study was to determine the ability of shilajit to act as pseudo-emulsifier, forming emulsions such as oil in water (O/W with thyme essential oil. The emulsions would be tested as plant biostimulants.

Materials and methods: Shilajit was characterized by FT-IR and UV-Vis spectroscopy. The critical micelle concentration (CMC) was determined by measuring the surface tension of shilajit powder in distilled water up to a constant value of surface tension. The value of CMC was obtained from the plot of surface tension against surfactant concentration. The surface tension was determined with the optical method, pendant drop, with optical OCA 50 dataphysics. The emul-sions shilajit – thyme essential oil were prepared by sonication with an Ultrasonic Homogenizer. The method used to obtain emulsions with shilajit and thyme essential oil was the low surface tension liquids method, with ultrasonic probe. The emulsions were visualized, and the size of the drops was measured with LEICA DM1000 LED optical microscope equipped with LEICA ICC50 W camera.

Results: FT-IR analysis of shilajit exhibited a broad band at about 3382 cm-1 which can be attributed to the stretching vibration of hydrogen-bonded OH group. Three bands, in the region of 1613 cm-1, 1411 cm-1 and 1081 cm-1 and a peak at 2930 cm-1 were observed. UV-Vis spectra showed absorption in the range 300 – 500 nm, characteristic to fulvic acids [4], the intensity of which increased with the concentration of shilajit. The CMC was found to be 1% and spherical micelles were observed microscopically starting with this concentration, the size of the micelles being between 3.12 and 32.64 μm. The different concentrations of shilajit induced a reduction in the surface tension of water (72.94 mN/m), which indicates can be used to form emulsions with thyme essential oil. Following sonication, the emulsions acquired a homogeneous, monodisperse macroscopic appearance.

Conclusions: Preliminary studies show that fulvic acids are a major component of shilajit. They have pseudo-emulsifying properties and can form (micro) emulsions with essential oils. These emulsions are planned to be tested as plant biostimulants.

Acknowledgements: *This work was supported by project POC-A1-A1.2.3-G-2015-P_40_352-SECVENT, My_SMIS 105684, "Sequential processes of closing the side streams from bioeconomy and innovative (bio)products resulting from it, subsidiary project "Nano-amphiphilic biostimulants for plants, based on essential oils recovered from spare biomass (1229/2020). The SECVENT project was co-funded by European Regional Development Fund (ERDF), The Competitiveness Operational Programme (POC), Axis 1.*

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THE EFFECTS OF LIGHT ON THE ENZYME PRODUCTION OF *TRICHODERMA ATROVIRIDE*

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Keywords: laser, blue-light, enzymes, Trichoderma

Introduction: The behavior of living organisms is influenced by sunlight, which is an environmental key factor. Ambient light influences many processes involved in growth, development, and reproduction metabolism [1]. Processes like signal transduction, blue-light perception and related responses have been extensively studied in plants, bacteria, algae and fungi [2]. A common soil fungus, *Trichoderma atroviride* can be used as a biocontrol agent because it has the capacity to parasitize phytopathogenic fungi. Conidiation, asexual reproduction, is influenced by light and the presence of certain nutrients [3]. The expression of some enzymes, such as lignocellulolytic ones, was shown to be regulated by light as well [4]. The aim of the study was to test the effects of blue-light laser radiation on the production by *T. atroviride* of enzymes that degrade lignocellulytic biomass.

Materials and methods: *T. atroviride* were grown on PDA medium at 28°C for 5 days. The mature spores were removed and inoculated into ISM medium. To induce biomass-degrading enzymes the mycelium from ISM was incubated in water supplemented with rice husk in Erlenmeyer flasks on a rotary shaker at 28°C for 15 days. The samples were subjected to blue-light laser for 60 and 300 seconds at three laser intensities and at different incubation time intervals. The supernatant was sterilized by filtration and used to determine the enzymatic activities, cellulases, proteases and laccases.

Results: Irradiation of *T. atroviride* with blue-light laser was found to influence the cellulase and protease activities. The highest cellulase and protease activities were observed in the case of 60 seconds irradiation at a laser intensity of 0.271µmol/s. Some effects seem to follow a hormesis behavior which needs further investigation. Neither the treated samples nor the controls presented any laccase activity.

Conclusions: Our results indicate an increase in enzymatic activities for *T. atroviride* when exposed to medium intensity of blue-light laser for 60 seconds.

Acknowledgements: *This work was funded by Subsidiary contract 1477/2020, TrichoSpor, 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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BIOCATALYTIC PREPARATION OF PERILLIC DERIVATIVES AS AN ALTERNATIVE FOR LIMONENE VALORIZATION

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Keywords: biocatalysis; perillic derivatives; ALDH.

Introduction: Perillic-type derivatives of limonene from the class of the oxygenated derivatives have been little exploited to date, despite a large number of applications that they provided based on their phytochemical properties [1]. Perillyl derivatives (e.g. alcohol, aldehyde and acid) are plant compounds designed as monoterpenes with low toxicity and prominent biological action, called phytochemicals, which are considered valuable intermediates for functional foods and novel therapies. They are increasingly important for their flavors, antimicrobial properties and also anticancer properties [2, 3].
The aim of this study was the development of an alternative for the biocatalytic preparation of perillic acid from perillic aldehyde. Aldehyde dehydrogenase will catalyze the biocatalytic transformation of perillic aldehyde.

Materials and methods: The tests were performed in 2ml Eppendorf tubes. The sample has contained 1mM perillic aldehyde, 1mM NAD+, biocatalyst (F-ALDH, ALD-S1, ALD-S2) and buffer, until a volume of 1000 µL is reached in each reaction vessel. The mixture was vortexed for 10 minutes in the thermoshaker for 24h, 1000 rpm, at temperature of 25 ˚C. After reaction, the sample content was monitored using HPLC-DAD system. Before analysis, the sample was mixed with the mobile phase (1:1, v/v)/ The analysis was performed in isocratic regime using 20:20:60 acetonitrile / sulfuric acid / water as composition of the mobile phase, 1 mL / min of flow rate, reaction time of 30 min, 10 µL the injected volume, at a temperature of 60 ˚C of the detector.

Results: The oxidation reaction of perillic aldehyde to perillic acid was studied. The reaction was catalyzed by aldehyde dehydrogenase in the presence of the NAD+ cofactor. Screening of the enzyme biocatalyst was performed initially in the presence of 3 different enzymes, aldehyde dehydrogenase type (F-ALDH, ALD-S1, ALD-S2). Also, the experimental parameters of the biocatalytic system have been optimized in order to increase the process efficiency. The performance of the system was evaluated by calculating the conversion of perillic aldehyde and selectivity to perillic acid. The biocatalysts ALD-S1 and ALD-S2 showed a similar behavior. Substrate conversion of 80 % has been achieved with a total selectivity in perillic acid.

Conclusions: We developed a biocatalytic approach for an efficient conversion of perillic aldehyde into acid derivatives, which is a valuable alternative for limonene valorization from the biomass residues.

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

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OPTIMIZATION OF ENZYME PRODUCTION OF *TRICHODERMA ATROVIRIDE* USING RESPONSE SURFACE METHODOLOGY

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Keywords: Trichoderma atroviride; enzymes; blue-light; response surface methodology.

Introduction: *Trichoderma atroviride* is well known as a filamentous fungus used as biocontrol due to its capacity to produce various enzymes that degrade the cell wall of phytopathogenic fungi [1]. It is also an important microorganism for the industrial production of enzymes and metabolites. Light, especially blue-light, is known to regulate the expression of many enzymes [2]. By means of response surface methodology (RSM), we aimed to optimize the production of enzymes of *T. atroviride*, using blue-light and side-streams from a flourishing industry.

Materials and methods: A three factors-two levels RSM was used for the enzyme production of *T. atroviride* that provided a total of 25 experiments, generating relevant combinations among the three variable factors. *T. atroviride* was incubated for 10 days at 28°C in minimal medium (MM) supplemented with 20% whey and 1% yeast extract. After 5 days, the samples were exposed to blue light, varying the light intensity and exposure time. To analyse the effect of irradiation on enzyme production in time, the irradiated samples were incubated for various amounts of time, according to the factorial model. The protease activity was assayed using casein and Folin-Ciocalteu reagent, against a tyrosine (Tyr/Y) standard curve [3]. The cellulase activity was assayed using carboxymethylcellulose (CMC) and DNS (3,5-dinitrosalicylic acid) reagent, against a glucose standard curve [4].

Results: Blue-light was found to influence the protease and cellulase activity. The ANOVA analysis provided information about the influence of variables on the enzyme production of *T. atroviride*, along with their synergic effect. Both numerical and graphical results from data processing pointed out to a relevant ratio between the variable factors in order to increase enzyme production yield.

Conclusions: By means of response surface methodology, we developed a biotechnological method for using by-products resulting from diary industry and blue-light for inducing enzyme production in *Trichoderma* cultures.

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number 107PCE/2021, within PNCDI III. We also acknowledge financial support from the Ministry of Research and Innovation, Nucleu Programme, grant number P.N.19.23.01.01 Smart-Bi. We thank Dr. Bogdan Trică for helpful discussions in designing the optimization plan.*

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OPTIMIZING THE ENZYMATIC-ASSISTED EXTRACTION OF AROMATIC COMPOUNDS FROM RED WINE LEES

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Keywords: aromatic compounds; red wine lees; enzymatic extraction, optimization

Introduction: In this research we aimed to optimize the enzymatic-assisted extraction of volatile oily compounds from red wine lees, which give cognac flavor to the wine. By recovering the wine lees by-products, the following can be obtained [1]: wastewater, ethanol, antioxidants, tartrate (as calcium tartrate and tartaric acid) and yeast cells. The chemical analysis showed that the volatile composition of wine lees [2, 3] consists of esters, acids, alcohols, aldehydes, furanic compounds, terpenes and C_{13}-norisoprenoids; and the phenolic composition [4] contains flavonoids and non-flavonoids.
Materials and methods: In the first stage, an enzymatic treatment was performed before the extraction of light oils using different concentrations of β-glucanase/pectinase from Novozymes (2500 PGNU/g Polygalacturonase and 75 BGXU/g β-glucanase (exo-1,3-)), at different reaction temperatures and times. The treatment was performed to a mixture of 1.5/1 w/w wine lees aqueous sediment (from Ișalnița, Dolj county) and double distilled water, under agitation. In the second stage, hydrodistillation of the mixture was performed using a Clevenger installation, but with prior removal of the first distillation head from the collecting tube, followed by recirculation of the azeotrope in the system at reflux until the substrate was depleted, at 141°C in the heated bath for 4 h 20 min as previously reported [5]. The final concentrated distillate, rich in light volatile oils, was collected from the collecting tube and the concentration of the main esters was determined using Gas Chromatography-Mass Spectrometry from calibration curves of standard purchased from Sigma Aldrich. In order to maximize the concentration of esters in the volatile oils extracted from wine lees, the optimization of the necessary enzymatic-assisted extraction conditions (concentration, temperature, time) was performed using Response Surface Methodology with the Design Expert v11 application.
Results: The concentrations of the major esters ranged from 0.158% to 0.481% in hydrodistillate sample represent the distribution sum of the main esters (ethyl octanoate, ethyl decanoate, ethyl dodecanoate and ethyl hexadecanoate) that are present in the samples. The final polynomial equation of the estimated coefficients was calculated with the Analysis of Variance for the selected factorial model. The experimental values of ester concentrations of the volatile oily compounds are similar to the predicted values obtained using Response Surface Methodology. The extraction temperature and time had higher significance than the β-glucanase/pectinase concentration on the aromatic composition extracted from red wine lees. However, the enzymatic extraction treatment applied to the wine lees before the hydrodistillation process, increased the concentrations by more than 30% according to the data analysis.
Conclusions: We optimized the enzymatic-assisted extraction of volatile oily compounds from red wine lees. Applying an enzymatic pre-treatment with β-glucanase/pectinase before the hydrodistillation process, the wine lees releases a higher ethyl esters concentrations responsible for the aromatic smell and taste than without the enzymatic pre-treatment, which represents an encouraging process.

Acknowledgements: *This work was funded by Subsidiary contract 1518/2019 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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IN SILICO APPROACH TOWARD ANALYSING THE BIOACTIVEEFFECTS OF SPENT BREWERY YEAST PROTEINS

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Keywords: bioactive peptides; spent brewery yeast proteins; ACE inhibitor; antioxidant

Introduction: *Saccharomyces cerevisiae*, a yeast widely used in food and beverage production, was observed to provide a valuable source of different nutrients, most important being the bioactive peptides which can become a major supporter in pharmaceutical therapies [1]. In this paper, the main aim was to predict *in silico* the health effects of bioactive peptides sourced from spent brewery yeast proteins, with a focus on their antihypertensive and antioxidant effects.

Materials and methods: To identify the bioactive peptides of interested, we employed an integrative approach which can be observed in figure 1.

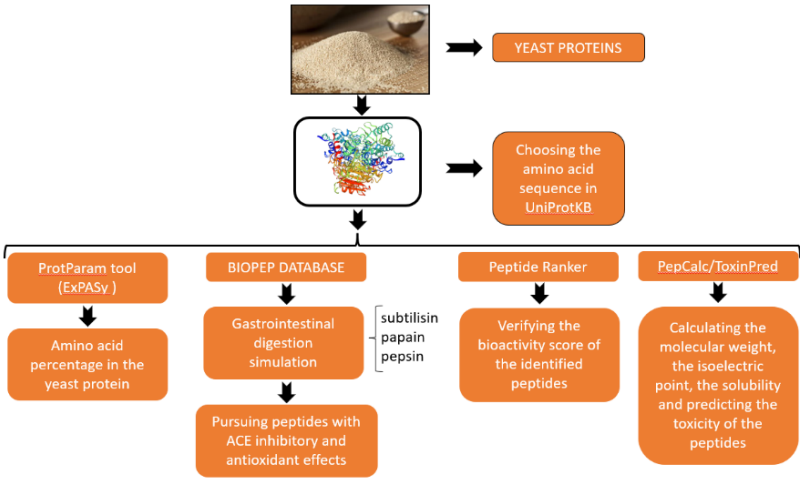

Fig. 1. The workflow used for the identification of bioactive peptides from spent brewery yeast proteins.

We used the following tools and databases: UniProtKB, ExPASyProtParam, BIOPEP, Peptide Ranker, PepCalc and ToxinPred and we assessed the potential of the spent brewery yeast protein and observed the presence of bioactive peptides with different effects on health [2].

Results: The analysis of the spent brewery yeast residues of amino acids showed an increased presence of alanine, leucine, threonine, glycine and valine. Bioactive peptides were released by all the three analysed enzymes, with the most found in the case of pepsin, followed by papain and subtilisin. All of them showed high antihypertensive activity. Using the Peptide Ranker and PepCalc tools, we managed to point out that papain and pepsin aid in the release of significant sequences such as DF, SDF, RP and RWA, which showed high scores of bioactivity and have good physico-chemical properties.

Conclusions: In this paperwork, we showed that the spent brewery yeast proteins are an invaluable source of health compounds such as bioactive peptides with potential antihypertensive and antioxidant effects. The modern bioinformatics approach used in this study provided us with efficient base for further experimental studies and offered a less costly process using databases that can simulate processes for gastrointestinal digestion.

Acknowledgements: *This work was funded by Subsidiary contract 1519/2019 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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CLASTOGENIC EFFECTS OF THYME ESSENTIAL OIL ON VICIA FABA

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Keywords: essential oil, ecotoxicology, clastogenic, mitotic index, vicia faba

Introduction: Indiscriminate use of pesticides in agriculture has many negative implications on both abiotic as well as biotic components of the environment [1]. One of the alternative methods to maintain productivity and quality of life is the possibility to use compounds produced by the secondary metabolism of plants, such as essential oils [2]. Due to their rapid efficacy and degradability essential oils are used as bioherbicide, bio-stimulants, anti-microbial agent, insect repellent, etc. Evaluations of the toxic, cytotoxic, and genotoxic potentials of essential oils, by means of ecotoxicological bioassays, are of great importance in determining possible risks [3]. For the determination of genotoxicity and clastogenic effect of various factors the mitotic divisions are used, the evaluated parameters being the mitotic index (MI) and the frequency of micronuclei [4]. The aim of this study was the analysis of the potential phytotoxic effect of thyme essential oil in view of its potential use as plant bio-stimulant. This was done by investigating the clastogenic effect on *Vicia faba* root meristems.

Materials and methods: After sterilization, seeds were left to hydrate for 24 hours in sterile water. Sterile deionized water was used for the control variant and thyme essential oil at 0.1% concentration for the sample. The seed plates were placed at 23ºC under dark conditions until rootlets reached 2–3 cm in length. For cytological analysis of mitotic index (MI) and micronucleus (MN) test, 1-2 cm of rootlets were subjected to Carnoy fixation solution for 24 hours. The samples were then rinsed with distilled water and hydrolyzed with 1N HCl at 60°C for 6 minutes. Schiff's reagent was used for staining. The mitotic index was calculated as the number of cells in mitosis divided by the total number of cells, x 100, per 1000 scored cells/sample resulting from 10 separate roots for each group.

Results: The mitotic index on *Vicia faba* in the 0.1% essential oil sample did not show significant differences compared to the control sample. The mean values of MI were 31.4% for the control, and 31.2% for the sample with thyme essential oil, which indicate a similar ratio of cell divisions. Also, this concentration of essential oil did not significantly lead to the formation of micronuclei at root meristems, relative to control. Various types of physiological (C-metaphase, stickiness, bridge, laggard etc.) and clastogenic chromosomal aberrations (chromosomal breaks, fragments etc.) were not observed analyzing the cell division phases.

Conclusions: Following the study performed on *Vicia faba*, it was noted that 0.1% thyme essential oil has no cytotoxic effect, as no chromosomal aberrations were observed in the samples, and it did not induce inhibition of cell proliferation in root meristems. The relative frequencies of the various mitotic phases were not affected by thyme essential oil.

Acknowledgements: *This work was funded by Subsidiary contract 1229/2019 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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ENHANCEMENT OF LIGNOLYTIC ENZYME ACTIVITY IN GANODERMA LUCIDUM BY CO-CULTIVATION WITH BACTERIA

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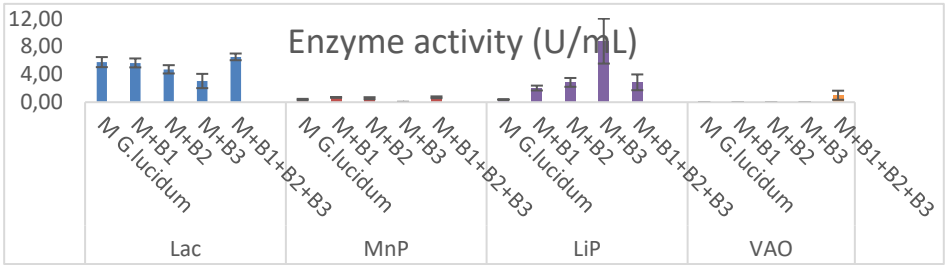
Keywords: Ganoderma lucidum; bacteria; co-culture; enzyme activity

Introduction: Fungi are known for their capacity to produce two main categories of enzymes, cellulolytic and lignolytic, both valuable for biodegradation of lignocellulosic biomass. *Ganoderma lucidum* is one of the widely grown basidiomycete white fungi for the production of lignolytic enzymes. Co-cultures of macrofungi with different microorganisms have been previously shown to boost the production of bioactive components and expression of functional enzymes [1]. Our aim was to co-cultivate *G. lucidum* with several bacterial strains in order to find optimal co-cultures that increase the production of lignolytic enzymes.[2]

Materials and methods: *G. lucidum* was tested in interactions with 9 strains of bacteria. The growth medium used was potato dextrose agar (PDA) for the synergetic-antagonist test because both fungi and the bacterial species studied grew well on the medium [3] and potato dextrose broth (PDB) for the enzymatic study. All enzymatic activities were determined by UV-Vis spectroscopy. Laccase (Lac) activity was determined measuring the absorbance of ABTS at 420 nm (ε=36000 $M^{-1}cm^{-1}$), Ligninperoxidase (LiP) the oxidation of veratryl alcohol at 310 nm (ε=9300 $M^{-1}cm^{-1}$), Manganese peroxidase (MnP) the absorbance of 2,6-dimethoxyphenol at 469 nm (ε=53200 $M^{-1}cm^{-1}$) and Veratryl alcohol oxidase (VAO) the absorbance of veratryl alcohol at 310 nm (ε=9300 $M^{-1}cm^{-1}$).[4]

Results: In the case of Lac there was no significant improvement in the enzymatic activity given by co-cultivation of *G. lucidum* with bacteria. For MnP and VAO, there was a slight increase in the activity for the experimental variants containing *G. lucidum* and bacterial strains. LiP activity was significantly improved due to co-cultivation. The bacteria cultures did not have enzymatic activity.



Conclusions: We co-cultivated *G. lucidum* with several bacterial strains, achieving an improvement in the activity of some lignolytic enzymes.

Acknowledgements: *This work was supported by project POC-A1-A1.2.3-G-2015-P_40_352-SECVENT, My_SMIS 105684, "Sequential processes of closing the side streams from bioeconomy and innovative (bio)products resulting from it, subsidiary project 382/2021 "Cellulose whitening by using enzymes produced by consensus microbial consortia and environmentally friendly oxidizing agents"*

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THE BENEFITS OF APPLYING COMPOST IN AGRICULTURE AS *ARONIA* CROPS FERTILIZER

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Keywords: Chokeberries, composts, vitamin C, anthocyanins, phenolics, leaves minerals

Introduction: This paper presents the preliminary results of a study that aims to emphasise the compost effect when used as fertilizer in *Aronia melanocarpa* crops [1-3]. The study was conducted at the Research Institute for Fruit Growing Pitesti-Maracineni, Arges county, Romania during 2019-2020 growing season on *Aronia melanocarpa* five years old plants.

Materials and methods: Two different origin composts, A (in 30 and 40 t/ha doses) and M (in 20 and 40 t/ha doses), were administrated, and the results compared to those of untreated plants. Dry weight (DW), total titrable acidity (TTA), total sugar content (TSC), vitamin C (Vit. C), total phenolics, and total anthocyanins content as quality indicators were quantified in berries and N, P, K, Ca, Mg, Zn, Cu, Mn, and Fe levels were determined in Aronia leaves.

Results: In the first experimental year, the influence of compost treatments was focused on berries, and non-significantly on vegetative organs (leaves). A-30 type compost decreased berries DW by 12.45 %. Total titrable acidity was decreased by 10,64% and total sugar content was 10.58% higher than control when A-40 was applied. A-40 fertilizer decreased by 21.56% Vit. C, and by 37.61% TAC and M-20 reduced TPC by 16.68% in Aronia berries. The foliar mineral content was non-significantly influenced by compost fertilization, except Zn (reduced Zn by 57.51% under A-30 fertilization), Cu, and Fe (M-40 reduced Cu by 59.03% and Fe, by 30.73%). By decreasing TPC (total phenolic content) and TAC (total anthocyanins content), compost fertilization proved a helpful instrument in reducing plant abiotic stress.

Conclusions: As the ANOVA test results showed, in the first experimental year, the influence of compost treatments was focused on berries and less on vegetative organs (leaves).
The M-40 type compost significantly increased berries DW only if compared with A-type compost treatments and M-20 reduced TPC and A-type fertilizer significantly decreased DW (A-30), TTA (A-40), Vit. C (A-40), TAC (A-40) and increased total sugar content (A-40) in Aronia berries;
Compost application reduced the foliar content of Zn (A-30), Cu (M-40), Fe (A-40);
By decreasing TPC and TAC, compost fertilization proved a helpful instrument in reducing plant abiotic stress.

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NUMERICAL SIMULATION OF COUPLED PROCESSES OF MEMBRANE FILTRATION AND ADVANCED OXIDATION (AOPS) IN PHOTOLYSIS REACTORS FOR WATER DECONTAMINATION

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Chemical pollutants disposed of various branches of industry pose a significant threat to both the aquatic environment and human health. A specific class of pollutants is given by hardly biodegradable organic compounds coming mainly from pharmaceuticals, personal care products and industrial dyes.

These pollutants are identified in water bodies (surface or underground) used as a source of water in drinking water treatment plants, the classic technologies for their elimination being inefficient.

Exploring new processes and transposing them on an industrial scale in order to develop innovative, operationally and energy efficient technologies is a complex approach, supported by both theoretical and experimental investigations, numerical modeling and virtual experiment being basic steps in shortening the time required and increasing accuracy for developing new methods.

Based on laboratory-level and functional model studies, the combined advanced oxidation processes (by photolysis and photocatalysis) and separation at the interface of photocatalytic ultra-filtrating membranes impregnated with elements based on carbon nanotubes (MWCNTs) decorated with ZnO particles, in the presence of active oxygen species (dissolved ozone), were investigated. The paper presents a methodology and a numerical model for modeling hybrid processes of advanced oxidation and membrane separation in photolysis reactors, as a preliminary step in the development of a water decontamination technology on an industrial scale.

The model deals with a coaxial reactor configuration, being based on concepts from fluid mechanics (CFD-Computational Fluid Dynamics) assembled in a multi-physical model that incorporates elements of fluid flow, radiation distribution in the reactor, the dynamics of dissolved ozone photolysis processes, both in the reactor volume and at the filter membrane interface.

The results obtained from virtual experiments, at different operating parameters of the reactor, allowed the determination of the flow regime in the reactor with highlighting of active areas, evaluation of the efficiency of disinfection processes and photochemical processes (photolysis, photocatalysis) by analyzing the reaction dynamics of dissolved ozone in the presence of UV radiation, useful in establishing the technical specifications necessary to make the model on a real scale.

PHYTOTOXICITY OF *CLEMATIS VITALBA* L. (RANUNCULACEAE) AQUEOUS EXTRACT AND NANOSTRUCTURED MIXTURE

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Keywords: Clematis, extract, nanoparticles, phytotoxicity

Introduction: Known in traditional medicine as a good source for the treatment of various diseases, *C. vitalba* L. is also quoted in the dictionary of toxic plants. In this study, the phytotoxic activity of the aqueous extract of *Clematis vitalba* L. prior to and after silver nanoparticles (AgNPs) was evaluated on the growth of roots and stem of dicotyledonous *Pisum sativum* L.

Materials and methods: The overground parts of *C. vitalba* dried at room temperature and finely ground were macerated in distilled water at 100°C in water bath for 15 min, and then for 24 hours at room temperature. AgNPs were biosynthesized as described by Sutan *et al*. (2019) [1]. The seeds of *P. sativum* were hydrated in distilled water for 1 hour and a half and transferred in the *C. vitalba* extracts with (CAg) and without (C) AgNPs for one hour. Distilled water was used as negative control (M). The seeds were kept in the dark and watered periodically. After 4 days the length of the root and stem were measured with graph paper and the fresh and dry biomass were determined by the method of Azooz et al. (2012) [2].

Results: The growth of the root and stem of the dicotyledonate was stimulated by *Clematis* extract compared to control, while the presence of AgNPs in the extract had an opposite effect. The growth inhibition was significant for both root and stem. The biomass was less affected by extract *C. vitalba* prior to and after AgNPs biosynthesis (Fig. 1).

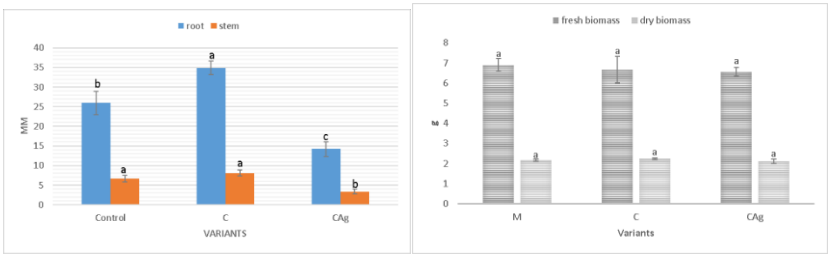

Figure 1. The influence of extracts from aerial parts of *C. vitalba*, prior to and after the AgNPs biosynthesis on the root and stem length (left), fresh and dry biomass (right) of *P. sativum* (a, b, c: interpretation of significance of the differences by means of the Duncan test, $p < 0.05$).

Conclusions: *C. vitalba* extracts prior to and after AgNPs synthesis showed significant antithetical effects on the growth of *P. sativum*. AgNPs induced a significant reduction in root and stem length.

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-0620, within PNCDI III.*

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EMPHASIZING THE GENERAL METHODS FOR THE USE OF THE NATURAL MINERAL WATERS LOCATED AROUND THE SALT MINES, ACCORDING TO THEIR THERAPEUTIC PROPERTIES

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According to the studies conducted in Europe [1,2], the environment plays a crucial role in physical, mental and social development of the population. Despite significant improvements made previously, there are still major differences in quality of the environment and public health, both between and within European countries.

Complex relationships between environmental factors and health of citizens, manifested by a multitude of issues and interactions, should be considered in a broader spatial, scientific, socio-economic and cultural context.

The value of the mineralized water resources in Romania is given by the great diversity of qualitative and quantitative mineralization of these springs and their therapeutic qualities.

Assessment of a water source as mineral is based on a determination of its physico-chemical and microbiological properties and in addition, based by emphasizing its balneal effects, scientifically demonstrated.

Figure 1. A salted lake and its green environment

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ENZYMATIC DEGRADATION OF P.E.T.

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Keywords: lipase; biocatalysis; PET; degradation; hydrolysis.

Introduction: Due to the fact that PET is almost impossible to degradate and has such a negative impact on the environment, new methods for PET recycling are constantly required. In order to improve the degradation process of PET, to valorise the relised products and to prevent the environmental pollution with PET, it is important to design efficient degradation process [1].

We study PET degradation using lipase biocatalysis in deep-eutectic solvent (DES) based on the BHET hydrolysis [2].

Materials and methods: BHET was used for optimizing the system for future use in PET degradation. An attempt was made to build reaction systems based on different types of DES. Six types of DES were created starting from the solubility of BHET in different solvents. The system of BHET and DES was completed by adding free (lipase from *Aspergillus niger*) and immobilized enzymes (Lypozime RMIM, Lypozime TLIM, Novozyme 425 and Transenzyme) as catalysts.

PET from four different sources and with different durity was used in the experimental processes: ST (PET from a bottle of juice), TA (PET from a packing tray), CU (PET from an ice cream box) and CF (PET from a bottle of Cif). The PET was cut into pieces of around 0.5 cm x 0.5 cm. The catalyst used in the degradation of PET was the enzyme *Aspergillus niger*. After the reaction, the PET pieces were washed with distilled water and then weighed. Their final weight was compared with their initial weight.

Results: *BHET hydrolysis* - after the HPLC analysis, the conversion for each type of DES and each type of enzyme was calculated. Graphics were made to see which type of DES is the best system for each enzyme. As a general remarks analysing the graphics, the best systems are: DES 1, 3 and 5 with Transenzyme, DES 6 with Lypozime TLIM, DES 5 with Novozyme 425 and DES 5 and 6 with Lypozime RMIM.

PET degradation - it can be observed that first and third method have the biggest sums of relative areas, so the degradation went better in these conditions. Although the second method had an error (the liquid phase of the CF reaction evaporated), it can be considered a valid method.
Pretreatment method 1, 2 and 3 allowed achieving the most degraded PET surface. Positive difference between masses could be the effect of DMC attached on the PET surface (carboxy methylation).

Conclusions: Lipase biocatalysis in DES allowed to perform efficient conversion of BHET. The experiments will be continued looking for process optimizing and application for PET samples.

Acknowledgements: *This work was financially supported by The Education, Scholarship, Apprenticeships and Youth Entrepreneurship Programmer – EEA Grants 2014-2021, Project No. 18-Cop-0041.*

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GREEN SYNTHESIS OF BIMETALLIC NANOSTRUCTURES USING VINE SHOOTS EXTRACTS – CHARACTERIZATION AND ANTIMICROBIAL EFFECTS

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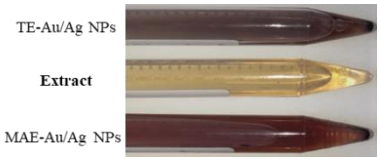
Keywords: vine waste management, green synthesis, nanoparticles, phytochemicals, antimicrobial activity

Introduction: Romania has a rich viticulture history, being one of the largest wine-growing countries in the world and the 5th country in Europe in terms of vineyard, with about 150,000 hectares of vineyards used for wine production [1]. However, the practice of viticulture presents the disadvantage of accumulating large amounts of vineyard wastes. Thus, after pruning the vines in October and March are produced considerable quantities of vine shoots and canes [2]. Furthermore, these residues represent a valuable source of bioactive compounds, which may have different medical, cosmetic and food applications [3]. The present work evaluates classical and modern extraction methods of phytochemicals from local vine shoots wastes in order to obtain phytosynthesized bi-metallic nanoparticles (Ag and Au) with antimicrobial and antioxidant effects.

Materials and methods: To extract the phytochemicals from vine shoots wastes, two solid-liquid extraction pathways have been approached: classical extraction (using an oven) and microwave assisted extraction with MILESTONE ETHOS EASY (microwave digestion system). The ratio between solid material and solvent was 1:10 (w/v)**.** The total phenolic content of extracts was determined using Folin Ciocâlteu method while the antioxidant capacities of extracts and phytosynthesized bi-metallic nanoparticles were determined using a DPPH assay. The formation of nanoparticles was monitored by UV-VIS spectrometry, in the wavelength range of 300-700 nm. Transmission Electron Microscopy (TEM) was used to visualize the size and shape of bi-metallic nanostructures. The antimicrobial activity of both extracts and bi-metallic nanoparticles was determined on gram-positive, gram-negative and fungi strains.

Results: The obtained results suggest the formation of Au/Ag nanoparticles in both extraction methods.



Conclusions: Microwave extraction method improves the ability of recovering the phenolic compounds from viticultural wastes in order to obtain Ag/Au bimetallic-nanostructures with significant antioxidant and antimicrobial activity.

Acknowledgements: *The authors gratefully acknowledge the financial support obtained through grants of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P3-3.5-EUK-2019-0226, contract 220/2020, and project number PN-III-P2-2.1-PED-2019-3166, contract 299PED/2020, within PNCDI III.*

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THE MOLECULAR SPECIES IDENTIFIED BY GC-MS IN SOL-GEL PROCESS. OPERATIONAL MASS SPECTRUM LIBRARIES

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Keywords: molecular species, sol-gel process, GC and MS arguments, user mass spectrum libraries

Introduction: The aim of this article is the presentation of mass spectrum libraries created based on unambiguous assigning of the mass spectra of the identified molecular species in the sol-gel process.

Gas-chromatography coupled with mass spectrometry (GC-MS) was used to unambiguous identify the molecular species obtained in the hydrolysis, transesterification and condensation reactions of tetraethoxysilane (TEOS) in nonparental solvents (MeOH and n-PrOH).

GC arguments were: The restrictive conditions imposed on the initial reaction mixtures and the retention times in the gas chromatogram of molecular species obtained by hydrolysis, transesterification reactions and condensation in the sol-gel process [1-5].

The MS arguments were: Linked scans, accurate mass measurements and M+1, M+2 isotopic effects [6-10]. The mass spectra of the methoxy transesters are similar to that of TEOS esters, but contain molecular and fragmentation ions with 14 units less, which correspond to the difference between the mass of the CH3 - and C2H5 - groups. The mass spectra of the propoxy transesters are similar to that of TEOS esters, but contain molecular and fragmentation ions with 14 units higher, which correspond to the difference between the mass of the C2H5- and C3H7- groups [10].

An additional theoretical argument for assigning structures for these molecular species are complex quantum calculations with the ALCHEMY, MOPAC, HYPERCHEM programs, among which the distribution of net charges on fragmentation ion atoms is very important for the interpretation of mass spectra [6,10].

Materials and methods: The experimental data for this paper were obtained on a GC-MS tandem produced by VG-Analytical:
The HP 5890 Hewlett Packard gas chromatograph with a fused silica high performance capillary column with 70,000 theoretical plates; stationary phase Silicone oil OV-1.
VG Analytical double focusing mass spectrometer: Acquisition mode SCN at standard and high resolution; B/E and (B/E) (1-E)1/2 linked scans.

TurboMass Software procedure was used to create mass spectrum libraries [11], run the Spectrum application, and select the first spectrum that we want to add to user library. Enter the name for the new library. Using the TurboMass Spectrum application, select spectra one at a time to put into user library. In the Library application, set up the text data for each entry. Create the Presearch file for the new user library. Once we have created a user library, we can add new spectra to it at any time by repeating these steps [11].

Results: In addition to the libraries available (NIST, NBS etc), we create "user" libraries that contain user spectra from raw data files obtained by GC-MS method. By unambiguous assigning the mass spectra for the precursor alkoxides and for the hydrolysis, transesterification and condensation products from the sol-gel process, based on the above-mentioned arguments, mass spectrum libraries were realized. These mass spectrum libraries were stored in the memory of the data acquisition and processing system of the double focus GC-MS tandem type 70-SE

Table 1 presents a few mass spectrum libraries created on the basis of somes reaction mixtures with parental and nonparental solvents.

A. Type of precursor alkoxide: Acid (HCl) catalysed systems			
Reaction systems	Mass spectrum library name code	Number of entries	Observations
TEOS: H_2O: EtOH	ICECHIM0 to ICECHIM9	10-33	start mixture to 9 days
TEOS: H_2O: MeOH	TRANSME0	35	methoxy transesters
TEOS: H_2O: PrOH	TRANSPR1	19	propoxy transesters

Table 1. Operational mass spectrum libraries creating in Analytical Department

In Fig.1 and Fig. 2 are presented the first 5 and the last 5 entries of the operational mass spectrum library TRANSME0 with 35 entries.

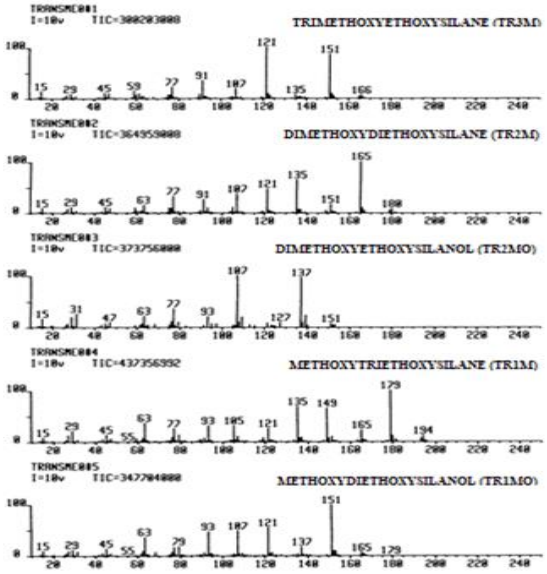

Fig. 1. TRANSME0 Mass spectrum library. Entries 1-5

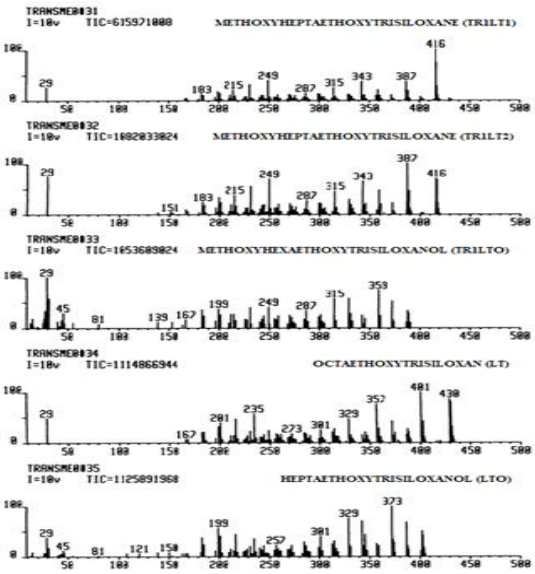

Fig. 2. TRANSME0 Mass spectrum library Entries 30-35

Conclusions: Mass spectrum libraries were created based on unambiguous assigning of the mass spectra of the identified molecular species in the sol-gel process.
Gas-chromatography coupled with mass spectrometry (GC-MS) was used to unambiguous identify the molecular species obtained in the hydrolysis, transesterification and condensation reactions of tetraethoxysilane (TEOS) in nonparental solvents (MeOH and n-PrOH).

GC and MS arguments for unambiguous identify the molecular species in sol-gel process were presented. Quantum calculations programs were used as additional theoretical argument for assigning structures for these molecular species.
A few mass spectrum libraries made on the basis of some reaction mixtures with parental and nonparental solvent were realized with TurboMass Software.
The first 5 and the last 5 entries of the operational mass spectrum library TRANSME0 with 35 entries are presented.

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POTENTIAL APPLICATION OF APATITIC MATERIALS SUBSTITUTED WITH Co AND Zn AS ANTIMICROBIAL TREATMENT IN THE PRESERVATION OF CULTURAL HERITAGE

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Keywords: nanomaterials**,** hydroxyapatite, cultural heritage**.**

Introduction: Cultural heritage has a major importance, as it represents human identity and evidence of existence and activities that people have left over time. Any heritage object, whether movable or immovable, represents a small part of human history, passed down from generation to generation. By using the term tangible cultural heritage, we refer to different types of artifacts (paintings, drawings, prints, sculptures, etc.), monuments and historical buildings, as well as archaeological sites.

The factors that lead to the degradation of cultural heritage are multiple, uncontrollable, caused by nature (rain, temperature, light, biodegradation) or by humans (pollution, urbanization, agglomerations, acts of terrorism, corruption or incompetence). For this reason, it's conservation represent a major objective, and the development of different compounds with a consolidating or protective role that do not affect the different properties of objects (appearance, color, etc.) is of major importance [1].

Nanomaterials represent a new and innovative solution under development with the role of saving heritage without affecting it and extending its lifespan for many generations to come [2]. Hydroxyapatite is a product highly studied in recent years due to the many positive results obtained in various fields such as: implantology, orthopedic surgery, catalysis, biosensors, adsorption, protection of cultural heritage, etc. In this study we synthesized two types of substituted apatitic materials with heavy metals (Zn, Co), using two different methods (co-precipitation and ultrasonication), at different molar ratios, as well as their antimicrobial properties [3].

Materials and methods: The synthesized materials were characterized by the following methods: X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), while their antimicrobial activity was evaluated using the method of minimum inhibitory concentrations and method of minimum concentrations of biofilm eradication.

Conclusions: The obtained results allows the proposal of the synthesized materials as viable alternatives in the protection of cultural heritage artifacts.

Acknowledgements: *The authors gratefully acknowledge the financial support obtained through a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PTE-2019-0579, contract 61PTE/2020, within PNCDI III. The authors also acknowledge the financial support of the Romanian Ministry of Research and Innovation MCI (Ministry of Research, Innovation and Digitization – MCID) through INCDCP ICECHIM Bucharest 2019-2022 Core Program PN. 19.23 - Chem-Ergent, Project No.19.23.03.*

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CONVENTIONAL VERSUS MODERN – NOVEL MATERIALS IN ENVIRONMENTAL DEPOLLUTION

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Keywords: advanced materials, water purification, green technology.

Introduction: As a result of technological development in recent decades, nanomaterials obtained by advanced techniques have gained new valences compared to conventional materials, due to the need of maintaining "a green environment" for future generations.

Literature describes many technologies for removing contaminants from water. The conventional methods such as electrochemical ones, chemical precipitation or adsorption using carbon-based materials require high-energy consumption and the removal can be incomplete most of the time [1].

Currently, water purification technologies are based on basic structures, such as activated carbon, silica gel, zeolites or clay minerals, to more complex and expensive structures, such as three-dimensional carbon-based architectures or three-dimensional macrostructures.
Nanoscale materials like metallic or metal oxide nano-adsorbents, nanomembranes and metal organic frameworks showed exceptional results in water remediation. Adsorption is one of the most eco-friendly and efficient method for removing pollutants from water bodies, due to the nano-adsorbents large surface, which creates multiple adsorption sites [2].

Materials and methods: This paper represents a review regarding the advantages of advanced techniques in the field of water purification, compared to conventional techniques; the review includes studies published in the last years, selected using scientific databases such as Scopus, Science Direct and Elsevier.

Results: The present review aims to present the most recent findings in water remediation using advanced materials, showing that at the end of purification process a high adsorption capacity is obtained, also the possibility of reusage of these materials due to their high stability. Moreover, advanced materials present the possibility of easy integration into an integrated depollution technology.

Conclusions: In conclusion, advanced materials represent a promising and, also, a cost-effectiveness option for water purification.

Acknowledgements: *The authors gratefully acknowledge the financial support obtained through a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PTE-2019-0222, contract 26PTE/2020, within PNCDI III. The authors also acknowledge the financial support of the Romanian Ministry of Research and Innovation MCI (Ministry of Research, Innovation and Digitization – MCID) through INCDCP ICECHIM Bucharest 2019-2022 Core Program PN. 19.23 - Chem-Ergent, Project No.19.23.03.*

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USE OF BACTERIAL CARBONATOGENESIS FOR CONSTRUCTION MATERIALS

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Keywords: *Bacillus, carbonatogenesis, microbially induced carbonate precipitation (MICP), urease.*

Introduction: Concrete is the most used construction material, but its industrial production from lime consumes 2-3% of the global energy demand, generating 0.73–0.99 t CO_2/t of cement produced [1]. At the same time, concrete structures are susceptible to physical, chemical and biological factors which affect its mechanical and durability properties. A viable alternative to reduce cost and environmental impact is considered the incorporation in cement matrix of bacteria capable to precipitate calcium carbonate [2-3]. Microbially induced calcium carbonate precipitation (MICP) is possible through following metabolic pathways: urea hydrolysis, ammonification of amino acids, denitrification, sulfate reduction and photosynthesis. Among them, urea hydrolytic metabolism is the most studied [4]. The aim of this study was to evaluate the capability of several *Bacillus* strains to precipitate calcium carbonate. Each bacterial strain was cultivated on urea-$CaCl_2$ medium of different concentrations and $CaCO_3$ precipitation was evaluated.

Materials and Methods: The experimental study was carried out with bacterial strains from Microbial Collection of ICECHIM, as follows: *Bacillus amyloliquefaciens*, *B. licheniformis* and *B. subtilis.* The bacteria were cultured on media with different composition: i) tryptic soy broth (TSB); ii) nutrient broth (NB) with different concentrations of urea and Ca^{+2}. The cultures were incubated and then centrifuged, the obtained pellets being analyzed with different techniques (FTIR-ATR, SEM and TGA).

Results: SEM investigations presented several morphological aspects of pellets. The bacterial pellets from cultures were characterized by TGA analysis. The results indicated that the pellets from media with calcium and urea the occurrence of two main weight loss steps, 17-24 %, (138-145°C) and 19-20 % (343-350°C), respectively. The residue at 700°C corresponded to a significant weight loss of 45-50%. The behavior of control samples from medium without urea and calcium was quite different: loss of 65-68% (248-281°C) and 27-31% residue. This aspect indicated that on medium with urea and Ca^{+2} ions bacterial strains were able to precipitate calcium carbonate. FTIR spectra of pellets presented the following distinguishable regions: 3000-2800 cm^{-1} for cell membrane fatty acids and carbohydrates; 1700-1500 cm^{-1} for amide I; band around 1401-1416 cm^{-1} assigned to CO_2; 1200-900 cm^{-1} polysaccharides or carbohydrates of microbial cell walls.

Conclusions: The corroboration of present results with those obtained previously regarding the secretion of urease [5] indicated *Bacillus subtilis* to be a microorganism with great potential for application in cementitious materials. Further investigations regarding the immersion of bacterial cells in cement will be carried out.

Acknowledgements: *This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project PN-III-P2-2.1-PED-2019-0991/392/2020.*

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BIO-CHAR PRODUCTION FROM ALGAL BIOMASS

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Keywords: algal biomass, pyrolysis, bio-char

Introduction: Biochar is a form of charcoal produced from biomass, by a process known as pyrolysis. Bio-char is also another product from pyrolysis and has carbon content over 50%. Biochar has unique properties that make it a valuable soil amendment to sustainably increase soil health and productivity, also canbe used for sequestering atmospheric carbon dioxide in soils [1]. Algal biomass was used in pyrolysis process at 350-450 ^{0}C temperatures range in a Parr reactor, obtaining bio-oil, bio-char and residual gaseses.The aim of this study was tovalorify a by-product, bio-char obtained from algal biomass pyrolysis. The results showed that the pyrolytic biochar has the characteristics for carbon raw material.This materials has potential after activation to be used in agricultural plant production, as a fertilizer and soil conditioners. However, the nutrient contents in biochar and performance depend on the source of the feedstock, pyrolysis conditions. The thermogravimetric analysis, N_2 adsorption-desorption analysis and elemental analysis were performed to investigate the pyrolytic characteristics and essential components.

Materials and methods: The raw material used in this research was *Chlorella sp.*biomass, the biomass was 80% humidity. Catalytic pyrolysis was performed in a laboratory-scale stationary tubular reactor using a mesoporous catalyst. The chemical components and the physical characteristics of algae and bio-char were investigated by thermogravimetric analysis TGA (TA Instruments), N_2 adsorptio-desorptioin analysis (Nova 2200e) and elemental analysis.

Results: The thermo-decomposition of organic matter of algae under pyrolysis was investigated by TGA. This technique measures the amount and rate of change in the weight of material as a function of temperature. TGA is used to determine the relationship between the weight loss or gain and the temperature due to decomposition, oxidation, dehydration. The results of the TGA of the pyrolytic characteristics of the algae and bio-char sugested the presence of three common stages.The first stage is dehydration, which occurs from the starting at 50–200 °C, the second stage is release of volatile compounds, and the last stage is solid decomposition at a temperature range of 600–900 °C.

Conclusions: The chemical composition of biochar obtained from the pyrolysis of algal biomass includes carbon (>60%), nitrogen, hydrogen and nutritive elements (K, Ca, Na, Mg, Si). Bio-char can be used as a natural fertilizer or support material for controlled release of nutritive elements, due to positive effects on the environment (reduced eutrophication risk, atmospheric carbon capture and degraded soil amendment) and on agriculture production.Also, biochar has the ability to reduce soil acidity, can increase electric conductivity and cationic exchange capacity, as well as ulterior nutrient availability. Increasing soil pH by application of biochar is a well-documented mechanism for improving nutrient availability, especially N and P.

Acknowledgements:*This work was supported by a grant of the Romanian Ministry of Education and Research, project number PN 19.23.01.01*

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TREATMENT OF DAIRY WASTEWATERS USING NANNOCHLORIS SP. MICROALGAE STRAIN

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Keywords: Nannochloris sp., dairy wastewater treatment, microalgae, lactose.

Introduction: The dairy industry is one of the main sources of agro-industrial wastewater. The produced wastewater mainly consists of milk and milk products residues, byproducts of the processing operations, water used for the cleaning of the equipment and sanitary wastewater from the staff. In general, the two main types of wastewaters produced in dairy industry are: a) the high-strength wastewater (e.g., cheese whey, milk permeate) and b) the medium-strength dairy effluent (e.g., effluents from the production of yoghurt, butter ice-creams, cheese final wastewater effluents) [1].

The aim of the paper is to study the potential of microalgae to reduce the content of organic compounds from a residual stream in the dairy industry specifically the reduction of N, P and COD, as well as the effects of microalgae growth by monitoring growth curves and biomass productivity in the cheese whey environment after 7 days of growth.

Materials and methods: The growth medium chosen for the cultivation of microalgae was deproteinized cheese whey. The microalgae strain chosen for these experiments is *Nannochloris sp.*. The growth medium (specific Zarrouk) was prepared through the addition of the respective salts that comprise Z medium in deproteinized cheese whey, used as carbon source. The experiments were performed with samples of increasing concentrations of cheese whey, calculated as amount of lactose (0, 2.5, 5, 7.5, 10 g / L). Whey dosing was done based on spectrophotometric determination of lactose.
Results: Cultivation of the microalgae strain *Nannochloris sp.* on dairy wastewater - cheese whey - resulted in an increase in biomass productivity proportional to the concentration of lactose present. Also, following the analysis of the growth medium at the end of the experiment, an almost complete consumption of lactose by microalgae was obtained, small quantities being found in the samples of higher concentrations at the end of the cultivation process.

Conclusions: Preliminary results have shown the great potential of microalgae, specifically *Nannochloris sp.*, for water reclamation from dairy industry derived wastewater. A significant reduction in P, N, chemical oxygen demand and lactose of up to 82%, 94%, 94% and 99%, respectively was achieved. Biomass productivities increased directly proportional to lactose concentration, while the distribution of bioactive compounds in microalgae biomass remained similar for all cases.

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

Acknowledgements: *"This work was supported by a grant of the Romanian Ministry of Education and Research, project number PN 19.23.01.01"*

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SCREENING METHOD FOR MICROALGAE WITH BIOREMEDIATION AND PLANT BIOSTIMULANT POTENTIAL

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Keywords: microalgae; polluted waters; hydrocarbons; biomass; plant biostimulants.

Introduction: During the last decades, the high potential of microalgal products in different industrial and agricultural fields was demonstrated [1]. Microalgae are a sustainable solution in many applications and challenges, from polluted water treatment to plant biostimulants. We aimed to develop a method to select microalgae strains capable of hydrocarbon biodegradation from those with plant biostimulant characteristics. Such strains could be further used in various applications, especially for bio- and/or rhizoremediation of hydrocarbons polluted water and, respectively, soil.

Materials and methods: Three species of axenic microalgae, with plant biostimulant potential, *Chlorella sorokiniana*, *Desmodesmus communis*, and *Raphidocelis subcapitata*, were cultured in BG11 media in the presence of two long-chain alkanes, decane, and hexadecane, respectively. The concentrations tested were 1% and 5% v:v. The microalgae cultures were kept under atmospheric conditions of light and temperature, with daily orbital manual agitation. The optical densities, biomass quantities, and chlorophyll concentrations were used to determine the effect of the hydrocarbons on microalgae growth [2]. The residual alkanes were quantified at the end of the tests by the GC-MS method to evaluate the potential for bioremediation.

Results: Both hydrocarbons stimulated the microalgae growth, especially C_{16} alkane, the variants with 5% hexadecane recording the highest amounts of weighed biomass. The cultures with *Ch. Sorokiniana* had almost four-fold higher biomass than control. The hydrocarbon peaks areas from GC-MS chromatograms decreased in the presence of microalgae, mainly in the cultures with *Ch. Sorokiniana* microalgae.

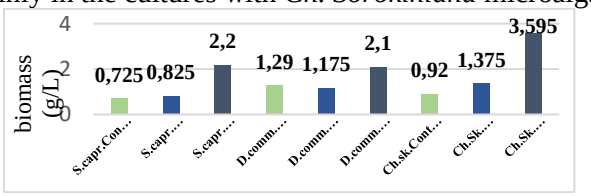

Fig.1. Quantities of microalgae biomass obtained in variants with 5% hydrocarbons

Conclusions: Microalgae were capable of growing in hydrocarbon-supplemented growth media with high rates of alkane biodegradability. *Ch. sorokiniana* showed the highest efficiency in bioremediation. Furthermore, a significant increase in microalgae biomass quantities was obtained in the presence of 5% hexadecane. Microalgae cultivation in hydrocarbon presence increases the efficiency of producing microalgae biomass with plant biostimulants potential.

Acknowledgments: *This work was supported by project POC-A1-A1.2.3-G-2015-P_40_352-SECVENT, My_SMIS 105684, "Sequential processes of closing the side streams from bioeconomy and innovative (bio) products resulting from it, subsidiary project 1882/2020 – Aqua-STIM. The SECVENT project was co-funded by European Regional Development Fund (ERDF), The Competitiveness Operational Programme (POC), Axis 1.*

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BIOSTIMULANT EFFECT OF HUMIC ACIDS FROM BIOMASS ON MICROALGAE

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Keywords: humic acids, lignin, microalgae, bio-stimulant effect.

Introduction: Humic substances (HS) are formed by chemical and biological transformations of vegetal and animal biomass through microbial metabolism, representing a major organic carbon source at the soil's surface. They contribute to the adjustment of many major ecological processes. For example, HSs enhance plant growth and terrestrial life in general, adjust carbon and nitrogen cycles in the soil, plant and microorganisms' growth, the fate and transportation of anthropogenic compounds and heavy metals and stabilize the soil [2]. Scientists define humic acids (HA) as humic materials that are soluble in aqueous alkaline solutions and presipitate when the pH is brought to 1 – 2 [3]. In this work HAs were obtained by humification of ligning that was extracted from beer spent grain (BSG) obtain in beer fabrication with deep eutectic solvents (DESs). The humification process used in this case was reacting the BSG extracted lignin with hydrogen peroxide in the presence of ferric sulphate heptahydrate. The biostimulant effect of HAs was tested on *Chlorella Sorokiniana* microalgae species. Also biostimulant tests were made using a commercial product containing HAs (BlackJak, BJK) and a coal extracted lignosulphonate (LsNa).

Materials and methods: For lignin extraction from BSG various DES were used. Humification of the extracted lignin was made by reaction with hydrogen peroxide in the presence of ferric sulphate heptahydrate. Bio-stimulant tests were made at 25°C±2°C, illuminating with a fluorescent light lamp at 100 µmol/m2·s (µEinstein) with a light/darkness period of 14/10 h for 9 days up to 2 weeks. Parameters like turbidity, optic density, cholorophyll content were studied. Concentrations of 10mg/l si 1mg/l in the case of BJK and LSNa and of 1mg/l in the case of the obtained HA were used.

Results: Lignin was extracted with various yields. HAs were identified using FT-IR spectra. HAs had the best bio-stimulant activity in the period of 9 days for the 1mg/l concentration.

Conclusions: The bio-stimulant effect showed promising results in every case, the obtained HAs having a better effect than the commercial product containing HAs after 9 days.

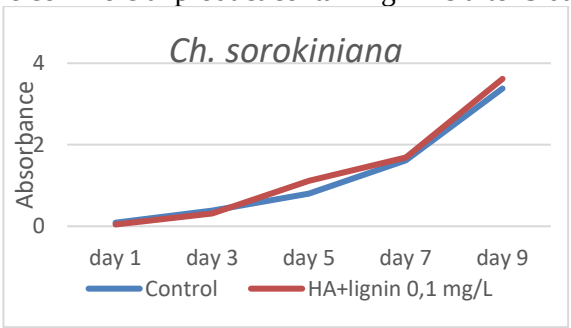

Fig.1. Optical density quantity for *Ch. Sorokiniana*.

Acknowledgements: *This work was supported by the POC-A1-A1.2.3-G-2015-P_40_352-SECVENT project, My_SMIS 105684, "Sequential processes of closing the side streams from bioeconomy and innovative (bio)products resulting from it", subsidiary project* 1500/07.08.2020 *BIOLIGNOL. The SECVENT project was co-funded by European Regional Development Fund (ERDF), The Competitiveness Operational Programme (POC), Axis 1.*

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THE INFLUENCE OF THE ZINC OXIDE NANOPARTICLES OVER DECONTAMINATION EFFICIENCY OF SOMAN AND SULFUR MUSTARD

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Keywords: decontamination; ZnO nanoparticles; chemical warfare agents; GC-MS;

Introduction: Metal oxide nanoparticles (NPs) has been intensively studied and showed promising results in various industries (alimentary [1], medicine [2], pharmaceutical [3], microbiology [4]). Metal oxide NPs offer promising outcomes such as small particle size, high specific surface area and unique physico-chemical properties which allow them to both adsorb and degrade toxic compounds due to their catalytic activity [5].
The paper presents the influence of the zinc oxide nanoparticles over decontamination efficiency of real nerve and blister agents with an internally developed amino-alcoholic decontamination solution. Through this paper, we aimed to evaluate the decontamination capacity of ZnO NPs embedded into an organic decontamination solution. The decontamination capacity was evaluated against two toxic compounds, sulfur mustard (HD) and soman (GD).

Materials and methods: The decontamination procedures were caried out at 25°C and magnetic stirring. Gas chromatography – mass spectrometry / electron impact (GC-MS/EI) investigations were performed on a GC Thermo Scientific Trace 1310 - TSQ 9000 MS/MS, TR5MS gold column, 250°C injector temperature, helium flow 1.5 mL / min.

Results: ZnO NPs utilization in the decontaminations of chemical warfare agents showed consisting and promising results. Several solutions with different concentrations of ZnO NPs (0,1% – 2%) has
been tested and comparted with the reference decontamination solutions (SD). The decontamination efficiency has been evaluated by GC-MS/EI analyses at 2, 10, 30 min, 1, 3, 5 and 24 h. The decontamination products formation has been observed and quantified over the process.

Figure 1. Organic solution (SD) and SD embedded with ZnO NPs with different NPs concentrations

Conclusions: The presence of ZnO NPs in the organic decontamination solution showed a better decontamination efficiency, which was increasing with the concentration of NPs added, on a concentration interval of 0,1 - 1%. The solution with 2% ZnO NPs showed a decrease in the decontamination efficiency in both cases, HD and GD.

Acknowledgements: *The authors would like to thank for the financial support provided by the National Authority for Scientific Research from the Ministry of Education, Research and Youth of Romania through the National Projects PN-III-P2-2.1-PED-2019-4222 ctr. no 427PED/2020 and PN-III-P2-2.1-PTE-2019-0400 ctr. no 49PTE/2020.*

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THE EFFECTS OF DIFFERENT TEMPERATURE CONDITIONS ON MARBLE PROPERTIES

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Keywords: marble, degradation, structure, analyze

Introduction: The term marble derives from ancient Greek and has the meaning of "shining stone". Marble is a rock that is formed through a metamorphic process of sedimentary rocks such as dolomite and limestone. In its pure state, the marble should consist only of calcite crystals and have a chemical composition of 56% calcium oxide and 44% carbon dioxide.

This is true only from a theoretical point of view, because there may be other foreign elements that can affect the color, shades, design. Some of the components that can be found are: quartz, pyrite, graphite, feldspar, iron oxides [1,2].

Materials and methods. The samples were exposed to two different types of treatments: 25 freeze-thaw cycles (according to SR EN 12371) and 3 cycles of exposure to high temperatures (400 ^{o}C for 1 hour). The analyzed samples are: Carrara Italy marble, Rușchița pink marble and Albești white marble. The aestetic parameters before and after treatments were measured using Chromameter Konica Minolta CR-410, Binocular Stereomicroscope Euromex and Glossmeter HG268. The freezing coefficient was determined with the following equation $\mu_g\% = (M_0 - M_i/M_0) \times 100$, where M_0= mass before FT cycles, respectively M_i after i numbers of FT cycles.

Results: Following the freeze-thaw cycles small differences in chromatic parameters (ΔE=2.2 for Carrara Italy marble and ΔE=7.2 for Rușchița pink marble) could be observed. The freezing coefficient for all the samples presents low values (0.016%-0.029%). Following the exposure to high temperature treatment, the samples show high differences in chromatic parameters (ΔE=43.47 for white marble) and significant changes in gloss. The surface of samples showed cracks and microcracks.

Conclusions: Based on the results of this study, the following conclusions can be drawn. Thermal cycles can cause mechanical disintegration of the outer part of the marble, starting from the discontinuities included in the rock and between the faces between the different minerals that form the stone. The exposure to high temperature will lead to a loss in adhesion between the superficial grains at the sample`s surface.

***Acknowledgements**: This paper was supported by the Romanian Ministry of Research and Innovation, Project 51PCCDI/2018 within PNIII and PN 19.23.03.01.11 within the NUCLEU program.*

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HYBRID CRYOGELS WITH ADVANCED ADSORBENT PROPERTIES FOR PENICILLIN

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Keywords: hybrid cryogels, peniciline, chitosan, clay, water purification

Introduction: In recent years, natural polymers (chitosan and biocellulose) sparked interest, especially when it comes to medical uses (wound healing, excipients for drug administration), due to their great biocompatibility and low toxicity[1-3]. However, the low mechanical properties of chitosan limit its use to some extent. For this reason, in this study, chitosan was used in mixture with a natural clay, i.e., kaolin. The choice for Kaolin was made considering both its low toxicity and the occurrence of hydroxyl groups, which make it suitable for hybrid cryogels with advanced adsorbent properties. Since 1941, penicillin has been used to cure infectious diseases, but it may be also used for food preservation. The presence of antibiotic residues in wastewater poses toxicity issues, requiring measures to reduce this pollution effect.[4,5]In this study, hybrid super-adsorbent cryogels capable of retaining penicillin from aqueous samples, were developed.

Materials and methods: In order to develop the aimed hybrids, two types of chitosan were used: Commercial Chitosan (CC) and Chitosan prepared in laboratory from shrimp shells (CS). Other reagents: acetic acid, was used in mixture with water, for chitosan dissolution; crosslinking agent; kaolin; γ-methacryloxypropyltrimethoxysilane, the organophilization agent and penicillin G, the antibiotic. The issues related to the rather limited compatibility between inorganic kaolin and organic chitosan requires organic modification of kaolin, in which case MAPTES was used.

Results: In order to confirm the organophilization and the structure of super-adsorbent materials, samples were characterized using various modern techniques (FTIR, BET, SD, UV-Vis). FTIR spectra confirmed the occurrence of characteristic bands of the involved raw materials. The developed hybrids possess adjustable porosity according to BET. The UV-Vis results confirmed that hybrid cryogels posed great retention capacity for penicillinin aqueous solutions.

Conclusions: Innovative super-adsorbent cryogels based on natural polymers and clays were successfully prepared. These materials showed a great adsorption capacity, mainly because of the high swelling capacity of chitosan. The use of Kaolin yielded improved mechanical properties.

Acknowledgements: *The authors would like to thank the ERA-NET COFUND ON THE BLUE BIOECONOMY and the EU for funding, in the frame of the collaborative international Consortium (BIOSHELL) financed under the ERA-NET BLUEBIO 2018 Cofunded Call and the National NFO Executive Unit for Financing Higher Education, Research, Development, and Innovation through, Project 157/2020, COFUND-BLUEBIO-BIOSHELL.*

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NANOCOMPOSITE BASED ELECTROSENSITIVE PLATFORMS FOR NITRITE AND BIOGENIC AMINES DETERMINATION

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Keywords: carbon allotropes, metallic nanoparticles, nitrite, biogenic amines

Introduction: Highly **e**lectrosensitive platforms have been developed using different nanocomposite materials based on carbon allotropes and different metallic nanoparticles for determination of nitrite and biogenic amines (BAs). The nitrification process occurred in soil represents an important source of pollution. The nitrification consists in biological oxidation of the relatively immobile ammonium (NH_4^+) to highly mobile nitrate, via nitrite. This process is carried out mainly by the ammonia – oxidizing bacteria (*Nitrosomonas* sp. and *Nitrobacter* sp.) present in the soil microbial population [1,2]. The nitrite contamination of ground and surface waters represents the major concern associated with the nitrification process. Also, the growing needs for food and environmental safety has led to an increase in research for the detection of biogenic amines (BAs) in last years. Despite the fact that BAs are increasingly present in food and beverages, causing toxic effects in the body, legislation that limits their presence in food chains needs to be updated, thus requiring sensitive tools for their detection [3,4].

Materials and methods: Miniaturized analytical tools have been developed based on nanocomposite materials obtained through combination of different carbon allotrope materials (nanoribbons, nanotubes - single and multiwalled and nanofibers) with metallic nanoparticles (Ag, Au-Ag, Pt, Cu). Thus, carbon based screen-printed electrodes (SPE) were chemically modified with the obtained nanocomposite materials and further characterized using different electrochemical techniques. In order to allow a selective and sensitive determination of analytes, an electropolymerized film was deposed on the modified sensors. For BAs determination were realized two configurations of biosensors, a bienzymatic one consisting in immobilization of diamine oxidase (DAO) and horseradish peroxidase (HRP) onto the modified sensors, and respectively a mono-enzymatic system based on immobilization of DAO onto the modified sensors. It was taken into account that the charge of carbon-based nanomaterials on the surface of the sensors should not exceed 5%, in order to ensure a low based current.

Results: Morpho-structural and electrochemical characterization studies of the modified SPEs have been performed in order to achieve a high sensitivity and selectivity of detection, applying a low overvoltage. The co-polymeric film ensured a better stability of the nanocomposite material layers at the electrode surface and an optimal matrix for enzymes immobilization. Optimization of the nanocomposite-based sensors were performed, and finally detection of putrescine, cadaverine and histamine was carried out using biosensors based on single-walled carbon nanotubes and Pt nanoparticles at an applied potential of -0.2 V vs Ag/AgCL. Nitrite determination was performed using multi-walled carbon nanotubes and AgNP modified sensors at 0.56 V vs Ag/AgCl.

Conclusions: The developed sensors and biosensors showed good sensitivities of nitrite and BAs detection. Although the enzyme DAO has a low enough activity to catalyze the oxidation of amine of interest, the detection limits were lowered due to the electrocatalytic activity of nanocomposite materials and the HRP enzyme used.

Acknowledgements: *The authors thanks to Ministry of Education and Research of Romania through National Programs PN19.23.03.02/2019, and respectively through International Program ERANET-MANUNET-NITRISENS no 216/2020.*

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FILM-FORMING POLYMERIC BLENDS DESIGNED FOR THE REMOVAL OF HEAVY METALS AND RADIONUCLIDES FROM CONTAMINATED SURFACES

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Keywords: decontamination, polymeric nanocomposites, strippable coatings, heavy metals, radioactive metals.

Introduction: Surface decontamination is a vast domain. The majority of the methods use a considerable quantity of water that needs further treatments. This study presents an ecological method for surface decontamination based on polymeric nanocomposites especially designed for the removal of heavy metals and radionuclides. Besides being effective in decontaminating the surfaces, these polymeric coatings also reduce the volume of the waste materials.

Materials and methods: The novelty of this work consists in the innovative path of combining the advantages brought by the film forming ability of polyvinyl alcohol, with the remarkable metal retention capacity of bentonite nanoclay, together with the chelating ability of alginate and with the one of two 'new-generation 'green' complexing agents': iminodisuccinic acid (IDS) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), for obtaining powerful, customizable, and environmentally-friendly film-forming water-based solutions for surface decontamination of heavy metal or radioactive metals.

Results: Decontamination test revealed a high decontamination efficiency for heavy metals (DF ≈ **95-98%** tested on glass surface) and also for radioactive metals (DF ≈ **91-97 %** for ^{241}Am, ^{90}Sr-Y and ^{137}Cs tested on metal, painted metal, plastic and glass surfaces).

Conclusions: This eco-friendly method can successfully be employed as alternative to classical methods for surface decontamination, due to its promising features.

Acknowledgements: *The authors would like to thank for the financial support provided by the Executive Agency for Higher Education, Research, Development and Innovation Funding (UEFISCDI) from Ministry of Education of Romania through the National Projects PN-III-P2-2.1-PED-2019-4222 ctr. no 427PED/2020 and PN-III-P2-2.1-PTE-2019-0400 ctr. no 49PTE/2020.*

MESOPOROUS SILICA NANORESERVOIRS LOADED WITH 1-H BENZOTRIAZOLE FOR ACTIVE ANTICORROSION PROTECTION

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Keywords: anticorrosion protection; mesoporous silica; corrosion inhibitors

Introduction: In recent years, scientists are paying increasined attention to the development of intelligent nanocontainers in applications such as biomedical, catalysis and anticorrosion [1]. Preparation of anticorrosion coatings containing smart nanocontainers loaded with corrosion inhibitors, which can be initiated when the barrier coatings are damaged, favor the long-term function, as uncontrolled loss by leaching is inhibited [2].
The aim of the present study is to optimize the amount of an organic inhibitor (1-H Benzotriazole (BTA)) that can be *in situ* encapsulated in a mesoporous silica nanocontainer, prepared by an original sol-gel formulation.

Materials and methods: For the synthesis of silica mesoporous nanoparticles loaded with BTA were used 3 silica co-precursors: tetraethylorthosilicate (TEOS), Phenyltriethoxysilane (PTES) and Octyltriethoxysilane (OTES), at a 5/ 1/ 1 gravimetric ratio. The synthesis was carried out in the presence of a solvent (ethanol) and of a surfactant (Igepal CA-630). The pH of the sol-gel system was adjusted to ~ 9 by dripping an aqueous solution of NH_4OH (25%). Prior to the addition to the sol-gel reaction system, BTA was completely dissolved in ethanol. Various amounts of BTA were loaded to the sol-gel systems: 0.25; 0.5; 0.75; 1; 1.25; 1.5 and 2 g (corresponding to 0.09; 0.18; 0.27; 0.35; 0.44; 0.53 and respectively 0.70 % grav. of the total amount of sol-gel mixture). Also, a similar set of samples was prepared in the presence of a constant amount of Rhodamine B, dissolved in ethanol.

This second set was obtained in order to perform a visual evaluation of the encapsulation efficiency. Particles dimensions, size distributions and particles charging in the final dispersions were evaluated by dynamic light scattering (DLS) technique and Zeta potential measurements. Surface morphology was observed by SEM. The structural characteristics of the silica mesoporous particles were investigated by N_2 adsorption-desorption analysis on the calcined samples.

Results: During the in situ synthesis of silica nanoparticles, the aromatic molecules of the corrosion inhibitor BTA were linked via a hydrophobic interaction with the phenyl groups from the silica pores formed by the hydrophobic functions of silica co-precursors PTES and OTES. Also, the corrosion inhibitor was trapped inside the surfactant micelles of Igepal and encapsulated together inside the silica pores formed by the surfactant. More than that, it has been observed that only a small amount of BTA can be encapsulated in the absence of the surfactant.

Conclusions: An optimized method has been developed to obtain mesoporous silica nanoparticles loaded with 1-H Benzotriazole (BTA) as a corrosion inhibitor. The optimal range of the BTA concentration was found to be between 0.18 and 0.35 %.

Acknowledgements: *„This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P1-1.1-TE-2019-2053, within PNCDI III, contract no. TE 85/2020".*

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HYBRID INKJET-PRITABLE PASTE FOR SCREEN-PRINTED ELECTRODES

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Keywords: inkjet printable paste, molecularly imprinted nanoparticles, LPS recognition

Introduction: Nowadays, Gram-negative bacteria (GNB) are among the most significant public health and environment concerns in the world due to their high resistance to antibiotics. According to a recent study [1], 47 out of 100 patients are infected with multi-drug resistant GNB such as *Pseudomonas Aeruginosa.* Since it occupies the second position on World Health Organization (WHO) list [2], regarding its widespread occurrence and being one of the major factors that cause endotoxemia and pulmonary affections [3], new methods of detection need to be developed. This work describes the preparation and characterization of a hybrid inkjet printable paste, which includes in its composition as recognition units molecularly imprinted polymer nanoparticles (MIP-NPs). The prepared MIP-NPs are capable of recognizing lipopolysaccharides (LPS), the endotoxin that compose the outer membrane of GBN, when printed on the surface of a working electrode.

Screen printed electrodes (SPE) are portable devices that represent a fast and cost-effective solution, as they can be printed on large scale from a low quantity of printable paste. SPEs have found use in detection and recognition processes, making them suitables for this type of application[4].

Materials and methods: In this study, we report the preparation and characterization of the inkjet printable MIP paste, obtained by incorporation of molecularly imprinted polymer nanoparticles (MIPs) in a lab-made formulation using commercial carbon paste. Thus, the incorporation takes place in two phases: (1) the homogenization of MIPs particles and ZnO electroactive particles in a compatible solvent, and (2) the addition of a commercial printable paste and a polyether as binder. Further on, the resulted paste is printed on the surfaces of working electrodes.

Results: The obtained printable paste is characterized using modern techniques, such as structural and rheological analyses to highlight the successful incorporation of MIPs nanoparticles and to establish an optimal flow profile for the formation of hybrid paste suitable for printing on screen-printed electrodes. The obtained screen-printed electrodes are subjected to cyclic voltammetry analyses for LPS recognition.

Conclusions: Consequently, the obtained printable paste holds a great potential for developing new generations of sensors for detecting the LPS from *Pseudomonas Aeruginosa.*

Acknowledgements: *The authors gratefully acknowledge the support of the Executive Unit for Financing Higher Education, Research, Development and Innovation (UEFISCDI) through Project no. 255PED/2020 "TOXINSENS" and the Ministry of Researrch, Innovation and Digitalization (MCID) through Project. Nucleu No. PN19.23.02.01.*

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ALPHA-FETOPROTEIN MONOCLONAL ANTIBODY-FUNCTIONALIZED GRAPHENE FOR THE FABRICATION OFSURFACE ACOUSTIC WAVE SENSORS

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Keywords: laser induced forward transfer, monoclonal antibody, liver cancer

Introduction: Increased selectivity, response speed, and sensitivity in the chemical and biological determinations of gases and liquids are arguably an important step towards future micro and nano sized sensing systems. Since their development by White and Voltmer in 1965, surface acoustic wave (SAW) devices have attracted much research attention due to their unique functional characteristics which make them appropriate for the detection of chemical and biological species. This work surveys our latest progress in engineered complex materials, i.e. graphene functionalized with monoclonal antibody anti-alpha-fetoprotein, for applications as recognizing elements in miniaturized surface acoustic wave sensor design and application [1].

Materials and methods: Graphene functionalized with monoclonal antibody anti-alpha-fetoprotein have been printed by laser induced forward transfer (LIFT) into 2-dimensional pixels onto the active surface of a SAW platform. First, a parametric study (i.e. laser fluence, donor film morphology and thickness as well as single versus multiple pixel deposition) was carried out to determine the optimum experimental conditions under which sensitive pixels are obtained. Following the morphological and structural characterization of the laser printed material, the responses of the coated SAW resonators are measured. The sensitivity of the monoclonal antibody anti-alpha-fetoprotein functionalized graphene coated SAW devices gives an indication these devices represent an enabling technology for monitoring liver damage.

Results: The obtained sensor showed a good signal for detection of alpha-fetoprotein (AFP) in range 1,2-145,1 μg/L with potential application in early detection of liver cancer forms.

Conclusions: Graphene functionalized with monoclonal antibody anti-alpha-fetoprotein have been printed by laser induced forward transfer (LIFT) into 2-dimensional pixels onto the active surface of a SAW platform with a good signal for detection of AFP in range 1,2-145,1 μg/L.

Acknowledgements: *This work was supported by a grant of the Ministry of Education and Research, CNCS UEFISCDI, project number PN-III-P2-2.1-PED-2019-1603 "Surface acoustic wave biosensor based on functionalized graphene with monoclonal anti-alpha-fetoprotein antibody for hepatic cancer diagnostic" within PNCDI III.*

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ALPHA-FETOPROTEIN FUNCTIONALIZED MULTI WALLED CARBON NANOTUBES FOR THE FABRICATION OF SURFACE ACOUSTIC WAVE SENSORS

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Keywords: liver cancer, SAW sensors

Introduction: Taking in consideration the multiple advantages of the surface acoustic waves (SAW) sensors as high sensitivity, fast response time [1,2] compact fabrication and easy usage and also the increase demand for fast and low-price sensors devices the field of application for this type of sensors it is in a continuous expansion. Therefore, in the field of biosensors the usage of SAW sensors has gained a lot of attention from detection of different viral and bacteriological diseases [3, 4] and even for the detection of allergic conditions like peanut allergy [5]. Thereby here we present our work in the detection of liver cancer by using sensors based on carbon nanotubes functionalized with antibody anti-alpha-fetoprotein (AFP).

Materials and methods: Multi walled carbon nanotubes functionalized with antibody anti-alpha -fetoprotein have been printed by laser induced forward transfer (LIFT) into 2-dimensional pixels on the active surface of the SAW platform. Firstly, after multiple trials we have established the optimal parameters (laser fluence, donor film morphology and thickness as well as single versus multiple pixel deposition) in order to obtain sensitive pixels. Furthermore, the obtained laser printed material has been morphological and structural characterized. Moreover, the calibration of the sensors has been made by using solutions with known antigen AFP concentration and UV-vis spectrophotometry has been used as a technique for validation of the results.

Results: The obtained sensor showed a good signal for detection of AFP with potential application in early detection of liver cancer forms.

Conclusions: Multi walled carbon nanotubes functionalized with monoclonal antibody anti-alpha-fetoprotein have been printed by laser induced forward transfer (LIFT) into 2-dimensional pixels onto the active surface of a SAW platform with a good signal for detection of AFP.

Acknowledgements: *This work was supported by a grant of the Ministry of Education and Research, CNCS UEFISCDI, project number PN-III-P2-2.1-PED-2019-1603 "Surface acoustic wave biosensor based on functionalized graphene with monoclonal anti-alpha-fetoprotein antibody for hepatic cancer diagnostic" within PNCDI III and another grant from Polytechnic University of Bucharest POC project "Biosensors with surface acoustic waves based on carbon nanotubes functionalized with prostate-specific antigen antibody and anti-alpha-fetus protein antibody for the detection of prostate cancer and liver cancer"*

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THE EFFECT OF GRAPHENE NANOPLATELETS ON THE PROPERTIES OF HYBRID POLYAMIDE/GLASS FIBER COMPOSITES

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Keywords: polyamides; glass fiber; graphene nanoplatelets; hybrid composites; mechanical properties

Introduction: Nowadays, the way of solving the issues related to the environment has become a topic of great interest, being approached by researching in several directions such as recycling or replacement of polluting materials [1]. Most glass fiber (GF) composite wastes are non-biodegradable and very bulky, causing serious environmental problems [2]. Given the requirements of the European Commission to reduce CO_2 emissions by at least 40%, it is possible to consider reducing the weight of automotive by replacing metal parts with high-performance polymer composites with a low impact on the environment [3]. Starting from the development of a new nanocomposite material based on bio-polyamide and 2D nanostructure that has improved properties [4,5] and can be used to obtain automotive parts, the possibility of reducing the content of glass fiber with graphene nanoplatelets in composite based on PA6 and 30% GF was studied.

Materials and methods: A full bio-based polyamide 1010 (PA1010), a polyamide 6 (PA6), a composite with PA6 and 30% glass fiber (PA6GF30), graphene nanoplatelets (M5) with a particle diameter of 5µm and an average thickness of approximately 6 – 8 nm were used in this study. Hybrid composites based on PA, GF and M5 were obtained using the masterbatch method. 39 wt. % M5 masterbatches were obtained based on both PA1010 (MB1010) and PA6 (MB6) which were diluted with PA6GF30 to the desired M5 concentration. Both masterbatches and hybrid composites were obtained under dynamic conditions using a double screw extruder. The resulting hybrid composites were characterized in terms of thermal properties (TGA, DSC), mechanical properties (tensile and impact test) and dynamic- mechanical analysis (DMA).

Results: Dilution of the MB1010 masterbatch with PA6GF30 composite, led to hybrid composites with a mixture of PA1010 and PA6 as polymer matrix, which at 5 wt. % M5 showed an interesting properties profile. In comparison with the starting PA6GF30 material, strength and stiffness of the hybrid composite was affected by approximately 29% and 25%, respectively. Also, impact strength decreased with approx. 18%. By contrast, a smaller decreasing was attained for the strength and stiffness by approximately 12%, respectively 8% with maintaining the impact strength, when the masterbatch MB6 was diluted with PA6GF30 composite.

Conclusions: It is possible to reduce at least 16 wt. % of the GF (from the overall 100 wt. % GF found in neat PA6GF30) with M5, with good compromise in comparison with the starting PA6GF30 and still meet the automotive field material properties requirements. By dilution of PA6 based masterbatch with PA630GF composite, hybrid composites with better properties are obtained.

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. ENGEL Austria GmbH and ENGEL Injecție Srl are kindly acknowledged for their support and enabling the development of the injection moulding equipment. EVONIK Industries AG is gratefully acknowledged for the full biobased PA1010 offering. ADDINOL Lubricants Romania SRL is also acknowledged for the equipment assistance.*

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SILVER NANOPARTICLES MEDIATED BY NATURAL EXTRACTS RECOVERED FROM WASTES AND BY-PRODUCTS

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Keywords: green synthesis; phenolic compounds; plant wastes; silver nanoparticles.

Introduction: Current environmental problems demand an eco-friendlier approach to the chemical synthesis of metal nanoparticles (NPs) [1]. By using plant extracts obtained from waste materials and by-products resulting from the essential oil and textile industry, the resulting green nanoparticles, represent a sustainable alternative for the classical synthetic route [2, 3].

In our study, we obtained silver nanoparticles (AgNPs) by using aqueous plant extracts from *Cannabis sativa*, *Thymus vulgaris*, *Lavandula angustifolia*, and *Origanum vulgare*.
The chemical composition of the extracts was determined by chromatographic and spectroscopic methods. AgNPs with less than 70 nm were obtained and characterized by UV-VIS, FT-IR spectroscopy, SEM. The antioxidant activity (DPPH and ABTS assays) and the antibacterial properties against Gram-positive and Gram-negative bacteria of some of the samples were evaluated.

Materials and methods: For the green NPs synthesis, the plant extracts were freshly prepared and filtered through a 0.45 mm PVDF, then, 0.5 mL extract was mixed with 0.5 mL 5 mM silver nitrate solution, and 0.7mL purified water. The total reaction time was 8 minutes at 90°C.

Results: The bio-reduction of silver ions was mediated by the phenolic compounds present in the aqueous extracts. This reaction was easily observed by a visual colour change from pale gold to a reddish-brown and confirmed by UV-Vis spectral analysis, with an average particle size of 35-70 nm. Nanoparticle morphology was observed using SEM and average spherical shapes were noticed.

Conclusions: The preparation of silver nanoparticles was successfully performed using aqueous extracts recovered from industrial wastes and by-products. Obtaining NPs through green synthesis is a fast, easy, and eco-friendly reaction that reduced Ag^+ to Ag^0 to spherical AgNPs with small average particle size.

Acknowledgements: *This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-PD-2019-0607, within PNCDI III.*

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5. Affiliated Workshops

CLOSING THE LOOP IN AN EFFICIENT MANNER – THE FEED-FORWARD CONTROL SOLUTION

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Keywords: circular bioeconomy, feed-forward control, Near-Infrared spectroscopy, Raman scattering

Introduction: Romanian economy is dominated by linear value-chains. Closing the loop in these value chains involves implementing biorefinery processes developed according to pyramid biomass value [1]. The main issue with using the bioeconomy side-streams as feedstocks for sustainable biorefinery processes is their high variability in the recoverable ingredients [2]. The feed-forward control systems adapt the biorefinery technology parameters to the specific features of the processed side-streams [3]. We aimed to develop a feed-forward system integrated into the biorefinery of the cyprinids side-streams, i.e., scale, skin, bones, into high-value products - bioactive peptides and ingredients for 3D and/or 4D- printed biocompatible scaffolds.

Materials and methods: The cyprinids side streams were mixed and grounded, and 12 samples from different batches were prepared for feed-forward method calibration. The crude proteins content was determined as 6.25 × nitrogen according to ISO 5983–2/2009. The total collagen content was estimated by determination of the hydroxyproline content - ISO 3496:1994. Two vibrational spectroscopic methods, Near Infrared (NIR) spectroscopy and Raman scattering, were used as candidates for the fast and non-destructive feed-forward techniques. The spectra were acquired for grounded sample arranged in plastic trays, with a surface equal to an A4 paper (210 x 297 mm) and a height of 2 cm. The NIR spectra were acquired in the range 900-1700 nm, using a NIRQuest+1.7 handheld spectrometer (Ocean Insight, Orlando, FL, USA). To acquire the Raman spectra, we used a handheld Raman-HR-TEC 785nm device (StellarNet, Tampa, Florida, USA). Partial least squares (PLS) regression was used to establish correlations between the proteins and collagen content determined by the ISO methods and NIR and Raman spectra. Protease and peptidases were added according to the determined protein/collagen ratio to produce (bioactive) peptides and (printable) polypeptides. To select and validate the spectroscopic feed-forward method, 6 samples were processed according to values estimated by spectroscopic techniques. The yields on peptides and polypeptides were determined by gel electrophoresis.

Results: NIR peaks from 1120–1350 nm were proven to have the best correlation with the total protein content – R^2=0.87. The peaks of Raman spectroscopy correlate well in the range of 850 cm^{-1}– 950 cm^{-1} with the ratio between protein/collagen ratio – R^2=0.78. Using the ratio between peaks at 861cm^{-1} and 916 cm^{-1}, a good prediction of the necessary activities of protease and peptidases in the biorefinery process was obtained.

Conclusions: Raman spectroscopy at 785 nm is a functional feed-forward solution and allows estimation of fish side-streams specific features for optimal protease/peptidase treatment.

Acknowledgments: *This work was supported by the project PN-III-P2-2.1-PTE-2019-0181 Biorefining of the side streams resulted from cyprinids commercialization – ColStim, contract 3PTE/2020.*

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PLANT BIOSTIMULANTS FOR AN ENHANCED SUSTAINABILITY OF HIGH RESIDUES FARMING SYSTEM

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Keywords: high residue farming system, nanoselenium, strigolactone mimics, ecotoxicology

Introduction: Besides multiple benefits, high residue farming systems have drawbacks: delayed development of the plant in early stages, nutrients availability, and enhanced risks for soil-borne diseases [1]. These drawbacks are targeted by the second-generation plant biostimulants delivered in the frame of an RO-NO project, STIM 4+. The STIM 4+ project objectives are: (i) to develop plant biostimulants intended to improve the resource use efficiency of high-residue grown vegetables; (ii) To assess and to characterize the new plant biostimulants effects on vegetables and rhizosphere microorganism; (iii) To investigate the safety and environmental impact of the newly-developed plant biostimulants.

Materials and methods: Vegetable cultivation in a hairy vetch mulch is the targeted high-residues farming system [2]. The plant biostimulants developed in the frame of RO-NO 540 STIM 4+ intended to compensate for the drawbacks of this farming system. These plant biostimulants include: microbial plant biostimulants that respond to rhizosphere endo-signals, strigolactone mimics formulated into a stimuli-responsive formulation based on glycodynameric chitosan, selenium nanoparticles, and microalgae extract containing betaine and polyamines. The application technologies are designed to exploit strigolactones functions as exo-signals for the better harnessing of the beneficial microbiome and as a cue for harmful organisms (e.g., to induce suicidal germination of parasitic plants)

Results: The ongoing STIM 4+ project activities refer to the delivery of (i) selected strains that respond to strigolactones, used to produce the microbial plant biostimulants; (ii) integrated process to produce zero-valent biogenic nanoselenium, as representative inorganic plant biostimulants and concentrated microbial microalgae extracts, as organic plant biostimulants; (iii) optimized synthesis reactions to produce strigolactone mimics, with enhanced exo-signal activities; (iv) glycodynameric hydrogel, for application on the plant residues and formulation of the plant biostimulants. These results will be further integrated with the application technology. The safety and environmental impact of the newly developed products are determined by state-of-art 3R techniques applied to soil solution samples collected *in situ* by suction lysimeters.

Conclusions: The integrated application of the plant biostimulants developed in the frame of the STIM 4+ project enhances the sustainability of the high residues farming system based on hairy vetch. Nutrient use efficiency and plant tolerance to the abiotic stress are improved due to applying the new plant biostimulants. Crop quality is enhanced due to secondary metabolism activation and higher accumulation of bioactive compounds in the edible yield.

Acknowledgments: *This work was supported by the project RO-NO-2019-540," Integrated use of the next generation plant biostimulants for enhanced sustainability of field vegetable high residue farming systems – STIM4+."*

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6. Author Index

The original title (in Romanian): Simpozionul international „PRIOCHEM”
Edited by: ICECHIM Bucharest, Romania

ISSN 2601 - 419X and ISSN-L 2601 - 4181 - English ed., CD-ROM,other Electronic Supports;
ISSN 2601 - 4181 and ISSN-L 2601 - 4181- English ed., Print;
ISSN 2601 - 4203 and ISSN-L 2601 - 4181 - English ed., Online;
ISSN 2285 - 8334 and ISSN-L 2285 - 8334 - Romanian ed., Print;

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