SICHEM 2020

BOOK OF ABSTRACTS

17 – 18 September 2020

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Support Institutions

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HOFIGAL IS ONE OF THE FAMOUS BRAND NAMES FOR NATURAL PRODUCTS

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Abstract*: Hofigal is one of the famous brand names when it comes to homeopathic, gemoderivative, and phytotherapeutic galenical products in Romania, made in the form of pharmaceutical products, dietary supplements, cosmetics, and teas. "Hofigal" is a share-held company comprising an exclusively Romanian private capital. The company utilises an area of 35 hectares. Approximately 400 employees work in the company, being continually motivated towards a professional and personal perfection; these people carry out their activities covering a wide range of fields: Agriculture, Production Planning, Production, Supply, Logistics and Distribution, Sales, Marketing, New Therapies, Total Quality Management, Quality Control, Regulatory Affairs, Research and Development, Human Resources, Legal, Administrative, Maintenance, and I.T. – all of which represent an integrated system.*

Key words: Hofigal, phytotherapeutic galenical products, dietary supplements, cosmetics, teas

Introduction: Hofigal is a company that is specialised in the manufacture of exclusively natural products, being characterised by the fact that they produce in their own greenhouses and agricultural lands the majority of the raw materials that they use.

The active raw materials that are used and obtained in controlled conditions, by way of a strictly organic agriculture.

Experimental and/or Modelling: The main objectives of the company are to apply the conditions and measures with regards to quality assurance, safety and efficacy of all products, as with the acquisition of natural vegetal active pharmaceutical ingredients (API) guaranteed to correspond in totality with current international ecological norms.

All of the stages of the process, from cultivation (pre-processing, plant processing), down to the finished product in the form of pharmaceutical products, dietary supplements, cosmetics, and teas conform to the international norms

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regarding the cultivation and harvesting of plants, as well as the rules for Good Manufacturing Practice,ISO 9001,14000,18000,22000 obtained from german TUV company.

Results and discussions: The products of Hofigal are the result of prolonged and sustained research or development activity carried out in our own laboratories by our own teams of specialists which include: researchers, and doctors in science (pharmacists, chemical engineers, physicians, biologists, microbiologists, biochemists, chemists, horticulturalists). This team collaborates with the most important higher learning institutions and the National Institute for Research and Development in Romania.

We currently cofinance research projects in the National Research Plan, to which are added a multitude of ongoing internal research projects.

As a result of these activities, the number of products successfully launched by Hofigal has risen from 3 products in the year 1990, to over 450 in the year 2020.

Being constantly engaged in the study and introduction of new therapies, we have recently added an innovative element to the Hofigal portfolio: the Gemoderivative range, in the form of hydro-glycero-alcoholic extracts in dilutions of 1:10 (1 DH), obtained from fresh plant tissues in their growth stages (buds, flower buds, inflorescences, shoots, young branch bark, internal root-bark tissue, sap, seeds). These are made up of embryonic tissues that have concentrated within them unique chemical compounds and the plant growth and development gene activated cell. These tissues are richer in vitamins, oligoelements, minerals, nucleic acids and growth factors than the plant has in general.

Conclusions: Throughout all of its activities, "Hofigal" promotes the newest leading concepts in nonpolluting production. From raw materials to finished products, everything is clean and natural.

No Hofigal product has counter-indications or adverse effects.

The National Institute for Research & Development
in Chemistry and Petrochemistry
www.icechim.ro

ICECHIM BUCHAREST – 70 YEARS OF CONTINUOUS RESEARCH IN CHEMISTRY AND CHEMICAL ENGINEERING

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Abstract: *A short history of ICECHIM, from its establishment to the contemporary challenges*

Key words: Research & Development, History, Current interests and challenges

Introduction: The year 2020 marks 70 years of continuous existence of one of the most renowned research institutes in Romania. What is now known as ICECHIM was established through the Decision of the Council of Ministers no. 604/1950, through the division of the Chemical Enterprises for Research, Design and Semi-Industrial Production (ICEPS).

Some of the ICECHIM employees were recognized personalities, and others later became reference names in the field: Costin Nenițescu, Ecaterina Ciorănescu, Margareta Avram, Ion Gavăt, Hipolit Sanielevici, Raul Mihail, Emilian Bratu, Ileana Necșoiu, Dan Costescu, Emil Ionescu and many others.

ICECHIM through the decades: In order to coordinate the entire Romanian chemical scientific research and to concentrate the forces on all the major problems, in 1970 the Central Institute of Chemical Research was established, whose main pillar was ICECHIM. This institute grouped all the departmental research institutes, research centers and laboratories attached to the industrial and chemical plants, as well as all the research activity in the higher education institutions. In 1973, the technological design institutes came under the direct subordination of the Central Institute, which thus became the Central Institute of Chemistry. In the period 1981-1989, the activity of ICECHIM had two basic components: modernization of technologies at the installations in operation and qualitative development of products, including those intended for export; putting into operation new industrial capacities on the national chemical platforms.

After 1990, it is known that research institutes faced very difficult conditions, as part of the industry disappeared, including the chemical industry. Even so, ICECHIM, through the efforts and perseverance of its researchers, managed to resist, even if a number of other institutes were abolished.

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ICECHIM as National Institute for Research & Development: ICECHIM has adapted to the new economic conditions due to the structural economic reforms preliminary to the accession to the European Union and to the new research financing systems, gradually orienting itself towards the requirements of small and medium enterprises. In 2004, the *Institute of Chemical Research* became the National Research & Development Institute for Chemistry and Petrochemistry - ICECHIM, providing applied research and theoretical studies in the field of chemistry and petrochemistry.

In our days, ICECHIM asserted itself as one of the main actors in the national research area, as well as an important component of the European Research Area, with applied research projects in multiple areas with a multitude of published research works, granted and requested invention patents, as well as technologies transferred into industry.

ICECHIM is proud to implement around 50 projects per year, an important part in national / international partnerships with other institutes, universities and SMEs, for more than half acting as coordinator.

Several representative results of the ICECHIM in its main research fields represented by:

- *Smart polymeric materials and nanomaterials,*
- *Biotechnologies, bioresources and bioproducts for bioeconomy*
- *New and emerging technologies*

will be briefly presented.

The complexity of the research developed in these projects lies in the integrated, inter and trans-disciplinary approach, while the connections between the complex activities and the human resource involved have an impact on the Romanian research. Creating an environment of excellence has led to increased visibility through publications in prestigious journals, attracting funds by applying to international and national projects, creating new opportunities for international scientific collaboration, contribution to the promotion of sustainable development and equal opportunities, as well as to the recruitment of a new generation of young researchers.

Institutul National de Cercetare-Dezvoltare Chimico-Farmaceutica

NATIONAL INSTITUTE FOR CHEMICAL-PHARMACEUTICAL R&D - CORE STAKEHOLDER OF THE ROMANIAN PHARMACEUTICAL RESEARCH

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Abstract*:* *The development of Romanian research in the field of medicines is closely linked to the evolution of the National Institute for Chemical - Pharmaceutical Research & Development (ICCF). With an adequate organizational structure and approaching a research methodology and directions in accordance with the dynamics of technical-scientific progress in the field, ICCF has maintained its essential competence, unique in Romania, to go through the entire development cycle of a drug, from synthesis/biosynthesis or plant extraction, to the elaboration of the documentation required by the introduction in the clinical trials*

Key words: synthesis, bio-synthesis, plant extraction, chemical-pharmacological characterization

Short history and description: Established in 1929 and operating uninterruptedly since 1949, ICCF was, until 1990, the sole provider of technologies for the pharmaceutical industry in Romania [1]. After 1990, in addition to industrial research and technological development, it approaches basic and pre-competitive research for new active substances of therapeutic interest [2] and carries out research services requested by Romanian and foreign drug manufacturers.

Current research directions include: (i) synthesis of bioactive substances, with two main objectives - innovative medicinal substances and competitive technologies for modern generic drugs; (ii) microbial biotechnologies for biomaterials and bioactive products with therapeutic role; (iii) plant extraction biotechnologies with good perspectives for capitalisation the diversity and richness of Romania's natural resources; (iv) pharmaceutical technologies for medicine formulations with controlled release of the active ingredient; (v) physical-chemical and pharmaco-toxicological (*in vitro* and *in vivo*) characterization of the products, according to GLP requirements.

Main achievements: - chemical entities with increased chances of becoming compounds of therapeutic interest: new quinolones for the treatment of infections with resistant microorganisms, nucleoside analogues [2] with potential antiviral or antineoplastic action (from the class of those that are experienced now for SARS-CoV-2); synthesis of compounds of prostaglandin class for use in human and

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veterinary therapy; studies of drug-design and molecular docking; and also - competitive technologies for modern generic drugs required by the market and the health system (candesartan, linezolid, memantine, acyclovir)

- biopolymers usable as vectors in therapeutic systems with controlled release of the active ingredient (polysaccharides) or in tissue engineering (polyhydroxyalkanoates), enzymes of therapeutic or industrial interest, such as asparaginase or xylanase, all obtained using a specific research infrastructure, the Collection of Microorgansims of Industrial Interest (CMII) of ICCF, which is affiliated to the World Federation of Culture Collection (WFCC) [3];
- plant extraction products (eg. an original product, eye drops, in phase II clinical trials or an original product with gastroprotective activity based on selective extracts isolated from two indigenous plant species) [4];
- pharmaceutical technologies for medicine formulations with controlled release of the active ingredient, using micro- and nanoparticles for target transport and higher bioavailability than known (supergeneric), such as transdermal or locally acting nanosystems, or synergistic combinations (cardiovascular, cytostatic - phytotherapeutics) [5].
- analytical research for development and validation of methods (physical-chemical) according to EU and international standards, development of the pharmaceutical data section as a component of a drug approval documentation (CDT-Quality).
- pharmaco-toxicological tests: antimicrobial activity of innovative substances and products, sterility control and microbial contamination of drugs and other pharmaceuticals; *in vitro* efficacy and safety on cellular and molecular models and *in vivo* pharmacological researches on adapted or developed (own) experimental models.
- internal microproduction and technological transfer of plant extraction products to phytotherapeutics manufacturers and internal microproduction of synthetic biological active structures commissioned by Romanian and foreign drug manufacturers

Conclusions: ICCF has developed based on its main competitive advantage - the existence of the necessary infrastructure and logistics to develop a new medicine.

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CEPROCIM – A PROACTIVE PARTNER IN ROMANIAN RESEARCH

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Keywords: Ceprocim, waste recovery / co-processing, special cements, circular economy

The first part is a brief review of the history of the Institute, founded in 1949, followed by a synthetic presentation of the activities currently undertaken.

The main part of our scientific paper is dedicated to outlining some successful research results achieved in the Institute lately:

- obtaining special and/or multifunctional cements and composite materials;
- a superior recovery of waste and its co-processing;
- development of innovative apatitic materials with high antimicrobial properties for construction materials and preserving of cultural heritage.

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Plenary

COMPARISON OF MECHANICAL AND BIOACTIVITY PROPERTIES OF NANO HYDROXYAPATITE COMPOSITES CONTAINING CERAMIC OXIDES

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Abstract: *Nanomaterials are an increasingly important product of nanotechnologies. They are coming into use in different areas like medicine, electronics and cosmetics. Their physical and chemical properties often differ from those of bulk materials. As in every field, studies on nanomaterials in the biomedical field show a rapid development. In this study, mechanical and in vitro bioactivity properties of nano hydroxyapatite (nHA) biocomposites containing different amounts of nano alumina (n*Al_2O_3*), nano magnesium oxide (nMgO) and nano niobium (V) oxide (n*Nb_2O_5*) were compared. 80 wt.% nHA- 20 wt.%* Al_2O_3 *(nAH1), 70 wt.% nHA- 30 wt.%* Al_2O_3 *(nAH2), 80 wt.% nHA- 20 wt.% MgO (nMH1), 70 wt.% nHA- 30 wt.% MgO (nMH2), 80 wt.% nHA- 20 wt.%* Nb_2O_5 *(nNH1), 70 wt.% nHA- 30 wt.%* Nb_2O_5 *(nNH2) composites including non-toxic binder were shaped by using dry-pressing method. The composites were sintered at 1000 and 1100°C for 2 hours, then microstructures, mechanical, technological and bioactivity properties were determined. The bioactivity properties were determined after soaking the samples in the simulated body fluid for 1, 2, 3 and 4 weeks. Density, compression strength and Vickers microhardness values of composites increased with increasing sintering temperature. The best density, compression strength and Vickers microhardness values were obtained with 70 wt.% nHA-30 wt.% MgO (nMH2) composite sintered at 1100°C as 3.16 g/cm 3 , 135 MPa and 438 HV, respectively.*

Key words: Nano, hydroxyapatite, bioactivity, mechanical properties, technological properties, alümina, magnesia, niobium (V) oxide.

Introduction: Nanomaterials are very important for nanoscience and nano technology. These materials have created a high interest in recent years [1,2]. As in every field, studies on nanomaterials in the biomedical field show a rapid development [3-5]. The aim of this study is to compare the mechanical and bioactivity properties of nano hydroxyapatite composites containing alümina, magnesium oxide and nano niobium (V) oxide to determine the effects of the reinforcement material and sintering conditions.

Experimental and/or Modelling: 80 wt.% nHA- 20 wt.% Al_2O_3 (nAH1), 70 wt.% nHA- 30 wt.% Al_2O_3 (nAH2), 80 wt.% nHA- 20 wt.% MgO (nMH1), 70 wt.% nHA- 30 wt.% MgO (nMH2), 80 wt.% nHA- 20 wt.% Nb_2O_5 (nNH1), 70 wt.% nHA- 30 wt.% Nb_2O_5 (nNH2) composites including non-toxic binder were shaped by using dry-pressing method. The composites were sintered at 1000 and 1100°C for 2 hours, then microstructures, mechanical, technological and bioactivity properties were determined. The technological and mechanical properties were determined by measuring density, firing shrinkage, compression strength and Vickers microhardness (HV). Structural characterization was carried out with X-ray diffraction (XRD) and scanning electron microscopy (SEM). The bioactivity properties were determined after soaking the samples in the simulated body fluid for 1, 2, 3 and 4 weeks.

Results and discussions: In figure 1 density, compression strength and Vickers Microhardness values increased with increasing sintering temperature for all composites.

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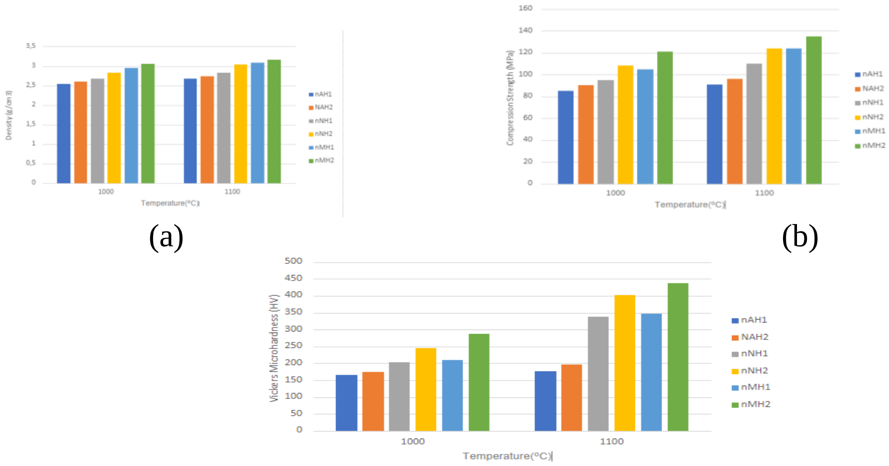

(a) (b)

(c)

Fig. 1 (a) Density (b) Compression Strength (c) Vickers Microhardness results of composites sintered at different sintering temperatures.

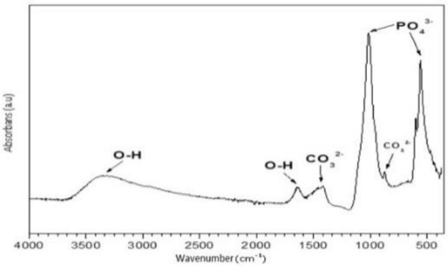

Fig. 2 TF-FTIR spectrum of the apatite layer during bioactivity tests [3].

Figure 2 exhibits the TF-FTIR spectrum of apatite layer on the nNH2 composite sintered at 1100ºC after the bioactivity test for 4 weeks. According to this figure solid formed in the SBF is the carbonated apatite.

Conclusions: 70 wt.% nHA- 30 wt.% MgO (nMH2) composite sintered at 1100ºC showed the best density, compression strength and Vickers microhardness values in all composites. The highest apatite thickness was obtained with nNH2 composite as 80 µm in all composites.

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SPARK PALSMA SINTERING AS EFFECTIVE WAY FOR COMPACTIZATION OF CARBON NANOMATERIALS AND SOLID ELECTROLYTES FOR BATTERIES

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Abstract: *The detailed description of SPS technique (spark plasma sintering) is given as well as it's application to compactization of different types of carbon nanomaterials and ion conductive solid electrolytes used in batteries. Other possible chemical and physical approaches to reach the same goal are discussed and compared with SPS. HR TEM, Raman spectroscopy, XPS and nitrogen porometry are used to support the data discussed.*

Key words: carbon nanostructures, spark plasma sintering, compacting, porosity, surface area, carbon electrodes, NASICON, solid electrolyte.

Introduction: Different carbon nanostructures, being rather new class of materials, demonstrate wide perspectives when used in various areas of power and chemical industry as well as in electronics. It is caused by variety of their chemical and physical properties together with possibility to influence on them by different types of treatment. For most of applications, especially energy storage, carbon nanomaterials must have ppm level of impurities and be compacted to maximal density. Nevertheless such properties as high specific surface area, electroconductivity, mesoporosity, heteroatoms content must be kept. For these purposes spark plasma sintering technique which is widely used in metallurgy and ceramic industry [1] might be an excellent solution. It also demonstrates high perspectives for NASICON-type ion conductors synthesis, that can be used in solid state batteries [2].

Experimental: The samples were synthesized by compactization of previously prepared pure materials using Labox-625 (Sinterland, Japan) apparatus at the temperature range of 900 -1800°C and holding time 5 - 15 min under the axial pressure of 10 - 50 MPa in a vacuum of 10^{-2} torr. The heating speed was 100 $^{o}C{\cdot}min^{-1}$. Graphite die set of 15 mm diameter was used for the experiments. High resolution transmission electron microscopy images were obtained using JEOL 2100 F/Cs (Jeol, Japan) operated at 200 kV and equipped with UHR pole tip as well as spherical aberration corrector (CEOS, Germany) and EEL spectrometer (Gatan, Germany). Specific surface area was determined by Autosorb-1C/QMS (Quantachrome Inc., USA) analyzer. The surface composition and binding type of atoms were determined using Axis Ultra DLD XPS spectrometer (Kratos

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Analytical, UK). Raman spectra were registered using LabRam HR800 UV (Horiba, Japan) spectrometer equipped with 5 mW argon laser (514.5 nm).

Results and discussions: It was shown, that being simple in practical realization, providing high vacuum level and inert gas filling during sintering, SPS technique allow to compact carbon materials up to 1.8 g/cm^3 density, remove any functional groups from surface of carbon nanotubes and nanoflakes, decrease of the amount of defects. Phase transitions between different carbon forms were detected during the sintering, that is reflected in Fig.1 summarized with literature data.

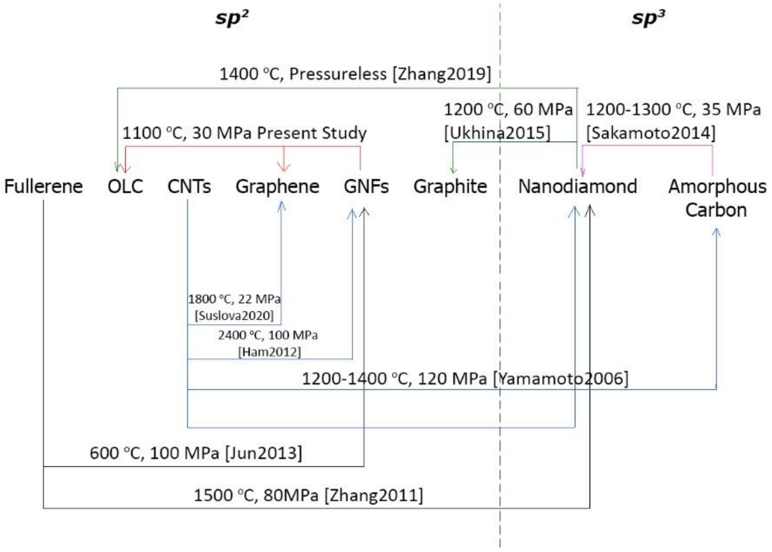

Fig. 1. Transformations of different nanocarbon structures under SPS condition.

As reference approaches the chemical compactization of carbon nanomaterials were utilized: synthesis on metal supports with its further removal, additional linking of nonconpensated bonds with divinylsulphone, hot pressing and implementation to polymer matrix. For NASICON type ion superconductors the optimal conditions to reach the density up to 90% from theoretical value with high level of conductivity can be achieved near the phase transition temperature.

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STABILITY AND SOFT INTERACTIONS OF NANOCARRIERS IN DRUG DELIVERY PROCESSES

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In recent years, a wide range of smart integrated nanosystems (including liposomes, polymeric and metal nanoparticles, silica and hybrid organic/inorganic nanostructures), have proven their effectiveness for various types of biomedical tasks [1-3]. More specifically, the study of the nanostructured drug delivery systems allows the development of novel platforms for the efficient transport and controlled release of drug molecules in the harsh microenvironment of diseased tissues of living systems, thus offering a wide range of functional nanostructures for application in biotechnology and nanomedicine [4-6]. The main aim of these delivery systems is to reduce the drug dose needed to achieve a specific therapeutic effect, thus lowering the costs and reducing the side effects associated with their use. On the one side, the *organic (soft) nanocarriers* (such as amphiphilic polymers and liposomes) present better properties to match the physicochemical condition encountered in biological (and pathological) tissues, thus furnishing the best examples of biocompatible nanostructures. On the other side, the *inorganic (hard) nanoparticles* (such as quantum dots and gold and mesoporous silica nanoparticles) propose the complementary functions for the diagnosis and detection of the pathological conditions within the diseased tissues [7, 8].

Although these nanomedicines show good performance against specific diseases, their inherent drawbacks, mainly connected with the limited absorption and request of frequent injection for patients, cannot be ignored. Furthermore, most of all nanocarriers' action is associated with a number of unwanted side effects that diminish their efficient use in biotechnology and nanomedicine applications. This highlights some critical issues in the design and engineering of nanocarrier systems for biotechnology applications, arising from the complex environment and multiform interactions established within the specific biological media [9-11]. One of the main difficulty to predict the behavior (and responses) of nanocarriers during the drug delivery processes is connected with the difficulty to fully describe (and model) the complex structural and dynamic processes involved in biological systems. Moreover, one of the major limitation in the use of such versatile and smart drug delivery systems is connected with their limited colloidal stability arising from the interaction with the complex environment and multiform interactions established within the specific biological media [12]. The complex microenvironment in living systems (and the special conditions within the diseased tissues) have a great impact on the functionality of nanomaterials and the

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delivery efficiency of nanocarrier systems, and may compromise their design goals. Therefore, a deeper knowledge and understanding of the real interactions involved in the diseased tissues is fundamental for the development of novel therapeutic approaches and protocols based on the employment of smart nanocarriers. In this respect, the choice of nanocarrier properties (such as the size, morphology, surface functionality), the mutual and cooperative interactions, as well as the initial spatial configuration (and environment conditions) play a crucial role in the design of efficient nanostructured materials and have a great impact on the evolution towards the desired functional products. The clear identification of these key factors for the design of efficient nanocarriers represents then the fundamental (initial) step to decipher the complexity involved in complex biological processes.

We discuss the main factors that influence the nanocarriers colloidal stability during their interaction with biological media during drug delivery applications. We also discuss some strategies that can be developed to overcome the biological barriers, and how these approaches have stimulated the development of advanced drug delivery systems.

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FUELS: FROM CHEMISTRY TO PHOTOREACTIVE SYSTEM ENGINEERING

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Abstract*: A chemical engineering approach to fully describe solar fuel production*

Key words: Solar fuels, artificial photosynthesis

Introduction: Considering the exhaustion of fossil resources and CO_2 emission rise due to their combustion, the use of solar renewable energy is an evidence to cope with a constant increase of human needs for energy. This resource being naturally fluctuating, it is necessary to convert it into storable energetic vectors. Among solar fuels, one of the first accessible is undoubtedly the H_2, whose production can be carried out in slurry photoreactors [1] making use of photocatalytic water splitting system [2] based on semiconductor or molecular catalytic systems (the combination of a photosensitizer with a suitable catalyst).

Modelling and Experimental:

We developed for both catalytic systems a multiscale and predictive model that comprises four levels: 1) Catalyst spectral optical properties determination which can be experimentally done or found in databases. 2) Calculation of spectral radiative properties (phase function, absorption and scattering coefficients) of the photocatalyst particle done by solving Maxwell's equations. 3) Resolution of the photon transport equation to determine luminance distribution over the entire system volume. 4) Formulation of thermokinetics coupling laws.

For the experimental part, the radiative properties are checked/determined thanks to transmittance measurement with an integrating sphere. The photocatalytic reaction for H_2 production (using semiconductor particles or molecular catalytic systems) is carried out in a lab-scale gas tight photoreactor [3] illuminated by a LED panel. H_2 production is indicated by the increase of the pressure in the headspace of the reactor measured with a pressure sensor and correlated with the H_2 production rate by a detailed mass balance on H_2.

Results and discussions:

In figure 1, for both systems, the variation of the mean volumetric rate of hydrogen production, $\langle \mathbf{r_{H_2}} \rangle$**,** is presented as a function of the incident photon flux density q. In the case of molecular catalytic system, the evolution is linear suggesting a linear coupling between photon absorption and reaction, this observation is in agreement with the thermokinetic coupling model established. On the contrary for the semiconductor system, the evolution is clearly nonlinear

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(closer to a square root evolution) due to recombination mechanisms inside the semiconductor.

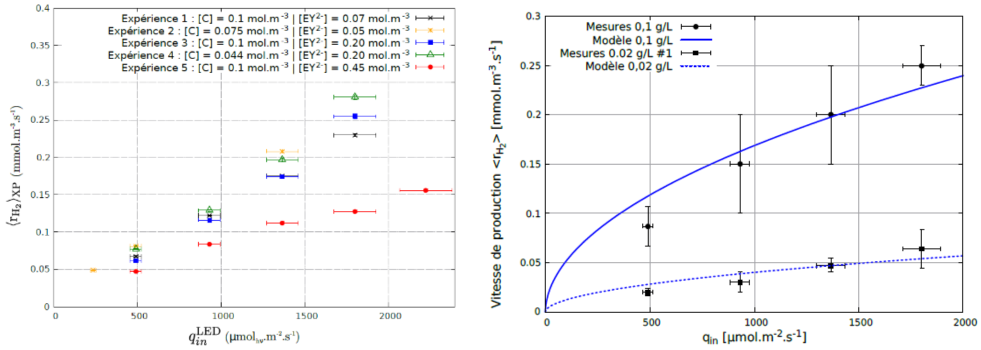

Fig. 1 Hydrogen mean volumetric rates as a function of incident photon flux density for molecular catalytic system (left) and semiconductor (right)

We also used our multiscale and predictive model to see if it is describing correctly the experimental tendencies, the agreement between model and experiment is rather good.

Conclusions: we described our method to thoroughly study photoreactive system to produce solar fuels, in order to conceive, implement, optimize a new demonstrator operating with solar light.

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BIOLOGICAL METHANATION: A CHALLENGE IN CHEMICAL ENGINEERING

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Abstract: *New process conditions and technological advances for biological methanation*

Key words: Biomethanation, Methanogenesis, H_2 mass transfer, bubble column bioreactor.

Introduction: Biological methanation (BioM) constitutes an attractive alternative to the catalytic pathway to convert CO_2 into CH_4 through hydrogenation within the framework of the Power-to-Gas strategy [1][2]. However, biological and technological issues are still to be solved for process scale-up and industrialization of *ex-situ* BioM. Here, these aspects are investigated, analyzed and discussed.

Experimental: *Hydrogen solubility:* A stainless steel magnetically-stirred cell (200 to 300 mL) where temperature, pressure, and rotation speed are controlled, and pH, ORP, dissolved H_2 are monitored under controlled gas flow rate (H_2+CO_2); *Bioreactors:* a PVC and a stainless steel bubble column (2 to 3 L) with an external loop for forced liquid recirculation, with additional outflow gas composition analysis (μ–GC) and outlet gas flow rate monitoring.

Results and discussions: A proof of concept of the counter-current bubble column technology was achieved; high interfacial area could be reached using an efficient porous sparger, due to the non-coalescing character of the inorganic culture medium (bubble size ~500 μm), with up to 80% conversion yield in CH_4 at 5 L/L/day in mixed cultures. Bubble columns can, therefore, compete with alternative technologies commonly found in the literature, such as stirred tanks [1–3]. The results depend, however, strongly on the preservation of the consortium and on pH which increases during the cultures. pH control through the renewal of the culture medium seems compulsory. Thus, a sustainable BioM process can be defined with a better societal acceptability than catalytic processes.

Conclusions: If an efficient bioreactor and a tailored gas sparger are required, pH control and maintenance of microbial consortium remain the key of the process.

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INTEGRATED PROCESS DESIGN

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Keywords: conceptual design; process simulation; optimization; plantwide control;

Chemical process design faces the challenge of sustainable technologies for manufacturing fuels, chemicals and various products by extended use of renewable raw materials. This implies a change in the education of designers, in the sense that their creativity should be boosted by adopting a systems approach, supported by systematic methods and computer simulation tools. Instead of developing a single presumably good flowsheet, modern process design activity generates and evaluates several alternatives corresponding to various design decisions and constraints. Then, the most suitable alternative is refined and optimized with respect to high efficiency of materials and energy, ecologic performance and operability.

This presentation promotes an integrated approach to conceptual design of chemical processes, illustrated by several case studies worked out by computer simulation. Typically, more than 80% of the total investment costs of chemical plants are determined at the conceptual design stage, although this activity involves only 2 – 3% of the engineering costs and a reduced number of engineers. In addition, a preliminary design allows critical aspects in research and development and/or in searching subcontractors to be highlighted, well ahead of starting the actual plant design project.

The design activity starts by analyzing the fundamental knowledge about chemistry, thermodynamics and reaction kinetics. Environmental problems are highlighted by examining the detailed chemistry. On this basis, the process synthesis is performed. The result is a set of process alternatives from which the most suitable is selected for refinement, energy integration, optimization and plantwide control. Computer simulation is intensively used for data analysis, supporting design decisions, investigating the feasibility, sizing the equipment, and finally for studying process dynamics and control issues.

The case studies illustrating the approach include dimethyl carbonate synthesis, biobutanol separation from the ABE fermentation mixture, acrylic acid production from glycerol, methyl amines production.

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BOOK OF ABSTRACTS

SICHEM – 2020

A – Chemical and biochemical engineering (CBE)

1. Keynotes

International Chemical Engineering and Material Symposium, SICHEM 2020, 17-18 September 2020, ISSN 2537-2254

FERMENTATION BIO COMBUSTIBLES

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Abstract*: The paper begins with a brief presentation of society energy needs, concluding that today's biofuels are promoted by global environmental requirements to the degradation of which all five industrial revolutions of our development have contributed. From fermentation biofuels the emphasis is on anaerobic fermentation biofuels namely biobuthanol, bioethanol and biogas. A short list of legislation in the field of biofuels is presented and commented. For each of these three biofuels, the most interesting data are brought regarding the technological and even social problems that the large-scale transition of their production implies.*

Key words: Solar energy, Subduction oil, Theory and modelling, Biobuthanol, Bioethanol, Biogas

Introduction: In the creation of the world, solar energy was given to be enough, even if it was not and is not evenly distributed. And because we did not know and still don’t know how to collect it, how to store it and then how to distribute it, it was necessary for Prometheus to set us on fire. And so we began to learn to burn wood, always biofuel to supplement our energy needs. With Prometheus legend and adding that the creator put in the man head, as fundamentals, the risk, minimization for his satisfaction, whenever he came, he took us where we are today with the problem of energy [1]. So, today in the post-industrial phase of the fourth industrial revolution, the energy problem seeks answers to two questions: i) what is to be done because photosynthesis can no longer consume the carbon dioxide generated by the production of energy from fossil fuels, which makes the effect more pronounced in the evening; ii) how to satisfy the energy demand of a population that is growing exponentially? It has been found that the focus on energy bioresources is a big part of the answer to the two questions. Fermentation fuels represent a part of the big response which is waited from the scientists from all over the world.

Experimental: The experimental part of the paper is based on literature data and on our processing data procedures. In this sense we enumerate the statistical models developed using literature data.

Results and discussions: An example of the results, that we attach, to what we describe briefly refers to the influence of the composition of the fermentation medium on the final solvents content in glucose fermentation to biobuthanol, with *Clostridium Acetobutilicum* [2].

Thus, in relation to a basic state regarding the starting composition of fermentation, given in Table 1, we found that the concentration of the product in acetone, buthanol and ethanol solvents depends on 4 factors: glucose concentration (x_1), butyric acid concentration (x_2), mass ratio C / N (x_3) and temperature (x_4).

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With data collected from the literature, organized in a second order orthogonal experimental plan (x_1, x_2, x_3, x_4 being dimensionless process factors) we have obtained interesting results. Here are two graphical representations and the relation (1) that shows a special result: the ratio between the concentration of butanol and that of acetone, for the considered conditions in the experimental plan, is between 3.1 and 4.5, with the linear connection by temperature.

Tabel 1. Standard composition of fermentation medium in ABE synthesis

	Compounds name	**u.m**	**Value**
1	Inoculum *Clostridium*	mL/L	75
2	Glucose	g/L	50
3	Butyric Acid	g/L	5
4	Ammonium acetate	g/L	2
5	Tryptone	g/L	5
6	Yeast extract	g/L	2
7	$MnSO_47H_2O$	g/L	0.3
8	$FeSO_47H20$	g/L	0.001

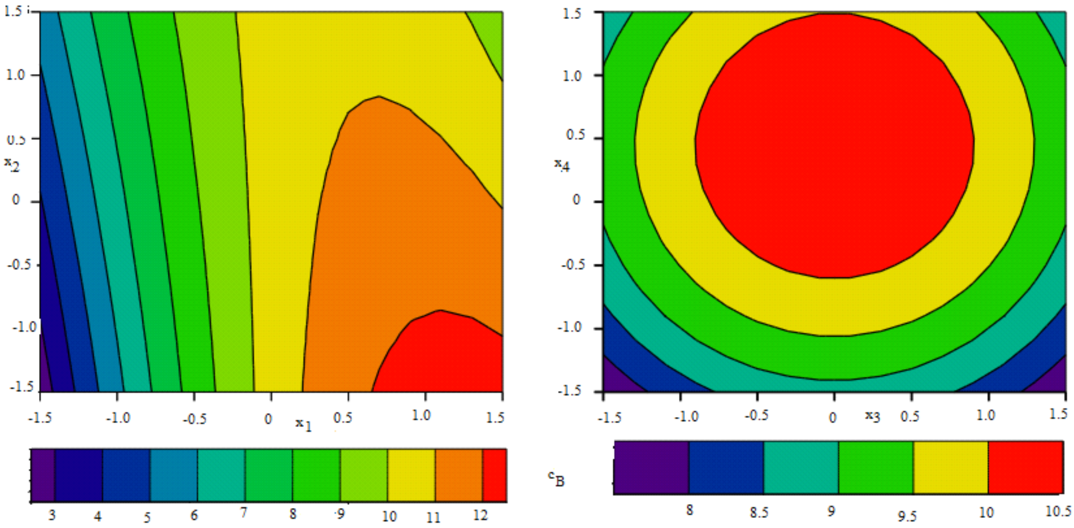

Figura 1. Influence of dimensionless factors on butanol content in ABE fermentation (left x3 = x4 = 0, right x1 = x2 = 0)

$$r_{BA} = \frac{c_B(x_1,x_2,x_3,x_4)}{c_A(x_1,x_2,x_3,x_4)} = 3.815 + 0.77x_3$$

In the case of ethanol obtaining starting from corn flour (bioethanol of generation 1) we bring to attention an orderly development of calculation and modelling.

Regarding biogas, the third fermentation biofuel, we present elements of interest, an example in this sense being the observations regarding the specific microorganisms for this process.

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BOOK OF ABSTRACTS

SICHEM – 2018

A – Chemical and biochemical engineering (CBE)

2. Oral presentations

International Chemical Engineering and Material Symposium, SICHEM 2020, 17-18 September 2020, ISSN 2537-2254

SORPTION PROCESS IN THE STATIC AND DYNAMIC SYSTEM WHEN RETAINING PETROLEUM PRODUCTS ON WOOL FIBERS

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Abstract: *Romanian Merino wool was tested as a biosorbent for removal petroleum products from either sea water or distilled water. The wool was packed into different nets and then placed on the surface of the oily water.*

Key words: wool fiber; static system; dynamic system; adsorption capacity; mathematical model

Introduction: For the development of large-scale processes, kinetic investigations are required. The 1st and 2nd order pseudo-kinetic models describe most of the dynamics of the adsorption microprocesses of petroleum pollutants, on different adsorbent materials. With respect to this, the merino wool from Romania was packed in different nets with a supporting role and then placed on the surface of the water polluted with petroleum products (Rebco oil and mixture of 50% gasoline - 50% diesel), the purpose being to choose the more suitable support [1].

Experimental and/or Modelling:

Experimental set-up in static sistem: crystallizer, Rebco Crude Oil, water layer (SW or DW), merino wool fiber sample (three nets N_1, N_2, N_3), system for sample weighing, electronic balance, computer, monitor, data acquisition system; The effects of the process factors were evaluated, the net mesh density (1.45, 3.07 and 42.5 mesh/cm^2), the concentration of water soluble salts (0 and 17 g/L) and the initial mass of the wool (10, 20, 30, 40, 50 g) on the kinetics of the sorption process and on the sorption capacity of the wool at equilibrium (2.12- 11.89 g/g).; *Experimental set-up in dynamic system*: crystallizer, GFL-3015 shaker with orbital shaking, merino wool fiber sample (two nets N_4, N_5) several initial densities of natural merino wool. It was tracked the effect of the initial concentration of crude oil in liquid phase and the effect of the diameter of the support. Experimental data were processed using kinetic and statistical models.

Results and discussions: The kinetic modeling of the suction process of the Rebco crude oil (persistent petroleum product) was presented by the merino wool adsorbent from Romania through two models: the pseudo-first kinetic model and the pseudo-two kinetic model. The Lagergren models were compared with the experimental data obtained at the oil sorption. The agreement between the

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experimental data and the values predicted by the model was expressed by means of correlation coefficients. A very good correlation of the experimental data was obtained: for the first three supports (R2> 0.998), and for support 4 and 5 (0,9845≤R2≤0,9995). Moreover, a good match was observed between the experimental and predicted values of the wool suction capacity at equilibrium (errors percentage less than 5.15%). The regression equations based on a factorial model 2^3 were established between the kinetic parameters of the model (the sorption rate constant and the sorption capacity at equilibrium) and the dimensional process factors [2, 3, 4].

Conclusions: The pseudo-two kinetic model, assuming that the nature of the adsorption is the chemosorption, offered a better correlation of the experimental results for all 5 supports tested.

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MIXING HYDRODYNAMICS IN AN ANAEROBIC DIGESTER

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Abstract: *Investigation of mixing hydrodynamics in a multi-stage anaerobic digester*
Key words: Multi-stage digester, Mixing, Particle image velocimetry, Multi-phase flow

Introduction: Anaerobic digester (AD) is an unit operation used to convert organic containing wastes into clean and sustainable biogas. Mechanical stirring is the most efficient mixing method for AD; however, stagnant or dead zones can occur, which was reported up to 77% of volume at active mixing [1]. Here, the features of mixed flow in AD comprising a complex multiphase system are investigated.

Experimental and/or Modelling: *Particle image velocimetry:* several non-Newtonian fluids (such as xanthan XG, or polyacrylamide PAM solutions) in a lab-scale digester have been studied and the velocity field measured; *Bubble mixing*: tracking and estimation of bubble size in these fluids under different rotation speed have been performed. *Numerical Simulation:* mixing of non-Newtonian fluid flow in AD using different turbulence models has been simulated using CFD.

Results and discussions: Figures 1a, 1b illustrate the contours of velocity and flow pattern for xanthan gum solutions at different concentrations, 0.2% and 0.1%, in multi-stage stirred tank. As the concentration increases, the active area of mixing gets smaller and as flow patterns show, the mixed region becomes limited. In figure 2, the distribution of bubbles in non-Newtonian media PAM 0.03% at 120 rpm was measured and presented when the gas bubble rate was adjusted as 5 L/h, representative of biogas production. At least 500 bubbles were considered to obtain the distribution curve. The results showed finally, that, bubbles did not significantly affect the liquid flow field due to the low gas holdup. The numerical simulations from CFD were compared with PIV data. For PAM fluids at different concentrations, the CFD results presented a good agreement with measured velocities.

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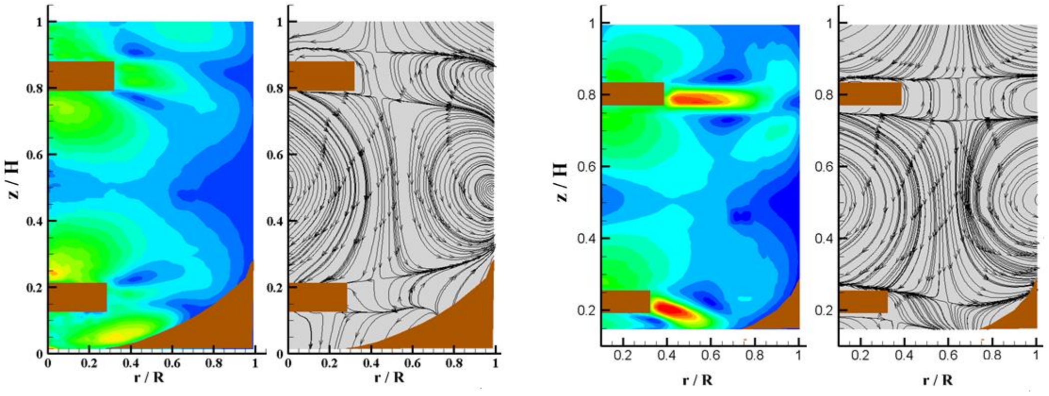

(a) (b)

Fig. 1 Contours of velocity and streamlines in mixing tank at speed 120 rpm for different xanthan gum solutions: (a) XG 0.2% (b) XG 0.1%

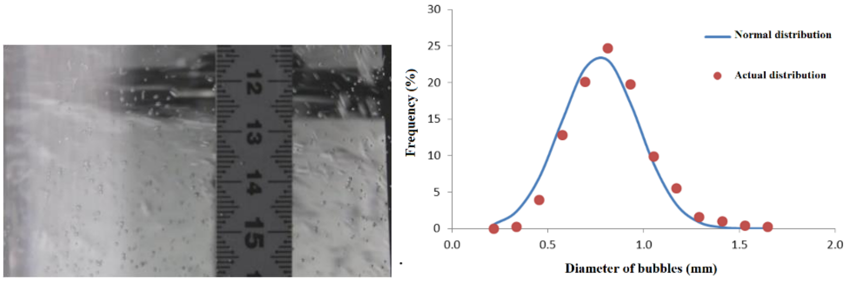

Fig. 2 Example of a bubble size distribution curve for PAM 0.03% at 120 rpm with gas flow rate 5 L/h

Conclusions:

The non-Newtonian character of the fluid strongly affects mixing and the bubble size distribution in AD conditions, but in such situations, the influence of the gas phase remains negligible and CFD is able to simulate experimental data.

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ENERGY SAVING IN A CRUDE DISTILLATION SYSTEM BY USING PREFLASH COLUMN – A CASE STUDY

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Abstract*:* *Reduce energy consumption of Crude Unit by Preflash unit implementation*

Key words: Process modelling, energy consumption, Preflash Column

Introduction: Crude distillation unit is an energy intensive process. A crude distillation system usually comprises a desalter unit, a preheat train and an atmospheric distillation column. The implementation of a Preflash column in a crude distillation system creates opportunities to reduce the demand for fired heater [1]. This paper presents a comparison between the energy consumption in the crude fired heater based on two different configurations of the Crude distillation unit, with and without a Preflash column. The process simulation model was developed based on real plant data.

Modelling: The simulation framework comprises the installation of a Preflash column at the end of the pre-heat train before the distillation column furnace. The crude fired heater is the bottleneck of the unit and by using a Preflash column it is possible to lower its energy consumption. A case study demonstrates the capabilities of the approach and illustrates that implementing Preflash units can reduce energy demand.

Results and discussions: In Table 1 an energy consumption and cost of operation comparison between the two processes configurations is made. Based on the simulation results it was found that the main advantage of the implementation of a Preflash column is the furnace duty reduction from 226.8 MMkJ/h to 199.8 MMkJ/h.

Table 1 Comparison between Crude Distillation system configurations

	Crude unit with Preflash column	Crude unit without Preflash column
Furnace Duty	199.8 MMkJ/h	226.8 MMkJ/h
Energy consumption	250.4 MMkJ/h	278.5 MMkJ/h
Operating costs	7.4 MM$/y	8.5 MM$/y

Conclusions: Considering the simulations results for both cases, the Preflash column implementation in the Crude Distillation system configuration associated

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with the furnace load reduction, is a good solution to reach semnificative savings in the energy demands and operating costs. The required capital investment for the Preflash column system is $1.6 million with a payback time of 1.45 years.

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COMPARATIVE LIFE CYCLE IMPACT ASSESSMENT BETWEEN THE PRODUCTION OF ZINC FROM CONVENTIONAL CONCENTRATES VERSUS WAELZ OXIDES OBTAINED FROM SLAGS

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Abstract*:* *Life Cycle Impact assessment between two different methods of producing zinc metal.*

Key words: Zinc; Life Cycle Assessment; Zinc concentrate; Zinc oxides; Waelz oxides; ISP Slag

Introduction:

The importance of zinc in today's life cannot be understated, being used in technology, architecture and even medicine for its durability, aesthetic and medicinal properties to greater degree each year. The purpose of the study is to compare two Life Cycle Impact Assessments: one of the conventional zinc production from concentrates (sulfide ores), the other using zinc oxides obtained through the Waelz process using existing slags as raw material.

Methodology:

The systems under study are considered "cradle-to-gate", meaning that each step starting with the extraction of raw materials is considered, but the system stops at the factory gate after the production of zinc metal. Using state-of-the-art consequential life cycle assessment methods together with recommendations for applying LCA in the metal and mining industry [1][2], the models were built in SimaPro 8 software using background data from the ecoinvent 3 database and compared using 7 impact assessment categories: 1) Climate Change; 2) Ozone Depletion; 3) Photochemical Ozone Formation; 4) Acidification; 5) Terrestrial Eutrophication; 6) Freshwater Eutrophication; 7) Marine Eutrophication. The comparison results were then calculated, extracted and interpreted further.

Results and discussions:

In figure 1 the results of the comparison can be seen for each of the selected impact categories, aggregated together to show the total impact score. This assessment uses the Single Score point system developed within the ILCD 2011 Midpoint+ calculation method [2].

It can be immediately noticed, that using Waelz oxides from existing waste slags a much smaller overall impact on the environment is obtained, than using conventional concentrates. This points out that it is the recommended choice when

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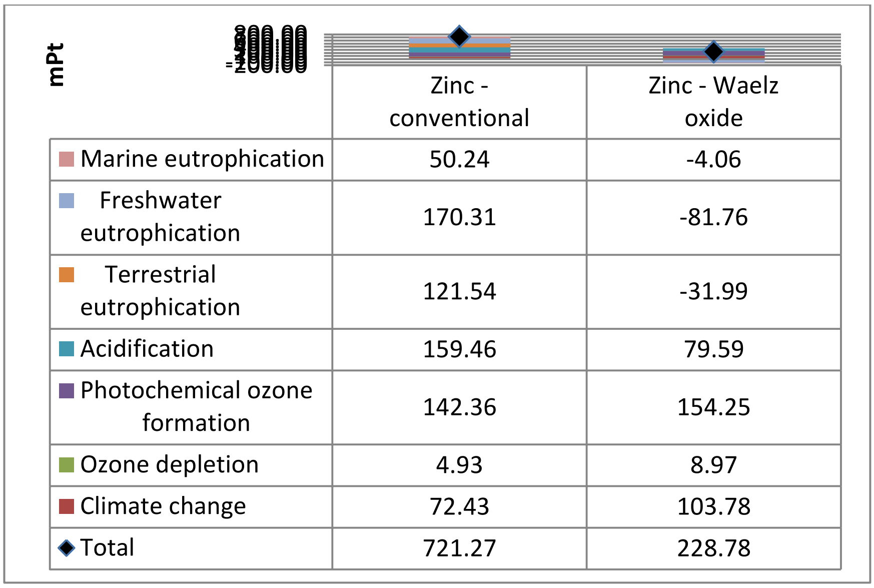
available. One can observe that the impacts on Climate Change, Ozone Depletion and Photochemical Ozone Formation are slightly higher when producing zinc using Waelz oxides due to the increased use of Coke in the production process, in all stages of production (Waelz kiln, Sintering and Smelting). However, looking upon the remaining categories, it can be noticed that not only the impact is lower, but negative in the case of Eutrophication – meaning that by using Waelz oxides, and thus avoiding the extraction and concentration of new conventional ores as per consequential life cycle thinking, the environment actually benefits and gains a respite.



	Zinc - conventional	Zinc - Waelz oxide
Marine eutrophication	50.24	-4.06
Freshwater eutrophication	170.31	-81.76
Terrestrial eutrophication	121.54	-31.99
Acidification	159.46	79.59
Photochemical ozone formation	142.36	154.25
Ozone depletion	4.93	8.97
Climate change	72.43	103.78
◆ Total	721.27	228.78

Fig. 1 Results of comparison, single score

Conclusions:

To sum up, it can be easily observed that the use of zinc oxides obtained through the Waelz processing of existing slags brings a great benefit to the environment, compared to the conventional method, and it should be an encouraged method of zinc production whenever slags are available.

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EFFECT OF FREQUENCY CHANGE IN THE HORIZONTAL MOVEMENT OF THE COLLECTOR ELECTRODE IN ELECTROSPINNING

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Abstract*: Effect of frequency change in the horizontal movement of the collector electrode in electrospinning*

Key words: Moving electrode, electrospinning

Introduction: Electrospinning is one of the fantastic ways to fabricate nanofibers. Changing one or more of the parameters that make up the electrospinning setup allows obtaining fibers with very different morphologies. Different results have been obtained by changing the factors such as voltage difference, flow rate, electrode type etc. In this study, the effect of periodically changing the electrode distance and the displacement speed of the electrode, which has not been studied in the literature before, was carried out.

Experimental and/or Modelling: The experimental setup was built on the Scotch-yoke mechanism. A grounded flat conductor plate, driven by a dc motor whose speed was adjusted by a separate voltage source, was moved horizontally back and forth. The plate size was 5cm x 5cm and covered with aluminum foil. PLA dissolved in chloroform was spun at a rate of 0.1 ml / h with a fixed electrode distance of 12 cm, 15 kV and a 3 cm stroke length. Changes in fiber diameters and distribution were determined with static, 15 Hz and 35 and 50 Hz systems.

Results and discussion : Similar results have been obtained in the literature by amplifying the alternating current at 50-60Hz. [1] Voltage fluctuates sinusoidally with time around zero volt due to the sequential movements of positive and negative charges in the system as in standard AC systems, which results in non-homogenous fiber diameters. However, changing the (tip-target) electrode distance in situ: (i) increases the fiber initiation by disturbing the Taylor cone at the tip of the nozzle, (ii) affects the evaporation time during the flight and the diameter thinning of the fiber, (iii) results in homogenous fiber diameter distribution compared to conventional AC amplification techniques.

Conclusions: As the system speed increased, fiber diameters decreased.

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IMPROVING THE EFFICIENCY OF THE SUPERCRITICAL CO_2 EXTRACTION PROCESS OF *CANNABIS SATIVA L.* SEED OIL

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Abstract

Hemp (Cannabis sativa L.) is a multifunctional plant from which many products such as oil, protein and fiber can be obtained. Hemp seeds have a high content of bioactive compounds such as omega-6 and 3 polyunsaturated fatty acids as linoleic acid (18:2) and linolenic acid (18:3), γ-tocopherol and β-carotene. This composition leads to a significant antioxidant activity of the hemp seed oil and gives it the possibility of being used in pharmaceuticals and food. The hemp seed oil content varies between 28-35% depending on some factors as variety, climatic conditions, geographical region, extraction method and process parameters [1].

The most commonly used methods of isolating hemp seed oil are cold pressing, Soxhlet extraction and supercritical CO_2 extraction. Among these methods, the supercritical technique sums up the advantages of the other two methods in terms of yield, extract quality, toxicity and avoiding thermos labile compounds degradation. The main parameters that influence the extraction of hemp seed oil are fluid flow and extraction temperature, pressure, and time. Simulation and process optimization based on mathematical models are crucial steps to simplify and understand the key process variables and their effect. As number of process variables may affect the extraction yield, it is preferable to apply statistical optimization techniques [2].

Based on this theory, the aim of this study is to improve the efficiency of the supercritical CO_2 extraction process of hemp seeds oil by setting up optimal operation conditions using 2^3 factorial design. This factorial design requires three factors, and each at two levels and needs only 8 supercritical extraction experiments. For this analysis, chosen factors are extraction pressure (X_1) of 350 and 400 bar, extraction temperature (X_2) of 53 and 63°C and supercritical CO_2 flow (X_3) of 11 and 13 kg/h. Further, based on the obtained experimental data, a statistical analysis of the process is made using ANOVA analysis and extraction yield is predicted using a polynomial regression model. Statistical parameters are followed, the influence of the factors on the response is analyzed by surface plots

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and optimal conditions are evaluated in terms of total desirability of all the three factors that affects the response.

Acknowledgement: The authors are grateful for financial support of POC project ID P_37_449.

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MODELING OF SOME CASES OF METAL PICKLING

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Abstract*:* *Mathematical models for metal pickling by immersion and by spraying techniques*

Keywords: metal pickling, mass transfer, modelling processes, convective boundary layer

Introduction: The aeronautic and automobile industry, and not only, uses various alloys of stainless steel, or titanium to manufacture various components for assembly theirs specific machines. Also the picking of steel is one basic process in steel factories. The component of machines must be pickled before their surface conditioning or treatment. In this sense it uses the chemical attack of component surface by components immersion or spraying with various pickling solutions. The commonly used pickling solution are aqueous mixtures containing HNO_3 (3 to 6 M) and HF (0.5 to 2 M), which could also be used to pick other non metals such as silicon [1]. In steel factory the pickling solution are formed with hydrochloric acid. The rate of the pickling and the state of the surface of the alloys after treatment are strongly conditioned by the pickling solution composition, by pickling temperature and by picking flow around the processed components. The aim of this paper is to propose models for rate of pickling for the bath picking procedures.

Basic Models. For pickling by immersion the basic phenomena occurs inside of natural convection boundary layer formed on the surface of metallic piece.

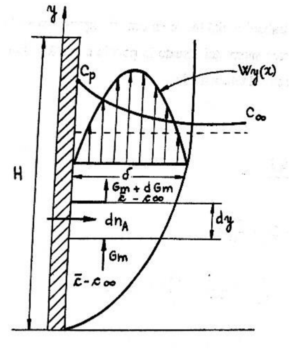

Figure 1. Schema for pickiling by imersion

Here the simultaneous solving of flow equation and species diffusion equation obtains that the local values of mass transfer coefficient depend on the local thickness of boundary layer. For flow in natural convection, driven by concentration difference c_p-c_∞ (fig1), the local thickness of boundary layer is given by relation (1). Immediately it obtains the mean values of mass transfer coefficient and the Sherwood number (2).

$$\delta(y) = 2.7\left(\frac{\nu\, D\, y}{g\,\beta_c(c_p - c_\infty)}\right)^{0.25} \quad (1) \qquad Sh = 0.99(Gr_H Sc)^{0.25} \quad (2)$$

For the case of pickling by spraying the simultaneous solving flow equation and species diffusion equation it obtains that the concentration field of pickled species follows a dependence after complementary function of errors. In these conditions the expression for Sherwood number is given with relation (3). It depends on

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Reynolds, Schmidt and modified Froude number.

$$Sh_H = 0.358\, Re_H^{0.33} Sc^{0.15} Fr_H^{0.15} \qquad (3)$$

Experimental: The experimental investigation of copper pickling using ammonium persulphate solutions was developed in natural convection. An experimental plan 2^3, where the process factors are temperature, ammonium persulphate concentration and respectively sulphuric acid concentration in the pickling solution was selected for the best data collection. Copper samples with 10 cm length (H= 0.1 m) and 2 cm width, was immersed, with vertical position, for a determined time, in 1.5 l of pickling solution. The pickling flux was computed, from experimental data, with relation (4) where m_τ - $m_{\tau+\Delta\tau}$ represents the mass of copper disolved during time period $\Delta\tau$.

$$N_{Cu,ex} = \frac{m_\tau - m_{\tau+\Delta\tau}}{S\Delta\tau} \qquad (4)$$

For pickling in spraying procedure, experimental part will be presented with the extended paper

Results and discussion: The pickling flux expressed with mass transfer coefficient from relation (3) is given by relation (5), where diffusion coefficient (D) and kinematic viscosity (ν) depend on pickling solution composition and temperature.

$$N_{Cu} = 0.99 \frac{D}{H} \left(\frac{g\beta_c (c_p - c_\infty) H^3}{\nu D} \right)^{0.25} (c_p - c_\infty) \qquad (5)$$

Experimental and model computed values for pickling flux are in table 1 (C6,C9)

Table 1. Experimental and model computed values of copper pickling flux

Nc	t ^{0}C	$c_{aps\ g/l}$	$c_{as\ g/l}$	$N_{Cu,ex}$	ν m^2/s	D m^2/s	N_{Cu}
1	40	150	15	2.075 10^{-4}	6.79 10^{-7}	5.34 10^{-10}	2.282 10^{-4}
2	40	150	7.5	1.813 10^{-4}	6.69 10^{-7}	5.45 10^{-10}	2.192 10^{-4}
3	40	75	15	1.296 10^{-4}	6.61 10^{-7}	5.67 10^{-10}	1.125 10^{-4}
4	40	75	7.5	1.031 10^{-4}	6.59 10^{-7}	5.71 10^{-10}	1.028 10^{-4}
5	20	150	15	8.85210^{-5}	1.13 10^{-6}	3.11 10^{-10}	1.338 10^{-4}
6	20	150	7.5	8.189 10^{-5}	1.11 10^{-6}	3.17 10^{-10}	1.286 10^{-4}
7	20	75	15	4.938 10^{-5}	1.08 10^{-6}	3.22 10^{-10}	6.515 10^{-5}
8	20	75	7.5	4.988 10^{-5}	1.04 10^{-6}	3.29 10^{-10}	5.973 10^{-5}
9	30	112	11.2	7.737 10^{-5}	8.07 10^{-7}	4.45 10^{-10}	1.326 10^{-4}
10	30	112	11.2	7.367 10^{-5}	8.07 10^{-7}	4.45 10^{-10}	1.326 10^{-4}
11	30	112	11.2	8.853 10^{-5}	8.07 10^{-7}	4.45 10^{-10}	1.326 10^{-4}

The comparison between the experimental values and those according to the model (column 6 and column 9 of the table1) shows that the model has an answer that finds the experiment well.

Conclusion: Referring to pickling flux of copper in persulphate solution, a good concordance between experiment and model was shown.

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BOOK OF ABSTRACTS

SICHEM – 2020

A – Chemical and biochemical engineering (CBE)

3. Poster presentations

EXPERIMENTAL AND NUMERICAL INVESTIGATION OF THE MIXING QUALITY IN BIOREACTORS CONTAINING NEWTONIAN AND NON-NEWTONIAN FLUIDS

Amaury Danican[1], Benoît Chezeau[1,2], Faten Dahak[1,2], Alina Violeta Ursu[1], Jean-Pierre Fontaine[1,*], Christophe Vial[1]

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Abstract*:* *Study of the difference in mixing quality between Newtonian and non-Newtonian fluids under the operating conditions of dark fermentation.*
Key words: Dark fermentation, Hydrogen, Mixing time, Non-Newtonian

Introduction: This study is part of the development of renewable energies, in order to decrease the use of fossil fuels. The final goal is the optimisation of 2nd generation biohydrogen by conversion of biomass (like agro-industrial waste, wastewater, etc.) thanks to a bacterial consortium through the “dark fermentation” process. The purpose of this work is to compare the mixing quality between Newtonian [1] [2] and non-Newtonian media with a shear-thinning behavior.

Experimental and Modelling: The initial study focuses on measuring mixing times as a function of digestate rheology and stirring speed. The experimental methods used are the chemical acid-base decolorization (Fig. 1,a) and PLIF (*Planar Laser-Induced Fluorescence*) (Fig. 1,b). In parallel, a numerical model was simulated with the *Phoenics*® software in order to determine the local structure of the flow (Fig. 1,c).

Results and discussions: The results on the mixing times are compared for the Newtonian [2] and non-Newtonian fluids using a model based on a variant of the mixing Fourier number. It shows that the difference in mixing quality between the two types of fluids is small in the main part of the tank. The difference lies in the areas of low shear, which are located around the walls and between the two turbines used for agitation. Close to the walls, the homogenization is not very good for Reynolds numbers below 440, and between impeller for Reynolds numbers below 200. These limitations are absent for Newtonian fluids.

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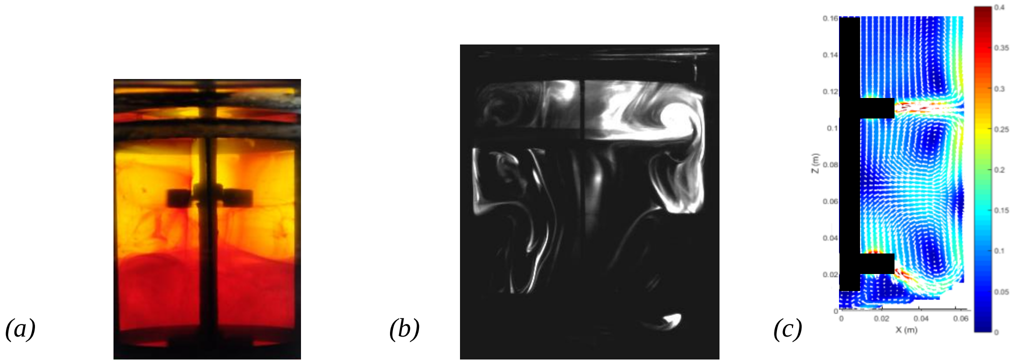

Fig. 1 Mixing time measurements by *(a)* chemical decolorization and *(b)* PLIF for non-Newtonian fluids; *(c)* Comparison with the local flow obtained by numerical simulation.

Conclusions: For non-Newtonian fluids, low shear stress around the walls and between turbines induces higher viscosities. This leads to low mixing quality in these regions for small Reynolds numbers, compared to Newtonian fluids.

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IMPACT OF TURBULENCE ON BIOHYDROGEN PRODUCTION UNDER "DARK FERMENTATION" OPERATING CONDITIONS

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Abstract*:* *Analysis of the impact of turbulence on microorganisms aggregates and bioH$_2$ production by dark fermentation*.

Key words: Hydrogen, Dark fermentation, Turbulence, Microorganisms

Introduction: The development of renewable energies production is now a major stake to reduce the use of fossil resources and the pollution resulting. One of the future solutions is the 2nd generation biohydrogen obtained by conversion of biomass (like agro-industrial waste, wastewater, etc.) thanks to a bacterial consortium through the "dark fermentation" process. For now, it needs to be optimized by the study of the flow in the reactor. The purpose of this work is to characterize the impact of turbulence on microorganisms (mainly *Clostridium butyricum*) during the mixing operation [1].

Experimental and Modelling: Firstly, the dark fermentation process was carried out in a laboratory-scale reactor. H_2 production was studied for different mixing conditions, represented by different Reynolds numbers [1]. Compared to the previous work, additional information are obtained thanks to samples of microorganisms, taken from the fermentation medium in order to perform microscopic observations of colony shape and size measurements of the bacterial aggregates. Secondly, a numerical model was studied with the *Phoenics®* software in order to apprehend local flow and global turbulence impact [2].

Results and discussions: The results of the biohydrogen production show a decrease in the H_2 yield with the Reynolds number in turbulent regime. This could be explained by the negative impact of turbulence on bacterial aggregates, especially during the growing phase of the colony. Microscopic observations (Fig. 1,a) and size measurements indicate that the order of magnitude of the microorganisms aggregates size is between 30 μm and 200 μm. Thanks to the CFD model, it is possible to estimate the size of the smallest eddies created by local turbulence using the Kolmogorov length scale (Fig. 1,b). The decrease in hydrogen production corresponds to the moment when the eddies become smaller than the aggregates (Fig 1,c). The developed model gives information about the regions of the reactor where high stress prevails locally on the aggregates.

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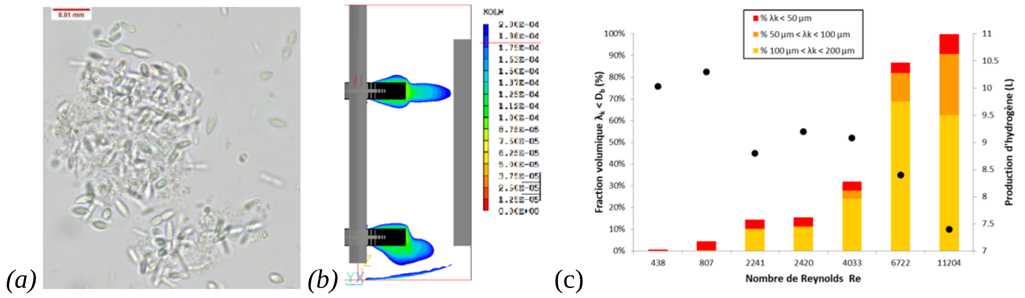

Fig. 1 *(a)* Microscopic picture of a bacterial aggregate ; *(b)* high stress local area for the aggregates using the Kolmogorov length scale thanks to numerical simulation ; *(c)* H_2 production and volume fraction of Kolmogorov length scale smaller than bacterial aggregates size plotted against Reynolds number

Conclusions: Turbulence can destroy the bacterial aggregates at high Reynolds numbers. This limits the syntrophic effects, and as a result reduces the process efficiency for H_2 production.

References:

[1] Chezeau B., Vial C. (2018). Combined effects of digestate viscosity and agitation conditions on the fermentative biohydrogen production, Biochemical Engineering Journal, 142, 105−116.

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EFFICIENCY OF MIXED PHYSICAL AND ELECTROCHEMICAL TREATMENTS ON LIQUID EFFLUENTS FROM AN ANAEROBIC DIGESTER

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Abstract*: New trends in treatment of liquid effluents from anaerobic digester*

Key words: Electrocoagulation, anaerobic digestion, liquid digestate, wastewater treatment

Introduction: Electrocoagulation (EC) is a compact, robust and eco-friendly treatment process that uses the electrical current to coagulate/flocculate contaminants from liquid effluents as wastewaters [1]. The coagulant are active metal cations produced in situ by electrolytic oxidation of a sacrificial anode. This study deals with the removal efficiency (RE) of pollutants in liquid effluents from an anaerobic digester using Fe and Al electrodes.

Experimental: The EC reactor (1 L, glass) was constituted by one pair of plate electrodes (aluminum, iron or combination between the two materials) positioned between 1.0 to 2.2 cm apart from each other; electrodes were installed vertically in the electrolysis cell. Each run was conducted in 0.4 L of liquid effluent and the sludge formed during EC treatment was eliminated by centrifugation (*10,000g*, 10 min.). This work deals with the effect of several EC operating parameters (inter-electrode distance, electrode combination, current density) combined or not with a pretreatment step (filtration on nylon filter cloth) on chemical oxygen demand (COD), total nitrogen (TN) and other physico-chemical properties (total carbon (TC), dry weight (DW), nitrate and phosphate contents, etc.) of the treated liquid effluent

Results and discussions: Analysis of several batches of liquid effluent show a dependency on the chemical composition of the digester feed. Thereby, COD (g.L^{-1}), TC (g.L^{-1}), TN (g.L^{-1}), and DW (%) of initial effluent are between 28.5 and 36.5, 13.3 and 21.1, 3.8 and 6.4, and finally between 2.8% and 7.5%, respectively. Low NO_3^- and PO_4^{3-} contents are detected in each sample (<10 ppm). Solid separation by cascade filtration pretreatment, CF (from 500 to 100 µm), allows decreasing up to 26.2% for DCO, 36.5% for TC, 60.0% for DW, and up to 23.4% for TN. EC without CF provides better results than CF, but the maximum RE is obtained when both methods are combined: 52.5% for DCO,

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58.3% for TC, 76.0% for DW and 64.1% for TN. Using Al electrodes generates an increase in the electrical resistance and the temperature, making the process more difficult. This phenomenon can be minimized when Fe electrodes are used.

Conclusions: Two-step cascade filtration followed by EC with iron plate electrodes induce a RE of DCO, TC, DW, TN greater than 50%.

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MICROBIAL RENNIN SYNTHESIS USING DIFFERENT CARBON SOURCES

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Abstract: *The aim of this work was to study the effect of carbon sources in submerged fermentation and surface solid state-fermentation on rennin production by Rhizomucor miehei (NRRL 3420).*

Key words: microbial rennin, mold, whey, wheat bran, coagulation efficiency

Introduction: Many microorganisms are known as producers of rennet such as proteinases, which can substitute for the calf rennet. The aspartyl protease from *Rhizomucor miehei* is commonly used as a chymosin substitute in cheese making. This enzyme has a high ratio of MCA/PA (milk clotting activity / proteolytic activity) which is an important requirement to substitute calf rennet [1]

Experimental: The carbon sources: whey for liquid submerged fermentation (LSF) and whey bran for solid-state fermentation (SSF). Other reagents used, such as corn starch, glucose and casein were purchased from Sigma-Aldrich. *Fermentation:* at 35°C and spore solution inoculum - (10^6 spores/mL); *Enzyme separation:* by filtration and centrifugal methods*; Enzyme activity* MCA was determined according to Arima [1] and expressed in Soxhlet units (SU).

Results and discussions:

In LSF the separation of the enzyme from the fermentation medium requires a more laborious separation sequence, with successive stages of filtration and centrifugation, in order to obtain a clear solution, free of other organic residues found in whey. In SSF, the separation of the enzyme from the fermentation medium can be done only through a filtration step, which represents an economic advantage. The yield of transformation of milk into cheese is better for the microbial rennet obtained on whey substrate (58%), compared to the one obtained on wheat bran substrate (35%), which indicates the importance of casein in the process of obtaining / purifying the microbial rennet. According to literature studies, in determining the coagulation activity, the microbial rennet obtained in SSF gives better results (1750 S.U.) than the rennet obtained LSF (1200 S.U.)

Conclusions: In this study we can observe that the SSF was a good method for rennet production. The results were close to LSF when supplemented with casein, which showed that casein had an important role in rennin production.

References:

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USE OF THE THREE-PHASE FLUIDIZED BED FOR WASTEWATER TREATMENT

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Abstract: *The study tackles an actual problem, in the context of integrated systems of technological processes environmental: the intensification of aerobic / anaerobic biological process of wastewater treatment by multiphase fluidized bed treatment.*

Key words: three phase fluidized bed, wastewater treatment, denitrification bacteria

Introduction: The Three-Phase Fluidized Bed (TPFB) can be used in the processes of biological, biochemical or chemical reactions, as the intensification technique in simultaneous transfer phenomena to generate height degree of utile transformation. As specific utilization TPFB can be used in environmental treatment of wastewater. [1]

Experimental: The experimental follow the determination of hydrodynamic and mass transfer conditions for the aerobic/anaerobic biological continuous treatment of wastewaters containing ammonium ions. The experimental plant was design with removable sections which confer to the column flexibility in function and multi functionality in treatment process (the TPFB for biological aerobically process, and bi-phase system – biological anaerobic process).

Results and discussions: The TPFB is created by the biofilm formation on the volcanic rocks under aerobic condition. The ammonium ions adsorption tuck place under anaerobic condition (only Bi-Phase Fluidized Bed, BPFB). For those two operating techniques it was determined qualitative and quantitative principal parameters which describes its. For the BPFB – minimum fluidization velocity, the fluid phase fractions and the bed porosity, for TPFB - considering two phase fluid flow, the initial bed height, the diameter, the shape and the density of the solid particles, in the conditions of a three phase fluidized bed operating at a fluid velocity under the value of the liquid - solid minimum fluidization velocity. Also it was determined the efficiency of ammonium ions removal.

Conclusions: The study shows that the increasing of ammonia ions separation efficiency can be achieved using a multi-bed system with the bed height decreasing for upper sections for a better stability of the biofilm formation

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TEMPERATURE PROFILE SIMULATION FOR BIODEGRADABLE POLYMER INJECTION MOLDING

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Abstract: *Cooling of biodegradables polymers in injection molding process is studied by heat transfer simulation for air in natural convection and cooling water agents***.**

Key words:, poly-butylene succinate, poly-lactic acid, mold cooling

Introduction: Biodegradable polymers are considered promising materials for replacing conventional polymer plastics for various applications. The study of their mechanical properties is generally performed using injection molded flexural specimens. A uniform temperature distribution in the mold may is considered to ensure a diminished shrinking effect.

Modelling: The heat transfer was considered mainly in the thickness of the sample (L=3.2 mm). The general heat transfer equation, considering heat generation by solidification: $\rho \cdot c_s \frac{\partial T}{\partial \tau} = \frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x}\right) + q_s$ with boundary conditions: $-k \frac{\partial T}{\partial x} = h \cdot \left(T - T_{cooling}\right)$, x=0,L was integrated using Matlab software**.** Polylactic acid (PLA) and polybutylene succinate (PBS) were studied considering water and air as cooling agents. The physical properties were taken from literature [1, 2].

Results and discussions. Due to the small thermal conductivity of PBS (*k*=0.19 W/mK) and high solidification heat (96 J/g), during solidification the temperature remains high. After the solidification the temperature decreases more rapidly (Figure 1). Similar profiles were obtained for PLA.

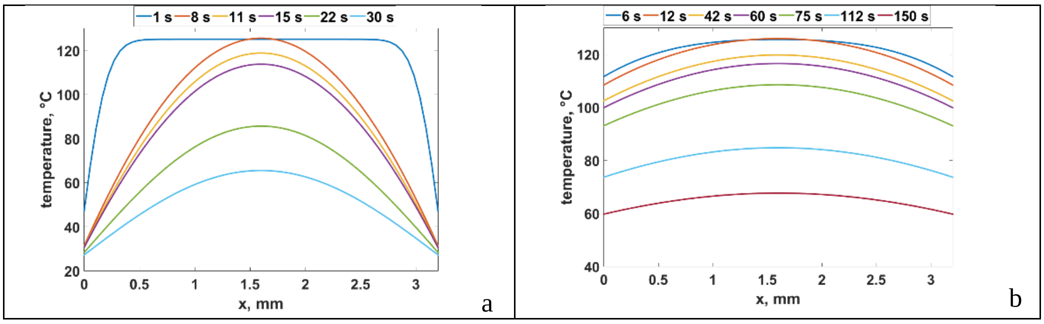

Fig. 1 Temperature profiles in PBS samples: a) water cooling, b)air in natural convection.

Conclusions: Cooling in air at natural convection can ensure a very steady temperature profile but increases significantly the time.

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KINETIC STUDY ON THE CONTROLLED RELEASE OF CIPROFLOXACIN FROM POLYMER MATRIX TABLETS

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Abstract: *The goal of this study was to evaluate the controlled release of ciprofloxacin from modified matrix tablets. Several release models were investigated in order to identify the most appropriate ones, for a better predictability of the drug release. The models best fitting the experimental release profiles reported by Shankar et al.[1]) were the diffusion and the interaction-reaction models.*

Key words: Ciprofloxacin, drug delivery, controlled release

Introduction:

Ciprofloxacin is a fluoroquinolone, a synthetic antibiotic of the quinolone drug class and recently was pointed out as the most used antibacterial agent worldwide. Ciprofloxacin is effective in the eradication of most strains of bacterial pathogens responsible for respiratory, urinary tract, gastrointestinal and abdominal infections. Ciprofloxacin can cause serious side effects, including tendon problems, nerve damage, or low blood sugar, thus it is important to optimize the dosage and correctly predict the way the drug is delivered.

Modelling: The oral route of drug administration is the most important method of administrating drugs for systemic effects. Tablets offer safe and convenient ways of active ingredients administration and provide accurate dosing. In the design of a drug delivery system it is necessary to study the drug delivery dynamics. Based on the experimental data from literature and hypothesized drug release mechanisms, several mathematical models were used to predict the release kinetics of ciprofloxacin from polymer matrix tablets: zero order and first order kinetics, Korsmeyer–Peppas, Higuchi, diffusion and kinetic interaction/reaction models.

Results and discussions: Best fitting models proved to be the diffusional and interaction/reaction models.

For many drug delivery systems, the release process can be modelled by using the classical unsteady state Fick's diffusion equation having appropriate boundary conditions. The dosage forms represented by tablets were considered as sheets [2]. Because some release processes are dependent on the interaction between the drugs and the ionic components of the release medium, they are well described by a kinetic interaction/reaction model [3].

$$R = \frac{R_e^2 \cdot k \cdot t}{\frac{1}{C_0} + R_e \cdot k \cdot t}$$

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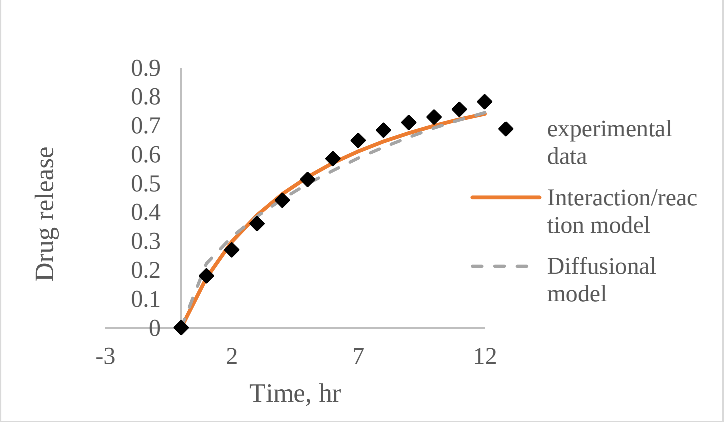
The parameters of the model are the percentage release in bulk liquid at equilibrium, R_e , and the kinetic constant k.



Experimental and calculated ciprofloxacine release profiles from polymer matrix tablets, for one of the formulations

Conclusions: The study showed that different pharmaceutical formulations lead to different release models, even in the case of the same additives used in the formulations, but with different concentrations.

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ASSESSMENT OF SOME HEAVY METALS IN *M. GALLOPROVINCIALIS* BIVALVE MOLLUSCS FROM NW BLACK SEA SHELF (ROMANIA)

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Abstract: *Bivalve molluscs were collected from five sampling stations (water depths within 43–54 m), in an offshore area located at approximatively 30 km of Sfantu Gheorghe branch (NW Black Sea), during the research cruise aboard R/V Mare Nigrum conducted in May 2019. Concentrations of Hg, Cd and Co were determined by specific techniques.*

Key words: Heavy metals, *Mytilus galloprovincialis*, ICP-MS, DMA 80, multivariate analysis

Introduction: One of the most severe categories of pollutants in the marine environment is that of heavy metals. Being filtering organisms, mussels can concentrate metals in their soft tissues that are then transferred to humans through consumption [1,2]. Due to their well-known capacity to accumulate the pollutants in different tissues through intense filtering feeding activity, the abundant mussel population is a good indicator and sentinel of the environmental quality [3].

Experimental part: Samples were collected using a dredge with a length of 5 m. The concentrations of Cd and Co were determined using an ICP-MS ELAN DRC Perkin Elmer, where the mussels were digested with HNO_3 65%. The total Hg content was measured using an automatic mercury analyser DMA 80 Milestone and quantified by atomic absorption spectrophotometry at 253.7 nm.

Results and discussions: Measured values of Cd, Co and Hg concentration of samples of molluscs from each site emphasize the following aspects:
(i) the highest values of Cd concentration (4.7–5.4 mg/kg) were detected in the mussels under the Danube's influence, due to the high river discharge, whereas minimum values (0.50–0.92 mg/kg) were found in the eastern part of the studied area; values of Cd concentration in the mussels flesh exceeded the maximum level set by Commission Regulation (EC) No. 1881/2006, *i.e.*, 1 mg/kg;
(ii) the highest values of Co concentration (1.91–3.0 mg/kg) were noticed also in the Danube's mouth area and the lowest values (1.01–1.43 mg/kg) were measured in the southern part of the studied area;

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(iii) the highest values of Hg concentration (0.11–0.12 mg/kg) were detected in the northern part (Danube`s influence), whereas minimum values (0.03–0.08 mg/kg) were found in the eastern part of the studied area.
Multivariate analysis was performed to establish correlations between the metal level in mussel tissue and seawater parameters.

Conclusions: This study provided information on the concentration of toxic elements Cd, Co and Hg within the tissues of mussels collected on the muddy sediments. The order of accumulation in the investigated samples in the study area was as follows: Cd > Co > Hg. Cd concentration exceeded the maximum value set by Commission Regulation (EC) No. 1881/2006, *i.e.*, 1 mg/kg.

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FREEZE-DRYING OF GARLIC. A COMPARATIVE STUDY WITH CONVECTIVE HOT AIR-DRYING. EFFECT ON ALLICIN YIELD

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Introduction: Allicin is one of the most studied bioactive compound from garlic and the scientific evidence shows that it plays an important role in the therapeutic potential of garlic [1, 2]. Drying process of garlic cloves is a crucial step in obtaining dried garlic with high allicin potential [3, 4]. The influence of freeze-drying on allicin potential of garlic was studied compared to convective hot air-drying.

Experimental: *Material:* garlic cloves cultivated in a Romania area were carefully peeled and used as whole and chopped in medium-large pieces. *Drying:* Chopped cloves were put in a convective air-dryer at different temperatures. Freeze-drying process was applied on fresh and pre-frozen whole and chopped cloves. Drying kinetics were measured for each drying technique. *HPLC:* Allicin content was determined by HPLC in fresh and dried garlic.

Results and discussions: Drying technique, using the cloves as whole or chopped and hot air-drying temperature influenced allicin yield of dried garlic. Hot air-drying curves were different based on air temperature. Freeze-drying curves and allicin yield were different for the pre-frozen and fresh freeze-dried cloves, suggesting that pre-freezing the cloves is necessary for reducing drying time and preserve the allicin potential of garlic. Significant change in color of pre-frozen whole cloves was observed during freeze-drying process, resulting in low allicin yield. Chopped pre-frozen freeze-dried cloves showed the best allicin yield, although not significantly more than hot air-drying of chopped cloves at 50 °C. It is important to note that the freeze-drying process was achieved with a bench-top freeze-dryer with non-heated shelves, at a 2.1 mbar vacuum pressure and at a condenser temperature of -48, -51 °C.

Conclusions: In adequate conditions, freeze-drying has a positive impact on allicin potential of dried garlic, being more protective than convective hot air-drying at different temperatures.

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CONTINUOUS FLOW REACTOR FOR ULTRASOUND ASSISTED ENZYMATIC ESTERIFICATION

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Abstract*:* *In this paper an ultrasonic reactor suitable for enzymatic reactions was designed, built and characterized. The reaction used as a model was the esterification of acetic acid with isoamyl alcohol. The reactor has a loop configuration, with ultrasound working in pulse mode, at a constant temperature and the water produced in the esterification was continuously removed [5]. The efficiency of the reactor was determined in relation to ultrasonic power density (measured by 4-nitrophenol dosimetry), position of ultrasonic horn and temperature. The results show that ultrasound can enhance the process efficiency and also reduce the reaction time. The reactor was assessed in terms of minimizing cavitation activity and maximizing mass transfer.*

Key words: Esterification, Isoamyl Acetate, Process Intensification, Ultrasounds

Introduction: Biocatalysts are increasingly used to replace chemical catalysts, especially due to their high specificity, regio- and stereo- selectivity in mild conditions [1]. A method to overcome the limitations related to immobilized enzymes is the use of ultrasounds [2]. Ultrasounds causes increase in the mass transfer rate of the reagents to the active site of enzyme [3], and influence protein conformation, unfolding the polypeptide chain and reveling the active site.

Experimental: *Esterification Process:* The esterification reaction was conducted in a loop reactor [4] (flow rate of 0.16 mL/min and different volumes of stock solution) at various reaction temperatures (30 to 50C) with an acetic acid-to-isoamyl alcohol ratio 1:2 molar. Ultrasound was introduced via a probe system (VibraCell VCX-750), using different ultrasound pulses and amplitudes. The water was removed from the system by passing the reaction mixture through a column containing molecular sieve (2.3 g molecular sieve, with a water holding capacity of 22% wt., enough to retain the whole water formed during the esterification). The concentration of isoamyl acetate formed from the reaction mixture was determined by gas chromatography.

Results and discussions: To prevent enzyme denaturation caused by the ultrasounds, the setup of the ultrasonic reactor should be arranged in such a way as to reduce cavitation bubble collapse within it. One method of monitoring the production of HO radicals generated by ultrasonic bubbles collapse is to use the conversion of 4-nitrophenol (4-NP) to 4-nitrocatechol (4-NC). The 4-NP disappearance was monitored both in the reactor itself (R), and in the coupling

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liquid (CL) used for both the transmission of ultrasonic waves and as the water jacket (WJ) coolant. The lowest degradation of 4-nitrophenol is obtained at a distance of 4.5 cm of the probe from the enzymatic reactor. 4.5 cm is the distance which generates a minimum number of cavitation bubble collapse events which would provide the preferred geometric arrangement of the reactor for minimal enzyme degradation (see Fig. 1).

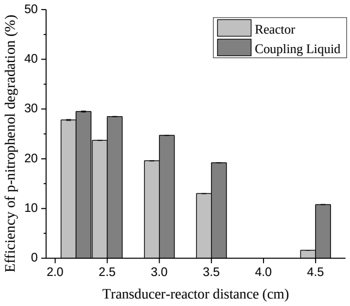

Fig. 1 The degradation efficiency of 4-nitrophenol depending on the distance between the ultrasonic probe and the reactor in the reactor and in the coupling liquid at 50°C with an ultrasound energy of 107 J (20% ampl, 3on/3off).

Conclusions: The results show that ultrasound can enhance the process efficiency and also reduce the reaction time.

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SUSTAINABLE APPROACH IN BIOETHANOL PRODUCTION FROM BROWN ALGAE

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Abstract: *This paper evaluates the potential of brown algae for bioethanol production through alcoholic fermentation.*

Key words: *Cystoseira barbata*, alcoholic fermentation, mathematical model, bioethanol.

Introduction: *Cystoseira barbata* is a brown alga found on the southern shore of the Black Sea. This species represents an important source of polysaccharides (alginates, laminarans, and fucoidans), a promising feedstock for bioethanol production.

Experimental: The algae were collected, washed with tap water, dried at 50 °C and crushed. The transformation of polysaccharides to fermentable sugars was performed by enzymatic hydrolysis with *Aspergillus niger* cellulase, then alcoholic fermentation followed with *Saccharomyces cerevisiae* yeast. The volatile compounds concentration was determined after the distillation of the fermented broth, and the bioethanol production was related to the amount of carbon dioxide released in the alcoholic fermentation.

Results and discussions : For mathematical modeling, the experiment was designed according to a 2^3 factorial plan. The three factors were: the temperature of the alcoholic fermentation (t, ^oC), solid-to-liquid ratio (S, g algae/g water), and cellulase ratio (U, cellulase units/g d.m), each being considered at two levels. Correlations between these independent variables and the process responses: volatile compounds yield (V, g/g d.m), and ethanol yield (E, g/d.m) were established in the general form of a first degree equation:

$$y = -a + b^{\cdot} t - c^{\cdot} S + d^{\cdot} U \qquad (1)$$

where y is either V or E and their sign show the direct (+) or inverse (-) proportionality of the response with the respective factor. The coefficients of the equation (1) where validated by ANOVA analysis.

Conclusions: Brown algae represent a sustainable resource for ethanol production via enzymatic hydrolysis of polysaccharides then yeast fermentation.

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

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EXPLOSION RISK ASSESSMENT OF AMMONIUM NITRATE STORAGE IN WAREHOUSES. CASE STUDY: THE BEIRUT DISASTER

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Abstract*:* *Qualitative and quantitative evaluation of the potential risks of ammonium nitrate explosions in chemical fertilizers factories and warehouses*

Key words: fertilizers, ammonium nitrate, risk assessment, explosion, major accidents

Introduction: The growing interest in improving safety actions for the storage, transportation and handling of hazardous substances, such as ammonium nitrate (AN), stemmed from a series of catastrophic events worldwide[1]. Recently, the explosion of approximately 2750 tons of AN in a warehouse located in Beirut port, had demonstrated again the major risk of explosion and destructive potential of this substance, if it is involved in a fire or stored improperly. The paper presents the case study of this disaster, by comparing simulation results with the damages observed on satellite images.

Experimental and/or Modelling: *Risk assessment for the ammonium nitrate explosion scenario*: According to the methodology, the risk is expressed mathematically using the following formula: Risk = Consequences x Frequency of the event. The consequences are estimated using the TNT Equivalent model, by considering different equivalency factors from scientific literature. The frequency is derived from literature data for warehouse explosions.
Scenario description: The quantity involved in the explosion scenario refers to the declared 2750 tons of fertilizer grade AN, stored in the warehouse. The ignition source was the fire propagating in the warehouse.
Short description of the effects: The explosion of AN itself occurs suddenly, and the effects are immediate, but the event can continue for a period of time, by igniting other fires or explosions due to the domino effect, or the toxic dispersion of combustion gases that form in case of AN fire and decomposition reaction.

Results and discussions: PHA (Preliminary Hazard Analysis) is the starting point for a more detailed risk analysis applicable to the next phases in the "life" of a system and is the preliminary security analysis technique needed to lay the groundwork for safety programs[2]. At this stage, the hazards of the storage process are identified and evaluated, estimating the qualitative risk level of each hazard identified. The results of the qualitative risk assessment show a medium risk of explosion, with low probability of explosion, but catastrophic consequences. The quantitative risk assessment consists in the consequence analysis of the explosion, considering two different TNT Equivalency factors, from literature[3]: 14% and 32 %.

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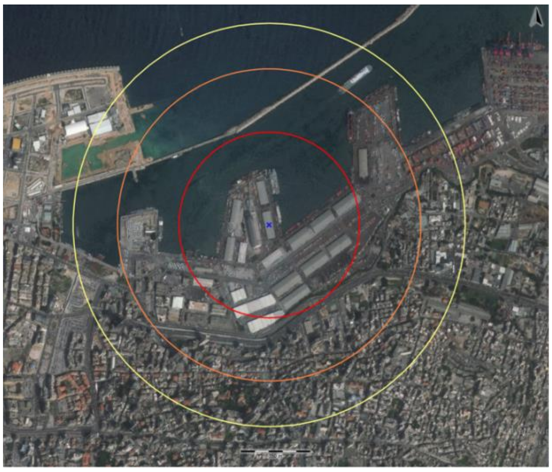

Fig.1. Overpressure contours of the explosion – 14% TNT Equivalency factor

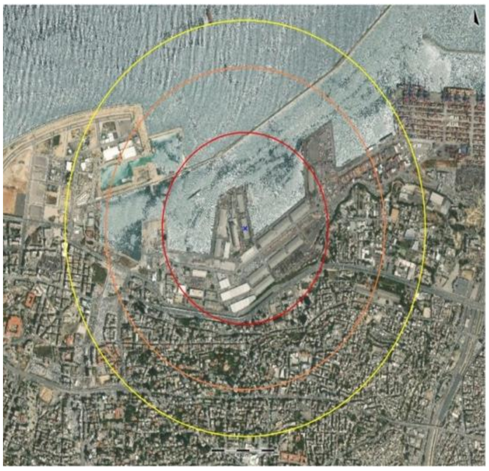

Fig.2.. Overpressure contours of the explosion – 32% TNT Equivalency factor

Legend: Red – total destruction - high lethality area (300 mbar); Orange – beginning of lethality area (140 mbar); Yellow – irreversible effects area – shattered windows (100 mbar)

Conclusions:

From the analysis of the accident it can be concluded, that for AN quantities bigger than 300 tons it is advised to consider a bigger TNT Equivalency factor.

Moreover, the TNT Equivalency model has also a certain degree of uncertainty when it is used for other substances than TNT. Considering the lack of data about the accident, such as exact quantity of AN involved in the explosion, type of AN and nitrogen content, density, porosity, ignition source energy etc., the results have a certain degree of uncertainty.

Risk and vulnerability reduction measures are necessary for a proper risk management.

The appropriate identification and risk analysis underlying potential explosions involving chemical fertilizers is the key to avoiding catastrophic consequences.

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BOOK OF ABSTRACTS

SICHEM – 2020

B – Applied organic, inorganic, and supramolecular chemistry (AOISC)

1. Keynotes

SEARCHING FOR A NEW POSITRON MODERATOR: RF-MAGNETRON SPUTTERED NANOSTRUCTURED THIN FILMS

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Abstract*: The goal of the present work was to generate a methodology for fabrication, processing and structural/functional characterization of nanostructured thin films in order to obtain a prospective new positron moderator, by correlating the compound structure with its interaction with positrons.*

Key words: GaN, heterostructures, thin films, RF-magnetron sputtering

Introduction: Several parameters are considered vital for associating a certain material to its potential use as positron moderator. The goal of the present work was to generate a methodology for fabrication, processing and structural/functional characterization of nanostructured thin films in order to obtain a prospective new positron moderator, by correlating the compound structure with its interaction with positrons.

Experimental: Commercially available GaN films deposited on different substrates were subjected to a complex study, involving structural and functional characterization [1-2]. Moreover, the present experimental study is focused on presenting a series of thin films, grown on different substrates by means of magnetron sputtering technique [3]. The most significant parameters for deposition are the target quality, substrate temperature, working pressure, gas feed, electrical input type, forwarded power and target-substrate distance.

Results and discussions: The structural features of the heterostructures were obtained assessing various characterization techniques. Firstly, the wafers were analyzed by means of high-resolution transmission electron microscopy (HR-TEM), in order to establish the crystallographic structure, substrate-buffer-film growth relationship, quality of interfaces, thicknesses of layers and elemental diffusion. Besides the HR-TEM description of the heterostructures, a high-resolution X-ray diffraction technique was implied to gather ω scans, upon which a mathematic model was applied in order to obtain the parameters (of the best

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simulated fit) that ultimately determine the values of edge and screw dislocation densities, along with their respective dislocation correlation lengths. The functional features of the wafers were studied with the help of a Doppler broadening spectroscopy technique, while being implanted with slow positrons, to determine the positron characteristic diffusion length, a measure that correlates with the moderation potential of the material at hand.

Conclusions: The quality of the substrate dictates the limitations that GaN thin films possess in field assisted positron moderation. The obtainment of highly oriented, low-defect GaN layers that surpass these limitations depends on the proper growth of a high-quality buffer layer.

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BOOK OF ABSTRACTS

SICHEM – 2018

B – Applied organic, inorganic, and supramolecular chemistry (AOISC)

2. Oral presentations

ADVANTAGES AND DISADVANTAGES OF RECHARGEABLE BATTERIES RECONDITIONING VERSUS RECYCLING

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This paper presents a comparative study of the advantages and disadvantages of the reconditioning procedure of rechargeable batteries versus the recycling procedure. Our previous studies successfully reported a reconditioning procedure of some lithium-polymer batteries that led to their reintroduction on the market, a good illustration of one of the circular economy principle [1,2]. The reconditioning procedure has been performed on a number of rechargeable lithium-polymer batteries, but the results showed that it may well be performed also on other various types of rechargeable batteries, with similar or different chemical composition, such as lithium-ion, nickel-cadmium, etc. In order to extend the reconditioning procedure study to an industrial scale application, one needs to establish if the procedure is suitable for large scale implementation or if it is limited to a small scale pilot plant. By performing a comparison between this reconditioning procedure and the recycling one, one may find certain applicable criteria to decide which method is suitable to be employed in certain given conditions. The results show that the reconditioning procedure is a secure, money, time and resources saving method, which may be performed on rechargeable batteries that are no longer working at acceptable output parameters.

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

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INFLUENCE OF THE SENSITIZER IN TiO_2-GO COMPOSITES ON THE KINETICS OF THE CATALYTIC PHOTODECOMPOSITION OF METHYLENE BLUE

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Abstract: *Photocatalytic nanocomposites based on TiO_2 sensitized with graphene oxide (TiO_2-GO) can be obtained and imbedded in water based styrene acrylic coatings and studied in view of photocatalytic behavior. Other physical and chemical properties of the photocatalytic coatings were also inverstigated by means of molecular spectroscopy, electronic and optical microscopy in relation with degradation efficiency.*

Key words: TiO_2-GO sensitized with iron (III) phtalocyanine, water-bore coatings, photocatalytic materials

Introduction: Photocatalytic coatings are a very active field in terms of research, (especially in the epidemic context) for antiviral, antibacterial and self-cleaning activity.[[1]]

Experimental: *Reagents:* TiO_2 (Evonik) doped with graphene oxide obtained in our laboratory by Hummers method. *Production of coatings:* Photocatalysts were imbedded in water based styrene acrylic coating (CHIMCOLOR). Were deposited on glass substrates, dried at room temperature and impregnated with methylene blue solution. Afterwards, the samples were exposed to artificial light in Xenotest chamber and reflectance spectra were recorded using a spectrophotometer (Jasco).

Results and discussions: Colour differences in CIEL*a*b* system were calculated from the reflectance spectra of the samples and from the total colour differences was estimated the photocatalytic behavior of the TiO_2-GO composites. Comparative tests developed at a various intervals of times during radiation with Xenon light lead to simplified kinetic formulation for the photocatalytic process. Interactions between MB molecules and photocatalytic composites determine the photodecomposition mechanism.

Conclusions: The study revealed the positive effect obtained on the efficiency of photocatalytic coatings at a very low GO loading.

Acknowledgements: This research was funded by the INCDCP ICECHIM Bucharest 2019-2022 Core Program PN. 19.23–Chem-Ergent, Project No.19.23.03.01.

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NOVEL BIOTANNING AGENTS AND NANOBLENDS FOR RECYCLABLE AUTOMOTIVE LEATHER

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Introduction: Sustainability is a global level challenge for tanning industry whose production lies on Cr(III) salts for more than 90%, negatively impacting both biotic and abiotic entities of various ecosystems. The aim of our research is to develop automotive leather that meets the OEM market performance requirements by significantly reducing chemical and environmental footprint of leather production.

Experimental: To this purpose a novel safe and non-toxic tanning agent based on sodium alginate (SA) derivatives, from 100% renewable sources, and hydrolysates from proteinous wastes of leather industry has been developed and tested at laboratory and pilot level. Safe and non-toxic wet finishing solutions based on various nanoparticle blends have been developed to protect leather against soiling and abrasion and confer it flame retardancy and tested at laboratory and pilot level.

Results and discussions: SA was selectively oxidized using KIO_4. The degree of oxidation /depolymerization was varied by changing the molar ratio between the monomer unit of the substrate and the oxidizing agent. The crosslinking ability of the oxidized sodium alginate (OSA) was higher compared to that provided by a commercial polyaldehyde tanning agent. Furthermore, significant enhancement was obtained by adding collagen hydrolysates to the SA solution prior to oxidation. By re-tanning with nanoSiO_2, nanoTiO_2 and nanohydroxyapatite (nHA) the hydrothermal stability of the collagen matrix further increased. Insights into the tanning mechanism were obtained using a multi-level analytical approach based on microDSC, NMR MOUSE and FTIR-ATR techniques [1-3].

Conclusions: Our results confirmed the suitability of OSA, nHA, nanoSiO_2 and nanoTiO_2 as non-toxic tanning agents for the automotive recyclable leather production [4].

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SYNTHESIS AND COMPARATIVE STUDY OF SOME AMINYL AND HYDRAZYL FREE RADICALS AND THEIR CONGENERS

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Abstract*:* *Several compounds of hydrazyl and aminyl type were synthesized and characterized, generating by oxidation nitrogen centred free radicals.*

Introduction: Nitrogen centered free radicals are a class of compounds that exhibit important acid-base and redox properties. Their stability is a sum of several factors, like conjugation and steric hindrance.

Experimental: Several methoxyamines and hydrazines were synthesized and characterized by IR, UV-Vis, and NMR spectroscopy; for few of them the X-ray structure was obtained.

Results and discussions: In the presence of a base, both methoxyamines and hydrazines generate the corresponding anions. This acid-base process is accompanied by color change (from yellow to blue in the case of methoxyamines and from yellow to red in the case of hydrazines). By oxidation, from methoxyamines are obtained persistent free radicals, while from hydrazines the free radicals obtained are more stable. All these free radicals were also characterized by ESR, thus demonstrating their open-shell structure. Besides, the oxidation process is again accompanied by color change (from yellow to pink or violet). Cyclic voltammetry was used for measuring the oxidation potential of such free radicals.

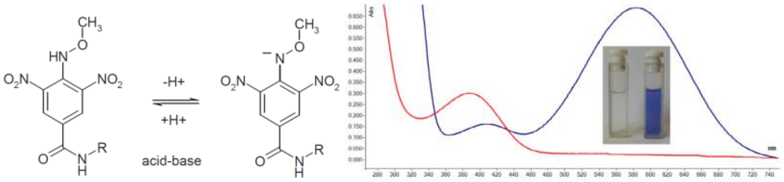

Fig. 1 UV-Vis spectra of a methoxiamine (in red) and of the corresponding anion (in blue).

Conclusions: These compounds can be involved in acid-base or redox processes that can be easily followed by color changes. This is useful for monitoring antioxidant capacity.

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MICROWAVES ASSISTED SYNTHESIS OF MESOPOROUS SILICA NANOPARTICLES

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Abstract: Spherical nanoparticles of mesoporous silica are synthesized by sol-gel method with cetyltrimethylammonium bromide (CTAB) as template, in two stages: first, the silica network is formed around the CTAB micelles, then the CTAB is extracted by refluxing, in acid solution, the obtained particles from the first stage. In the present work, extraction of CTAB was realized by heating the reaction mixture with microwaves, into a laboratory microwaves oven. The silica nanoparticles treated by microwaves were compared with those obtained by refluxing the reaction mixture in the synthesis flask, heated on the oil bath. The composition and chemical structure of the two silica obtained through different synthesis methods were analyzed by elemental analysis, infrared and Raman spectroscopy. Also, the particles structure was characterized by Scanning Electronic Microscopy (SEM) and X-Ray Diffraction (XRD) techniques. The influence of reaction time in the microwaves oven has been studied. It was found that using microwaves the same structure of silica could be obtained but the synthesis time is significant decreased.

Acknowledgments: The authors acknowledge the financial support of the Project PN 19110204 by the Ministry of Scientific Research and Innovation.

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CATALYTIC DEGRADATION OF DIRECT BLACK 38 BY PHYTOSYNTHESIZED SILVER NANOPARTICLES

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Abstract*: This paper describes the green synthesis of silver nanoparticles (AgNPs) using aqueous extracts from different vegetal materials (plants and their parts such as leaves, fruits, flowers) and their catalytic degradation of Direct Black 38 (DBk38, Figure 1) at different time intervals.*

Introduction: Textile industry is, unfortunately, a major source of pollutants for wastewaters and conventional degradation methods have some major drawbacks. Therefore, in recent years researchers shifted to unconventional routes that proved their efficiency and, among them, the use of silver nanoparticles (AgNPs) alongside a reductive agent clearly exhibited excellent results [1, 2].

Experimental: *Phytosynthesis of silver nanoparticles:* The plants used are all of pharmaceutical importance: Sea buckthorn, Jujube, Celadine and Hyssopus. AgNPs were phytosynthesized in different temperature conditions: room temperature and 50^0 C; *Catalytic degradation of DBk38:* The catalytic degradation of DBk38 using phytosynthesized AgNPs was determined based on the reductive degradation of dyes in the presence of a reductive agent and recorded at different time intervals at the specific wavelength of 520 nm.

Results and discussions: The first sign that AgNPs are phytosynthesized is the visual change in color of the aqueous extract which is then confirmed by UV-Vis recordings.

Conclusions: This paper presents the catalytic degradation of Direct Black 38 using phytosynthesized silver nanoparticles from different plant extracts.

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COORDINATING COMPOUND OF COPPER CHLORIDE - {2 - [(2 - [(METHYLSULFANYL) (PROP-2-EN-1-YL) CARBONOIMIDOYL] - HYDRAZINYLIDENE) METHYL] PHENOLATO} DI (AQUA) AS INHIBITOR OF SUPEROXIDE RADICAL

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Abstract: *Free radical-mediated oxidative stress plays a key role in the pathogenesis of many multifactorial diseases (MFDs), such as cancer, cardiovascular, neurodegenerative, and chronic inflammatory diseases. Therefore, the issue of developing, highlighting and selecting new effective compounds that could be used to combat MFDs remains an issue of great importance and practical value.*

Key words: {2 - [(2 - [(methylsulfanyl) (prop-2-en-1-yl) carbonoimidoyl] -hydrazinylidene) methyl] phenolate} di (aqua) copper (II) chloride, thiosemicarbazide derivatives, inhibitors of superoxide radicals.

Introduction: The compound - {2 - [(2 - [(methylsulfanyl) (prop-2-en-1-yl) carbonoimidoyl] -hydrazinylidene) methyl] phenolato} di (aqua) copper (II) chloride belongs to the isotiosemicarbazide class of metals transition. It is a biologically active compound, due to its remarkable properties as a superoxide radical inhibitor.

Experimental and/or Modelling: The compound: {2 - [(2 - [(methylsulfanyl) (prop-2-en-1-yl) carbonoimidoyl] -hydrazinylidene) methyl] phenolato} di (aqua) copper (II) chloride, was tested as an inhibitor of superoxide radicals, synthesized at the State University of Moldova in the Laboratory Advanced Materials in Biopharmaceuticals and Technology [1].

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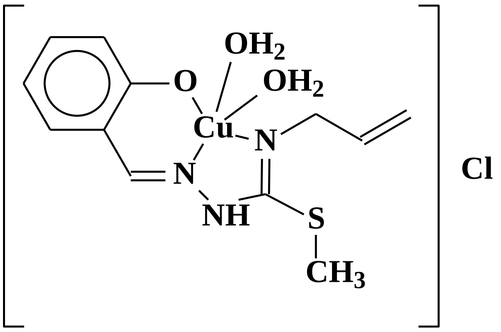

The superoxide radical was tested by the spectrophotometric method, described in [2, 3] with some modifications. The method is based on the generation of the superoxide radical by the phenazine metosulfate / nicotinamide adenine dinucleotide system (PMS / NADH) by oxidation of NADH, and the superoxide radical reduces the salt of tetrazolium - Nitro Blue Tetrazolium (NBT) to blue-purple formazane.

Results and discussions: The experimental data obtained, demonstrated the antiradical activity with the semimaximal inhibition concentration (IC_{50} = 0.04 μmol/L), which is 21.5 times higher than the activity of the structural analog nitrate- [2 - ({2 - [(ethylsulfanyl) (prop-2- en-1-yl) carbonoimidoyl] hydrazinylidene} methyl) phenolato] (aqua) copper (IC_{50} = 0.86) and 1547.5 times more effective than quercetin (IC_{50} = 61.9 μmol / L), used as a standard for the determination of superoxide radical inhibitory activity .

The detected activity of the highlighted compound is of particular interest for medicine in terms of expanding the arsenal of synthetic superoxide radical inhibitors.

Conclusions: The anti-ROS properties of new compound broaden the theoretical knowledge about the properties biological of a series of chemical compounds and at the same time offers new possibilities to obtain new effective remedies to combat the pathological processes caused by ROS, limiting cytotoxic lesions and damage to cellular DNA and not allowing their spread.

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NOVEL SUPPORT BASED ON RENEWABLE RESOURCES DOPED WITH CERIUM OXIDE NANOPARTICLES WITH TECHNICAL APPLICATIONS

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One of the significant drawbacks encountered when inorganic nanoparticles (NPs), are used in various applications, is their aggregation, which eventually lead to the loss of owned final activity. Among various metal oxides, CeO_2 has attained in the last years a lot of interest, as the most reactive rare earth material, being extensively used especially as catalyst, due to its crucial importance in the design of three way catalysts (TWCs) and photocatalysts. One efficient solution to overcome the intrinsic aggregation of the metal oxide NPs, is to use of an appropriate matrix for efficient incorporation of the nanoparticles, to enhance the performance, avoid the cluster growth and aggregation and improve the handling and recovery of the nanoparticles. In our work, cellulose acetate (CA) has been used to serve as matrix for the synthesis of transparent films containing various amounts (1–5 wt.%) of cerium oxide (CeO_2) NPs. In order to attain an improved dispersion and a better connectivity between NPs and the cellulose matrix, the surface of CeO_2 NPs have been previously functionalized by the reaction with 3-aminopropyl(diethoxy)methylsilane (APDMS). The uniform dispersion of the NPs in the homogeneous thin films has been evidenced by using Transmission Electron Microscopy (TEM) and Fourier Transformation Infrared Spectroscopy (FTIR) characterization. The optical properties of nanocomposite films revealed that these, exhibit intense absorption bands in the UV domain (around 312–317 nm) attributed to CeO_2 NPs; consequently, they can be successfully used as efficient UV absorbers, especially as UV-protective coatings in food packing.

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SYNTHESIS, ORGANIC FUNCTIONALIZATION AND IMMOBILIZATION OF CeO_2 NANOPARTICLES IN CELLULOSE MATRIX. EVALUATION OF THEIR PHOTOCATALYTIC EFFICIENCY

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The considerable interest shown to the synthesis, characterization and application of inorganic nanoparticles is given by their remarkably different properties relative to those of bulk counterparts. The unique attributes of metal nanoparticles recommend them for wide application in various fields, such as catalysis, (bio)sensors, biomedicine, optoelectronics etc. However, despite their outstanding properties, the small size of the nanoparticles brings some issues regarding certain difficulties in their separation and reuse, and also possible risks to ecosystems and human health caused by the potential release of nanoparticles into the environment. An efficient approach to overcome the above drawback is to immobilize the nanosized particles onto a host material of larger size, finally a new type of material, namely a hybrid composite being formed.

In this context, CeO_2 NPs were synthesized by two different methods, the attained nanoparticles being further organically functionalized in order to be immobilized in a cellulose derivative matrix, aiming to achieve an improved dispersion and a better connectivity between NPs and the organic matrix. The initial or organically modified CeO_2 NPs were characterized by appropriate techniques (UV-vis, Fluorescence, FTIR, ATG, RX, TEM) and we analysed whether the organic groups introduced on the surface of CeO_2 NPs change their characteristics. Also, after CeO_2 NPs immobilization in cellulose matrix, the photocatalytic performance of the films in the photodegradation of methyl orange was investigated.

Acknowledgement:

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BOOK OF ABSTRACTS

SICHEM – 2020

B – Applied organic, inorganic, and supramolecular chemistry (AOISC)

3. Poster presentations

ENHACEMENT OF IRON ELECTROCORROSION RATE IN DIFFERENT INORGANIC ELECTROLYTES

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Abstract: *The purpose of this research is to identify an appropriate electrolyte solution for electrochemical cutting by anodic corrosion (ECAC) of iron. The anodic dissolution tests were performed on a pure iron disc and using aqueous solutions of inorganic electrolytes ($NaNO_3$, Na_2SO_4 and H_2SO_4). Based on the preliminary tests, the highest cutting speed (evaluated based on the corrosion rate) can be obtained in the presence of $NaNO_3$ in acidic solution.*

Introduction:

Electrochemical cutting by anodic corrosion (ECAC) is an alternative for manufacturing products leading to smooth cutting surfaces and without changing the material structure at the cutting section level. ECAC can remove the disadvantages of the mechanical methods and ensure a high precision. ECAC is based on the controlled anodic dissolution of metals (Cu, Ni, Fe, Ti etc.) and their alloys [1].

Our research aimed to find an electrolyte solution for iron ECAC. The tests were performed on pure iron disc and using combinations of aqueous solutions of inorganic electrolytes ($NaNO_3$, Na_2SO_4 and H_2SO_4).

Experimental Part: A traditional electrochemical cell with three electrodes (WE – Working electrode, RE - Reference electrode, CE – Counter electrode) was used to accomplish all the electrochemical measurements. WE was represented by one pure iron rod (3 mm diameter), embedded with epoxy resin on all the side, leaving only a circular active area (7.07 mm^2) exposed to electrolyte. Before each experiment, it was polished with abrasive paper with granulations ranged between 320 and 2000, then cleaned in ethanol and bidistilled water. CE was from titanium net and the RE was represented by a SCE. All measurements were conducted at room temperature (23ºC) into potentiostatic mode and using an Autolab10 electrochemical workstation. The measurements consisted of cyclic voltammetry tests and Tafel polarization curves, recorded at 5 and 1 mV/s, respectively.

Results and discussions:

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In mono-component solutions of 1 M nitrate or sulfate the corrosion rate presents small values and therefore ECAC it is not fast enough. By acidifying the electrolyte solution by adding sulfuric acid (0.05, 0.1, 0.2, 0.5 M) the corrosion rate increases. Also, the addition of small amounts sulfuric acid shifted the iron passivation potentials to more positive values, favoring the ECAC process.

Conclusions: In non-acidified electrolytes, comparing to sulfate, nitrate represents a better choice for the ECAC process. Moreover, the addition of small amounts sulfuric acid (up to 0.2 M) to 1 M nitrate solution increases significantly the electrocorrosion rate of pure iron, enhancing the ECAC process speed.

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SELECTIVE ELECTROEXTRACTION OF Sn-Pb FROM CU FREE LEACHING SOLUTION OBTAINED DURING THE RECYCLING OF WASTE PRINTED CIRCUIT BOARDS USING THE KBr - HBr SYSTEM

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Abstract: *This paper presents our results concerning the selective electroextraction of Sn-Pb alloy from real leaching solution obtained by exposed metals dissolution from waste printed circuit boards and preliminary electroextraction of Cu.*

Introduction: Waste electrical and electronic equipment (WEEE) is among the largest categories of dangerous waste in the European Union, which grows with 3-5% per year [1]. Printed Circuit Boards (PCBs) are a metal-rich fraction of WEEE streams and their recycling to recover metals promotes the preserving of the nature resources [2]. The development of the recycling strategies is extremely important from the environmental point of view and because WEEE can be considered a valuable resource of secondary raw materials [3]. PCB waste is recognized as multi-metal urban ores and are recycled mainly for the recovery of copper, tin, lead, iron, nickel, gold and silver [4]. Their recycling can be done using electrochemical processes that have high environmental compatibility and energy efficiency and requires less auxiliary materials [5].

Experimental: The Sn-Pb selective electrodeposition experiments were performed in an electrochemical reactor divided by a ceramic porous membrane. A Fisher-type Pt electrode was used as cathode, a graphite block as anode and two $Ag/AgCl/KCl_{SAT}$ systems as reference electrodes (REF). 2 L of 2M KBr aqueous solution was used as anolyte. The catholyte consisted in 2 L of solution obtained by leaching the exposed metals from PCBs and preliminary electroextraction of Cu (see Table 1).

Table 1. The composition of the catholyte solution

Metal	**Cu**	**Sn**	**Pb**	**Fe**	**Ni**	**Zn**
(g/L)	0.008	7.9	3.97	5.09	0.618	7.48

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The measurements were performed at room temperature (+24 °C), by potentiostatic chrono-amperometry (PCA). The Sn-Pb selective electrodeposition tests were started at an imposed potential of -0.50 V/REF, which was progressively decreased up to -0.8. V/REF.

Results and discussions: During the successive tests, the composition of the cathodic deposit evolved, including Sn from 99.83 to 92.70%, Pb from 0.01 to 5.69%, while the Cu content did not exceed 0.03%. It is worth noting that the most susceptible impurities (Ni, Fe, Zn) start to be incorporated in the cathodic deposit (Sn-Pb alloy) only at the cathode potential of -0.8 V/REF. Current efficiencies and specific electricity consumption are reasonable if the process is properly controlled, ensuring the profitability of the process. A high concentration of Sn causes the formation of a dendritic deposit, after which, with its decrease, the Sn-Pb alloy deposits become smooth and compact, facilitating its extraction from the electrodeposition reactor.

Conclusions: The results concerning the efficiency and purity prove that the selective electrodeposition of Sn-Pb alloys by PCA from Cu-free leaching solutions is a feasible and cost-effective method, which allows to obtain good quality products that can be easily recovered and valorised. The process efficiency can be ensured by rigorous control of the main process parameters, such as the concentration of Sn and Pb ions, the cathode potential and the current level through it.

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CARBON DOTS FOR ENHANCED PHOTORESPONSE OF SELF-POWERED SENSOR BASED ON NANOSTRUCTURED SILICON

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Abstract: *In this work a photoactive material was prepared by surface passivation of carbon nanoparticles and demonstrated its capability to enhance the white light sensitivity of a self-powered sensor based on nanostructured silicon. The proposed system may pave the way for designing environmentally friendly sensing devices.*

Introduction: Carbon nanoparticles of graphitic nature and quasi-spherical shape with size less than 10 nm have been studied recently for their emerging potential as active layer in various devices from electrochemical sensors or biosensors to optoelectronic devices due to their numerous advantages including tunable band gap, strong luminescence or electrical conductivity. [1]

Experimental: *CDs Synthesis:* Water-soluble photoluminescent carbon dots had been prepared by covalent grafting of three amine-terminated polymers with average Mn~ 1500 [2,3] & 2000 on the tiny surface-oxidized carbon nanoparticles; The *nanostructured silicon surface* was fabricated using metal-assisted chemical etching technique; Further, the back and front contacts were deposited such that the 0.25 cm^2 actively absorbing area was defined at the front of the device.

Results and discussions: The prepared CDs displayed excitation dependent fluorescence in 300-700 nm domain owing to the presence of trap states energy levels associated with surface functional groups. They were drop casted on the porous silicon based photodetection platform and the device was further characterized under dark and white light illumination (100mW/cm^2) condition, at 0V bias. The results showed the reverse photocurrent was enhanced by up to 2 times and the responsivity (R) of the device can be tuned due to the diffusion of additional photo-generated carriers created at the carbon/silicon interface.

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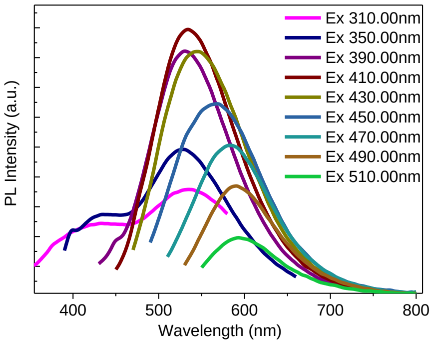

Fig. 1 Fluorescence emission spectra of NIPAM-carbon dots in aqueous solution at different excitation wavelengths.

Conclusions: The photoactive CDs layer showed promising results in terms of photoconduction and effective charge injection at the silicon interface leading to improved photodetection performance.

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EVALUATION OF THE BEHAVIOR OF RESTORATION MATERIALS EXPERIMENTALLY APPLIED IN ECCLESIAL MONUMENTS LOCATED IN CAVE SPACES

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Abstract: *Representing one of the major concerns that define the modern conservation and restoration of the built heritage, the evaluation of the behavior over time of the materials used in the interventions on historical monuments is a topical issue. Included in the specialized methodologies and in the fields of competence of the specialists and restoration experts, the observation of the evolution of conservation-restoration materials has become an interdisciplinary research direction. This paper is part of this line, being devoted to evaluating the behavior of materials for in situ consolidation interventions of murals located in cave environments.*

Introduction: The search for consolidants compatible with the material structure of the mural paintings from the ecclesiastical patrimony, led us to obtain materials that meet the general principles of conservation-restoration and the requirements imposed by the specifics of the monuments in which they were to be applied. These are murals in a cave environment, characterized by a severe microclimate, with variations in temperature and humidity, with large amplitudes of relative humidity caused by condensation and infiltration. The materials researched and produced by us were applied in situ, on an experimental basis, the evaluation of their behavior over time remaining a problem for the future. Now, more than a decade after the application of the new binding materials, with a role in strengthening the support of murals, conducting investigations on their evolution and possible effects on the constituent materials of murals has been the subject of new and necessary research.

Experimental: Two ecclesiastical monuments in which we tested the binding materials produced by us represented the current case studies within the 5PS / 2019 project: the church of the Saints Archangels (19th century) built in the cave of St. Gregory the Decapolis (Vâlcea County) and the church dug in the rock (14th century) from Corbii de Piatră (Argeș County). In situ observations were performed, as well as samples from experimentally applied restoration mortars, subsequently analyzed by X-ray diffraction and scanning electron microscopy coupled with X-ray dispersive energy.

Results and discussions: It was found that all mortars maintained a good adhesion to the rock wall, masonry and the support of murals. The mortars have

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no cracks, are compact and have a hardness compatible with the original. One of the mortars applied in the narthex of the church of the Saints Archangels became friable, like the support of the original painting, due to the capillarity and the recrystallization of soluble salts. In the absence of measures to improve the humidity of the walls and the microclimate, the applied mortars have, like the original wall surface, saline efflorescences (calcium sulphate, recrystallized calcium carbonate) and biological contamination (mycelium formed by branched or poorly developed hyphae, spore chains, bacilli).

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

CEMENTITIOUS COMPOSITES CONTAINING BARIUM TITANATE FOR REAL TIME DAMAGE ASSESSMENT IN SMART STRUCTURES

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Abstract

The study presents the manufacture processes and characterization of special engineered mortars based on Portland cement (PC) with addition of barium titanate nanopowder (BTNp). Cementitious composites containing barium titanate presents piezoresistive behavior. These materials, based on PC with BTNp, can sense strain through the variation of electrical resistance and as a result cementitious composites (mortars and concrete) can be used as sensors for nondestructive monitoring of infrastructures. The BTNp was obtained by a combination of sol-gel and hydrothermal methods starting form tetrabutyltitanate and barium acetate. The mortars based on PC and BTNp were characterized from the point of view of specific properties (electrical resistance, mechanical strengths). Variation of electrical signal when applying a mechanical strain was the main specific property studied in terms of self-sensing materials.

The composition and microstructure of mortars strongly influences the electrical signal and mechanical strength values. The compressive and flexural strength values were assessed on mortars cured for 28 and 90 days; those of mortars containing barium titanate, are comparable with the ones of PC mortars. The values of electrical resistance are strongly correlated with the composition, morphology and curing time of mortars. The experimental results presented in this study demonstrate that BTNp addition can reduce the electrical resistance of cement-based matrices. Regardless of the curing time, in all mortars, one can observe that the presence of BTNp does not change the nature of specific phases formed by hydration of Portland cement and does not lead to the formation of other new hydration phases.

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IN SILICO ANALYSIS OF REACTIVITY PARAMETERS OF 1,3,4-THIADIAZOLE DERIVATIVES

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Short Abstract: *Computational approach based on Density Functional Theory, using software predictions of molecular properties and structural descriptors was conducted on three thiadiazole derivatives containing azulene rings, in order to estimate global and local reactivity parameters, useful for electrochemical applications. From predicted energy levels of the frontier molecular orbitals, global reactivity parameters (ionization potential, electronegativity, global hardness and softness, chemical potential, electrophilicity index) and local reactivity descriptors (Mulliken, electrostatic and natural charges, electrostatic potential al local ionization potential) were obtained and discussed in terms of kinetic stability and reactivity, as well with regard of oxido and reduction potential estimation.*

Introduction: Our previous study on electrochemical properties of azulene compounds [1] were supplemented with a global reactivity analysis based on Koopmans’s theorem [2] on three azulene-diazenyl-thiadiazole derivatives. Kinetic stability and reactivity of molecules was predicted from molecular frontier orbitals energy values. Additionally, local reactivity parameters (atomic charges, atomic electrostatic potential and local ionization potential map), are provided. Redox potentials are evaluated using empirical equations of Bredas et all [3, 4].

Computational modelling:

The structures of 2-(azulen-1-yld)-5-phenyl-1,3,4-thiadiazole (**T1**), 2-phenyl-5-((4,6,8-trimethylazulen-1-yl)diazenyl)-1,3,4-thiadiazole (**T2**) and 2-(azulen-1-yldiazenyl)-5-(thiophen-2-yl)-1,3,4-thiadiazole (**T3**) were generated and optimized by energy minimization using molecular mechanics force fields [5] with Spartan’18 software, Wavefunction, Inc. Irvine, U.S.A. [6]. Property computations were performed using Density Functional Theory (DFT) and hybrid B3LYP functional [7], 6-31G* polarization basis set [8], for equilibrium geometry at ground state.

Results and discussions:

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Figure 1 illustrates the investigated structures of the thiadiazole derivatives **T1**, **T2** and **T3** (a), with their predicted electrostatic potential map (b) and Mulliken charges (c).

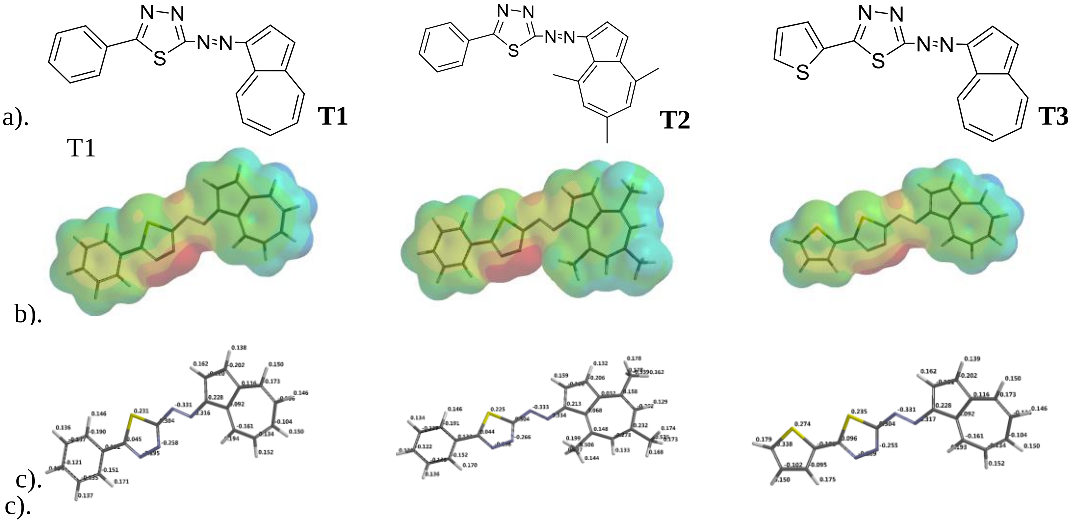

Fig. 1 a) structure of **T1**, **T2**, **T3**; b) electronic potential map of **T1**, **T2**, **T3**; c) Mulliken charges of **T1**, **T2**, **T3**.

The energy gap decreases in order: **T1**> **T2**> **T3**, the first being the most stable compound, with smaller reactivity. The substitution of the azulene moiety leads to increased reactivity and the introduction of a thiophen ring, adds a sulfur atom, increasing the capacity of interactions of **T3** compound.

Conclusions: Structural insights obtained by DFT computations as energy levels of frontier molecular orbitals prediction can be used to assess redox potentials.

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DENSITY FUNCTIONAL THEORY (DFT) AND THERMODYNAMICS CALCULATIONS OF L-VALINE AND L-SERINE

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Key words: Amino acids, density functional theory

Introduction: The goal of the present work was to evaluate the chemical reactivity of L-Valine and L-Serine using density functional theory (DFT) and thermodynamics modeling by calculating a series of molecular descriptors and properties of their optimized geometries.

Experimental and/or Modelling: The predictive calculations were achieved with Spartan software from Wavefunction, Inc. Irvine CA USA [1], hybrid algorithm B3LYP (the Becke's 3-term functional; Lee, Yang, Parr exchange Hybrid) [2, 3] and polarization basis set 6-31G (d, p) for equilibrium geometry at ground state in vacuum and in water, after minimization energy and geometry optimization.

Thermodynamic properties (zero-point energy, enthalpy, constant volume heat capacity, entropy and Gibbs energy) for these derivatives have been calculated and related to ligands electrochemical behavior. Reduction and oxidation potentials have been correlated to their calculated energy levels for LUMO and HOMO orbitals.

The results of this work were compared with those obtained for other amino acids, with different functional groups.

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Mn AND Fe IONS EFFECT ON Zn ELECTRODEPOSITION FROM ACIDIC LEACHING SOLUTIONS OBTAINED BY Zn-Mn SPENT BATTERIES RECYCLING

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Abstract*: High demand of Zn-Mn batteries include also high quantity of waste from batteries, and the necessity to recover the valuable materials. The aim of the present study is to evaluate the influence of Mn and Fe ions on Zn electrodeposition from acidic leaching solutions obtained by Zn-Mn spent batteries recycling.*

Key words: spent Zn-Mn batteries recycling, zinc recovery by electrodeposition

Introduction: The consumption of Zn-MnO_2 is steadily increasing due to popularity of electronic portable products that use those batteries as power source [1]. Due to high toxicity and increasing quantity, is necessary to recycle the batteries to recover the valuable metals and avoid pollution. Electrochemical selective recovery of Zn from acidic leaching bath obtained in the first steps of batteries recycling is an efficient method, but the other ions, like Fe and Mn, presented in the bath have an influence on the electrodeposition process and, therefore, it is necessary to study the influence of those elements [2].

Experimental: The study was performed using samples from a leaching bath obtained by dissolving the back powder from spend Zn-Mn batteries in H_2SO_4, and synthetic electrolytes with the concentration of the main 3 ions (Zn^{2+}, $Fe^{2+}$and Mn^{2+}) similar to the real solution. The electrolytes solutions are the pH = 0,63. The behavior of each ion in the solution was studied by cyclic voltammetry and cathodic electrodeposition of zinc in a divided electrochemical reactor. The cyclic voltammetry experiments were performed using a classic electrochemical cell with 3 electrodes: a vitreous carbon disk working electrode; Pb+ 1% Ag alloy plate as counter electrode and reference electrode - Saturated Calomel Electrode. The electrodeposition experiments were performed on an aluminum plate cathode.

Results and discussions: Cyclic voltammograms show the impact of Mn on Zn electrodeposition. At low concentrations of manganese, it has a positive effect on the electrodeposition of zinc, but at higher concentrations (> 1g/L), the

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effect is significant negative. The presence of Fe even in concentrations below 1 g/L it is strongly negative.

Conclusions: The presence of Mn^{2+} and Fe^{2+} in high concentrations inhibits the process of Zn^{2+}electroextraction from the solution. The current efficiency decreases by up to 12.9%.

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NEW PHOSPHATE CEMENT FOR THE IMMOBILIZATION OF HAZARDOUS WASTES WITH HEAVY METALS CONTENT

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Abstract: *Magnesium phosphate cement (MPC) hardens due to an acid-base reaction between magnesia (MgO) and orthophosphoric acid or an acid-phosphate solution. The main reaction products are the magnesium phosphates with binding properties. Due to several improved properties as compared with Portland cement (rapid setting and higher early and long-term mechanical strengths) MPC have numerous applications. Among these is the immobilization of hazardous wastes with heavy metals content.*

The main raw material used for the obtention of magnesium oxide is magnesite ($MgCO_3$), which is thermally treated at high temperatures in order to obtain dead burned magnesia (DBM); according to “Report on critical raw materials for EU” (2015) magnesite is a critical raw material. Therefore, in this paper new phosphate binders were obtained by the substitution of dead burned magnesia (DBM) with calcined dolomite. The phosphate binders were obtained starting from dolomite, previous calcined at 1400˚C, and sodium dihydrogen phosphate solution. The main properties assessed on these materials were the setting time and compressive strengths; these properties were compared with those of corresponding MPC based on DBM. These phosphate cements were used for the immobilization of two wastes with high nickel and lead content. The results obtained on the phosphate cements with waste content, after 28 days of hardening, using the leaching test presented in European Norm EN 12457-4:2003, show a good immobilization of Ni and Pb in phosphate cement based on calcined dolomite.

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THE INFLUENCE OF THE OPERATING PARAMETERS ON THE APPLICATIONS OF THE TITANIUM PASSIVATION PROCESS BY ANODIZING

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Short Abstract: *Preliminary studies on Ti6Al4V titanium alloy samples were performed in order to investigate the influence of the operating conditions of the anodizing process on the corrosion resistance and chromatic effect of the oxidized surface. The voltage of the power supply varied in the range of 10 – 30 V. Regarding the current density, it decreased continuously in the first 20 seconds, depending on the value of the supply voltage, then remain constant until the end of the electrolysis. As a result of the experimental results, a directly proportional increase of the amount of deposited oxide and, implicitly, of the thickness of the samples was observed, together with the increase of the power supply voltage. The direct relationship between the supply voltage, the thickness of the deposited film and the color of the titanium oxide layer obtained was also observed.*

Key words: titanium passivation, anodizing, operating voltage, colour durability

Introduction: Electrochemical passivation (anodizing) can be defined as the electrochemical growth of a solid film on the surface of a metallic/semi-metallic substrate, obtained by the anodic polarization of the substrate in an electrochemical cell. During anodizing, the electrons of the metal to be anodized flow to the cathode through the external circuit. Therefore the ionization of the metal atoms at the surface of the anode takes place. Subsequently, the anode surface reacts with oxygen-containing anions from the electrolyte, which will lead to the formation of a solid film, usually an oxide. Once the first layer of oxide film is formed on the substrate, the additional growth of the oxide film requires the metal cations, produced at the metal/film interface, to react with the oxygen-containing anions, inserted into the film at the film / electrolyte interface. Therefore, the growth of the oxide film is based on the transport of metal cations and/or O^{2-} anions over it [1]. Preliminary studies on Ti6Al4V titanium alloy samples were performed in order to investigate the influence of the operating conditions of the anodizing process on the corrosion resistance and chromatic effect of the oxidized surface.

Experimental: The electrochemical oxidation experiments were performed at room temperature, in 0.5M H_2SO_4 aqueous solution, having a pH of 0.3, at an average current density of 400 $A\cdot m^{-2}$. The supply voltage varied in the range of 10-30 V, being obtained from a stabilized DC power supply. The deposition time was about 80-90 seconds. The electrochemical cell used for the anodizing of titanium samples contains the Ti6Al4V titanium alloy working electrode, the negative porous graphite counter-electrode, and the saturated Ag/AgCl, KCl system as reference electrode, respectively.

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Results and discussions: The experimental data and the calculated results on anodized titanium samples at different supply voltage values in acid aqueous electrolyte at room temperature are presented in Table 1.

Table 1. Experimental results on anodized titanium samples at different voltages in 0.5M H_2SO_4 aqueous solution at room temperature

Titanium alloy samples	Supply voltage, V	Active surface, $10^4 \cdot m^2$	Deposited amount, g	Layer thickness, mm
1	10	2.4	0.0012	1.1442
2	20	2.8	0.0016	1.3076
3	30	3.2	0.0021	1.5017

The anodizing process may confer different colors to titanium oxide surfaces due to the interference between the light reflected at the oxide/air interface and the incident light part refracted by the transparent oxide film and then reflected by the metal/oxide interface. The result of this process is the appearance of different colors on the anodized surface [2, 3]. The shades generated depend on the spectral components of the incident light that are intensified or not by the interference, and thus on the difference of the optical paths due to the film thickness. [2, 3]. The colors of the anodized samples ranged from bronze to purple and light blue, respectively.

Conclusions: Titanium passivation is a simple, inexpensive and fast process that can be easily accomplished, presenting versatility in different industries.

The colouring process can be controlled by modifying the value of the supply voltage and hence the transparent oxide layer, thereby obtaining a range of colors.

Coloring is a clean process because it does not involve the use of paints and does not produce waste. The final products are biocompatible and have no residues.

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STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION OF SOME PLANT EXTRACT-MEDIATED METALLIC AND METAL OXIDE NANOPARTICLES

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Starting from the well-known methods of nanoparticles synthesis (e.g. chemical “top-down” and physical “bottom-up” techniques) recently, the growth of metallic and metal oxide nanoparticles in an eco-friendly approach by the use of natural materials (plant extracts) has gained considerable attention. This interest stems from the fact that, in addition to the characteristics of nanoparticles (especially size-and shape-dependent properties), the impact of toxic components into the environment is significantly reduced while the chemical stability of the compounds and their final properties are generally improved.

Consequently, a wide range of plant extracts from leaves, flowers and essential oils were employed into the manufacturing of green and sustainable nanomaterials. Besides their antibacterial, antimicrobial, and insecticidal properties in various therapeutic uses, these natural extracts work like chemical reducing agents of metallic salts and stabilizers of the systems, too [1]. For example, aromatic Thyme (*Thymus vulgaris*) was widely studied for its antifungal and antioxidant properties due to the occurrence of abundant active phytochemicals (thymol molecule), present both in plant extract and essential oil and known for its ability to kill bacteria by destabilizing the bacterial membrane. *Peppermint* is another abundant aromatic herb, widely use in medicine for its multifunctional properties including antibacterial, antifungal, antiviral, and anti-inflammatory activity. Both were successfully exploited in the green synthesis of nanoparticles (mainly Au, Ag and more recently, ZnO nanoparticles), when the plant extract was mixed up with the metal salts in solution, and the reaction was carried out completely in a few minutes [2,3]. As expected, various parameters affecting nanoparticles synthesis (like concentration of metal salt, pH, temperature, time, etc) and their final properties are under thoroughly investigation.

In the present study, an easy, efficient and eco-friendly method for the synthesis of metallic and metal oxide nanoparticles (Ag, Cu and ZnO nanoparticles) at room temperature is reported. *Thymus vulgaris* and *Peppermint* extracts were employed in the reactions as reducing and capping agents and the obtained nanoparticles

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were structurally and morphological characterized by various analytical techniques. The UV-Vis absorption spectroscopy evidenced the presence of the prepared nanoparticles in aqueous solution, while the crystalline structure and nanoparticles diameters were identified from the X- ray diffraction (XRD) pattern. Moreover, the surface morphology, the shape and size of the particles were evidenced by atomic force microscopy (AFM) and transmission electron microscopy (TEM), too.

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BOOK OF ABSTRACTS

SICHEM – 2020

C – Biomaterials and composites in chemical and biochemical applications (BCCBA)

1. Keynotes

RARE EARTHS DOPED ZIRCONIA NANOMATERIALS: SYNTHESIS, PROCESSING AND APPLICATIONS

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Rare earth oxides (REOs) are used in mature markets such as catalysts, glassmaking, metallurgy. During last decade increasing interest is to use REOs in newer, high-tech markets, including batteries, permanent magnets and coatings for energy harvesting applications. REOs may avoid grain size coarsening due to interface segregation in doped zirconia ceramics enhancing its thermo-mechanical properties. The use of ZrO_2 doped with mixed REO is considered as a challenge in designing of solid oxide fuel cells (SOFCs) membranes with high ionic conductivity, long-term high temperature performance stability, density, high long-term reliability (high strength, high durability). The properties of these materials depend on the nanopowders properties and are strongly influenced by the synthesis and processing routes.

Hydrothermal synthesis technology of nanomaterials produces high crystallization yield at high pressures and moderate temperatures in closed vessels, leading to important advantages such as controlled nucleation and growth of nanoparticles, high dispersibility, high compositional and granulometric homogeneity, low activation energy for sintering of the nanopowders. A key aspect is the ability to use small amounts of doping elements that may enhance the mechanical, thermal, chemical or optoelectronic properties of nanomaterials.

Here we present some results on the hydrothermal synthesis of nanocrystalline zirconia materials doped with one or more different rare earth oxides, including Ce, La, Y, Gd, Nd and Sm, at controlled temperature, pH and concentrations. XRD analysis of nanopowders obtained at different temperatures is used to evaluate the crystal lattice parameters, crystalline sizes and phase composition. The effect of doping zirconia with multiple rare earth oxides on the thermal stability of nanomaterials is analysed. Three applications of these nanopowders are further discussed: compact ceramics for SOFCs obtained by spark plasma sintering, porous materials obtained by powder extrusion additive manufacturing and coatings obtained by electron-beam physical vapour deposition.

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BOOK OF ABSTRACTS

SICHEM – 2018

C – Biomaterials and composites in chemical and biochemical applications (BCCBA)

2. Oral presentations

PRODUCTION OF DRUG REINFORCED ELECTROSPUN NANOFIBERS AS A DIABETIC WOUND DRESSING MATERIAL

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Abstract*:* *Drug reinforced nanofiber patches*

Key words: Diabetes, Anticoagulant, Anti-inflammatory, Antibiotic, Electrospinning method, Nanofiber, Wound dressing.

Introduction: Diabetes is among the most common chronic diseases of human age [1]. Due to the continuous increase in the number of diabetic patients, there is a need to develop a successful treatment system. Studies have been carried out to obtain anticoagulant, antibiotic and growth factor-loaded nanoscale wound dressing designed for this purpose.

Experimental and/or Modelling: *Reagents:* Polyvinyl Alcohol, Amoxicillin, Salicylic Acid, *Production of wound dressing:* In this study, Polyvinyl alcohol was used as matrix polymer for the treatment of diabetes. Salicylic acid is a group of drugs that prevent clots. Besides, it supplies antiinflammatory effect for wound healing. Amoxicillin was selected for antibacterial effect since it has antibiotic function against infections. Amoxicillin is used for antibiotic agent against infections. 13 wt(%)PVA was solved in distilled water and then drugs were added into this matrix solution. In the electrospinning process solutions were spinned to get the nanofiber patches. After the production, crosslink was done under 25%Glutaraldeyde vapour for 3 hours.

Results and discussions: To observe the efficiency of drugs for wound healing in PVA matrix, they were tested against the *Staphylococcus Aureus*, *Pseudomonas Aeruginosa,* and *Escherichia coli*. FTIR, SEM and DSC also performed to characterize the nanofiber patches to see the properties of nanofiber patches as a

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wound dressing. SEM images demonstrated that samples had uniform fiber distribution and beadles structure. The crosslink application increased the diameter of the nanofiber patches and didn’t disorganize the uniform microstructure of the nanofibers. The result of DSC was indicated that drugs can affect the thermal transitions points of the PVA matrix.

Conclusions: Drugs loaded uniform nanofiber patches were successfully fabricated with electrospinning method.

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IN VITRO BIOACTIVITY AND DEGRADATION EVALUATION OF BIOCOMPATIBLE AG DOPED HYDROXYAPATITE COATINGS

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Abstract*: A new insight into biocompatible hydroxyapatite-based coatings*

Key words: hydroxyapatite, acellular media, corrosion, antibacterial properties**,** magnetron sputtering

Introduction: The development of biomaterials is representing an emerging field, mainly due to improvement of their superior physical and mechanical properties, but also to the possibility of tailoring their degradation and bioactivity behavior [1]. The goal of this work was to evaluate through in vitro studies in acellular media the influence of Ag addition into the structure of hydroxyapatite (HAP).

Experimental: The HAP and Ag doped HAP coatings were deposited on Ti6Al4V alloys and Si substrates by using the RF-magnetron sputtering method. The in vitro and corrosion investigations were performed in three acellular media namely simulated body fluid (SBF), Dulbecco's Modified Eagle's medium (DMEM) and phosphate buffer solution (PBS) at 37 ± 0.5 ^{0}C. Also, it was investigated the coatings resistance to Staphylococus aureus, Salmonella Typhimurium and Candida albicans infection. All the coatings were exposed to SBF, DMEM and PBS media over a period of immersion ranging from 1 to 21 days and it were evaluated in terms of elemental, morphology and phase composition before and after the above-mentioned immersion period.

Results and discussions: For as-deposited coatings, the EDS analysis exhibited the formation of almost stoichiometric apatite, while the AFM images revealed smooth surfaces. By evaluating the mass evolution before and after immersion in acellular media one can note that the degradation rate is not affected by Ag addition. By comparing the coatings tested in SBF and DMEM, the addition of Ag leads to an improvement of corrosion resistance of HAP, while in the case of PBS the results indicated a corrosion resistance deterioration. After 1 and 7 days of incubation in media of suspensions containing C. albicans, a positive reaction was observed due the most probably insufficient Ag amount in the HAP coatings.

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Conclusions: The results showed that Ag addition into the HAP structure has enhanced both antibacterial and bioactive behavior.

Acknowledgements: We acknowledge the support of the Romanian National Authority for Scientific Research and Innovation, project COFUND-ERANET-RUS-PLUS-68/01.08.2018.

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CONTROLLED RELEASE OF RISPERIDONE LOADED POLYLACTIC ACID (PLA) MİCROPARTICLES USING ELECTROSPRAY

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Abstract: *Production of risperidone loaded microparticles for treatment of schizophrenia*
Key words: *Microparticle, polylactic acid (PLA), schizophrenia, risperidone, drug delivery, electrospraying*

Introduction: Schizophrenia is a neurological disease that effect mental status of patient and it is one of important disease among globally, considering the long-term experience of its symptoms and burden of disease of this disease. The current treatment approach is antipsychotic. Application of micro and nanoparticles has remarkably increased especially in the field of neurological diseases to overcome undesired effects and obstacles. [1].

Experimental and/or Modelling: *Formation of solution:* Polylactic acid (PLA) and dichloromethane (DCM) are chosen for solute and solvent respectively and formed particles loaded with risperidone and clozapine; *Production of microparticles:* Solution were sprayed on electrospray device by using various parameters at room temperature; *Evaluation of obtained microparticles:* Particles morphology were evaluated by SEM, FT-IR was used for molecular interaction between components, drug releasing test was carried out by UV spectroscopy and physical analysis such as density, surface tension, viscosity of particles was measured.

Results and discussions: It is seen that microparticles were optimized in 3 wt. % PLA in DCM solution concentration with 18 kV voltage, 20 µl / min flow rate by using electrospray method. Obtained microparticles were homogenous and had

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porous surface. The porous structure of the particles we create indicates that it has a good potential for use in the drug delivery system [2]. Risperidone and clozapine were loaded successfully into optimized microparticles.

Conclusions: Formed microparticles that are loaded with drug had a great potential to be used in treatment of schizophrenia by minimizing side effects and with maximum efficiency.

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CONTROLLED RELEASE OF DONEPEZİL-LOADED POLYVİNYL ALCOHOL (PVA) MİCROBUBBLES/NANOPARTİCLES USİNG MİCROFLUİDİC T-JUNCTİON DEVİCE

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Abstract: *Production of donepezil- loaded microbubble/nanoparticles for treatment of Alzheimer disease*

Key words: Microbubble, nanoparticle, microfluidic device, drug delivery, donepezil, alzheimer

Introduction: Alzheimer disease (AD) is a major cause of age-related dementia. AD is an incurable and progressive neurodegenerative disorder with a long presymptomatic period that is clinically characterized by cognitive and behavioural impairment, social and occupational dysfunction and, ultimately, death. In recent years, researchers have taken care to avoid the blocking of Aβ formation and its transformation into plaques in the treatment of AD. Currently, nanomaterials have great attention in effective drug delivery in AD due to their exclusive structural behaviors, extraordinary stability and particularly equipped aptitude to transporting into the blood-brain barrier of the human brain [1]. Drug delivery systems is one of the popular research area which aims at maximum therapeutic efficacy, drug-releasing stability, increased bioavailability with minimum side effects of the drugs [2].

Experimental and/or Modelling: *Formation of solution:* PVA solution was prepared and mixed with a magnetic stirrer for 1 hour at 90 ° C in 10 ml of distilled water for complete dissolution. Then donepezil was added to the PVA solution and mixed for 10 minutes. *Production of microbubbles/nanoparticles:* Monodisperse polymeric and donepezil-loaded nanoparticles at different concentrations were produced by exploding microbubbles using a T-junction device. *Evaluation of obtained microbubbles/nanoparticles:* Morphological analysis by SEM, molecular interactions between the components by FT-IR, drug

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release test by UV spectroscopy and physical analysis such as density, surface tension, and viscosity measurements were carried out for particles and solutions.

Results and discussions: The obtained microbubbles and nanoparticles had a smooth outer surface. When the microbubbles/nanoparticles were compared, it was observed that they were optimized with 0.3 wt.% polyvinyl alcohol (PVA) solution, 40 kPa pressure, and 110 µl /min flow rate. The diameters of the bubbles and particles were 110 ± 7 µm and 80 ± 7 nm, respectively. Donepezil was successfully loaded into nanoparticles in these optimized concentrations and parameters.

Conclusions: The resulting structures have a great potential to be used in the treatment of AD, especially in drug delivery studies, with nanoparticle forming ability.

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EFFECT OF FREQUENCY CHANGE IN THE HORIZONTAL MOVEMENT OF THE COLLECTOR ELECTRODE IN ELECTROSPINNING

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Electrospinning is one of the fantastic ways to fabricate nanofibers. Changing one or more of the parameters that make up the electrospinning setup allows obtaining fibers with very different morphologies. Different results have been obtained by changing the factors such as voltage difference, flow rate, electrode type etc. In this study, the effect of periodically changing the electrode distance and the displacement speed of the electrode, which has not been studied in the literature before, was carried out.

The experimental setup was built on the Scotch-yoke mechanism. A grounded flat conductor plate, driven by a dc motor whose speed was adjusted by a separate voltage source, was moved horizontally back and forth. The plate size was 5cm x 5cm and covered with aluminum foil. PLA (Mw) dissolved in chloroform was spun at a rate of 0.1 ml / h with a fixed electrode distance of 12 cm around 15 kV and a 3 cm stroke length. Changes in fiber diameters and distribution were determined with static, 15 Hz and 35 and 50 Hz systems. As the system speed increased, fiber diameters decreased.

Similar results have been obtained in the literature by amplifying the alternating current at 50-60Hz. Voltage fluctuates sinusoidally with time around zero volt due to the sequential movements of positive and negative charges in the system as in standard AC systems, which results in non-homogenous fiber diameters. However, changing the (tip-target) electrode distance *in situ*: (i) increases the fiber initiation by disturbing the Taylor cone at the tip of the nozzle , (ii) affects the evaporation time during the flight and the diameter thinning of the fiber, (iii) results in homogenous fiber diameter distribution compared to conventional AC amplification techniques.

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SELF-DOPED $Pr_{1-x}MnO_{3+\delta}$ PEROVSKITES: ELECTRON STRUCTURE AND MAGNETIC PROPERTIES

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Abstract: *Local electronic and crystal structures of self-doped $Pr_{1-x}MnO_{3+\delta}$ (x=0.0 and 0.2) perovskites are studied by x-ray absorption spectroscopy at Mn K-edge, and by soft x-ray spectroscopy at Mn L- and O K-edges. In high vacancy-doped x=0.2 oxide the lattice accommodates the distortions by the formation of trivalent manganese anti-site defects in the praseodymium position. The intensity of the $2p_{3/2}$ and $2p_{1/2}$ peaks increases with x correlating with the increase in magnetization and that results from the change in hybridization between the O 2p and Mn 3d orbitals. Decrease in oxygen and praseodymium contents is observed with Fourier transform of EXAFS spectra.*

Key words: Self-doped manganites; Electron structure; Magnetic properties; XANES; EXAFS

Introduction: Interesting properties of vacancy-doped $Ln_{1-x}MnO_{3+\delta}$ (LMO) open a way for their applicability [1,2]. The LMO features display the peculiarity caused by their cation deficient structure and anti-site defects formed at high value of vacancies. We report the study of $Pr_{1-x}MnO_{3+\delta}$ (x=0.0, 0.2) perovskites to shed light on the connection of magnetic properties and electronic structure.

Experimentals: The samples were synthesized by the nitrate method using Pr_6O_{11} oxide and metallic manganese. XAFS measurements, including x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS), were performed at Pohang Light Source (PLS), Republic of Korea.

Results and discussions: According to Mn *K*-edge XANES measurements the average manganese valence (v_{Mn}) equaled to ≈3.2 for both samples. The v_{Mn} value allows deducing the oxygen content on the base of the electroneutrality principle, and the deduced δ are 0.1 and -0.2 for the samples with x=0.0 and 0.2, respectively. At a high level of lattice vacancies, as in the Pr02 sample, the anti-site defects in Pr-position could be formed (see also [3] where the $La_{1-x}MnO_{3+\delta}$ oxides were studied). The above anti-site formation should lead to a change in the Mn *K*-edge line shape if the defects are created by the divalent manganese [4].

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But, no changes are observed in the line shape with increasing x. This evidences that the anti-site defects are formed by trivalent manganese, which agrees with [5] though in [6] the divalent manganese was reported to be responsible for these defects. Fourier transform of the EXAFS spectra shows the decrease of the intensities of the backscattering of photoelectrons by the oxygen and praseodymium positions coordination spheres with x increase manifesting the decrease of oxygen and praseodymium contents.

Mn L – edge spectra display the splitting into $L_3(2p_{3/2})$ and $L_2(2p_{1/2})$ peaks caused by the core hole spin-orbit coupling. Intensity of the $2p_{3/2}$ and $2p_{1/2}$ peaks increases with x. The results show that the change of magnetic properties, studied in [7], is caused by the change of level of hybridization of Mn 3*d* and the O 2*p* states. The position and intensity of the O *K*-pre-edge peak are the same for both samples indicating the invariable Fermi level with x increasing.

We discuss also the difference in the relation of magnetic properties to electron structure in self-doped oxides, and manganites doped in *A*- and *B*-positions of perovskites ABO_3 cell.

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BIODEGRADABLE COATINGS WITH CONTROLLABLE DEGRADABILITY

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Short Abstract: *The effect of Ag addition on in vitro bioactivity and degradation characteristics of hydroxyapatite in SBF, DMEM and PBS*

Key words: Hydroxyapatite, Magnetron Sputtering, Corrosion Resistance, Biocompatibility

Introduction: Nowadays great efforts are dedicated to the development of biomaterials with tuneable properties. In the clinical practice, there is a massive demand for implants with high resistance to infection, especially following a short period after insertion. Thus, the challenge is to find a solution for improving the antibacterial properties of implants, without affecting their osseointegration abilities [1].

Experimental: In vitro bioactivity and degradation characteristics of hydroxyapatite doped with Ag, prepared by a RF-magnetron sputtering, was investigated in simulated body fluid (SBF), Dulbecco's Modified Eagle's medium (DMEM) and phosphate buffer solution (PBS) over a period of immersion at 37 ±0.5°C ranged from 1 to 21 days. The corrosion investigations in all three media were carried out at 37±0.5°C. For the deposition, three cathodes with 1” diameter were used: two manufactured of hydroxyapatite and one manufactured of Ag (99.9% purity). The coatings were deposited on Ti6Al4V alloy and Si wafers.

Results and discussions: The coatings behaviour is modulated with respect to the testing media and indicated that the Ag addition into hydroxyapatite has enhanced the general behaviour of HAP by either preventing and/or reducing dissolution of the HAP in SBF and DMEM solutions, while in PBS media the Ag addition contributed to a very slow degradation of hydroxyapatite. Nevertheless, in PBS, the degradation process is more active for the Ag doped coatings, evidencing a better stability after a short time of immersion. The EDS analysis demonstrated that the deposited coatings were mainly composed of calcium and phosphorus, their ratio was ranged from 1.69 to 1.71.

Conclusions: It can be said that the Ag addition into HAP enhances the overall chemical stability and behaviour in acellular media.

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SYNTHESIS, CHARACTERIZATION AND SORPTION PERFORMANCES OF CHITOSAN-BASED COMPOSITE CRYOGELS

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Abstract: Heavy metal ions (HMIs) have been excessively released into the environment through industrial wastewaters due to the rapid industrializations, which has created a major global environmental concern. The industrial effluents contain toxic HMIs like copper which is an essential trace element for human being, but excess amount (usually higher than 1 mg/L) is very harmful. It can cause life threatening complications which inter alia, include kidney damage, hemolysis, respiratory problems, and severe vomiting [1]. Several treatment technologies for HMIs removal have been investigated extensively, such as chemical precipitation, ion-exchange, adsorption, membrane filtration, electro-chemical treatment technologies, etc. [1]. Among these methods, adsorption is generally preferred because of its high efficiency, availability, low cost, simplicity of design and easy operation, and the green adsorbents derived from natural polymers were more attractive [2]. Among the natural polymers adsorbent exploration, chitosan (CS), an abundant nontoxic biopolymer consisting of β-(1,4)-2-amino-2-deoxy-D-glucose units, had been widely studied owing to its effectiveness in contaminates removal from wastewater. CS could uptake HMIs from aqueous medium through adsorption due to its abundant -NH_2 and –OH groups [3]. The objectives of this study are (i) to prepare novel composite sorbents based on clinoptilolite particles entrapped within CS cryogels by combining the ion-imprinting and ice-templating methodologies; (ii) to systematically evaluate the effects of several parameters such as the solution pH, sorbent dose, number of sorption/desorption cycles, and temperature on the sorption performance of CS-based composite cryogels; (iii) to evaluate the selective sorption performance of CS-based composite cryogels using binary, ternary or multi-component synthetic mixtures of Cu^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+} and Cr^{3+} ions [4]. The tube-like morphology with interconnected unidirectional oriented pores of CS-based composites ensured a fast access of all HMIs to the functional groups of network, the equilibrium sorption being reached in only 150 min. The modeling of thermodynamic and kinetics experimental data indicated a spontaneous chemisorption process [4].

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BONE AUGMENTATION WITH NATURAL AND SYNTHETIC MATERIALS

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Abstract: *The analysis of filling a critical bone defect using different grafts.*

Key words: Demineralised bone, collagen sponge, polylactic acid

Introduction: Obtaining of a suitable graft for regeneration of bone tissue defects is a current problem notwithstanding existing contemporary techniques [1].

Experimental and Modelling: The rabbit bones were demineralised in 0.6 M HCl and cutted in discs of 8 mm in diameter. The collagen was extracted from bovine Achilles tendons. The 1% collagen suspension was prepared in 0.5M acetic acid and lyophilized at 0.05µbar. The obtained collagen sponge (CS) was crosslinked in 25% glutaraldehyde vapors (Sigma. USA). With a 3D printer (Ultimaker 2+ Extended. Netherlands) from polylactic acid (PLA) (Verbatim. UK), grille similar discs were printed. The prepared materials were transplanted in 8 mm diameter defects on rabbits skull (n=3). Demineralized bone discs were transplanted intact (DBD) and minced (DMB). As a control group served autograft minced bone from iliac wing. The animals were euthanized at 12 weeks after transplantation.The cranial bones were examined by computed tomography (CT), scanning electron microscopy (SEM) and histologically.

Results and discussions: At CT scan of the skulls, the complete closure of the bone defects was obtained in DMB allografts treated group. In the groups treated with DBD and the control, the defects were partially or incomplete restored, and in groups treated with CS and PLA discs the filling of defects was absent. At SEM, the group with DMB had a homogeneous bone structure, the DBD treated group and control group had a inhomogeneous structure, with the presence of unchanged pieces of grafts. In CS group, a membrane structure was present, and in PLA disc group, the graft remained unchanged. At histological examination in all cases with bone material utilisation, a new bone formation was present around existing bone trabeculae. Between the PLA discs grille spaces the restricted areas of calcifications were present. In all cases the increased amounts of collagen fibers, arranged in compact bundles, often linear but also at random were present, especially in the CS group.

Conclusions: The DMB allografts had higher regeneration potential compared to control group and other bone and synthetic materials.

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FIBROBLASTS ISOLATION BY VOLUMETRIC REGULATION CYCLES

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Abstract*: A simplified method of fibroblast isolation*

Key words: Fibroblasts isolation, explant, volumetric regulation cycles

Introduction: Fibroblasts are widely used cells for *in vitro* researches. The explant method is commonly used in fibroblast isolation. Various laborious techniques for explant attaching to the cell culture surface are described, such as fetal bovine serum, type I collagen, gelatin, fibronectin [1] and even by attaching tissue to the edges of defects created in the cell culture surface [2].

Experimental and Modelling: From a rabbit (n=3) piece of dermis was taken (32±8 mm^3) and placed in 15 ml steril tube with culture medium, composed of Fibroblast basal medium with 10% FBS (Lonza, Belgium). In the laboratory the dermis, in sterile conditions was washed with HBSS (Sigma. USA) and placed in a 12-well plate with 3 ml of culture medium. The explant was incubated for 2-3 days at 37°C, 5% CO_2 in a humid environment. After removing culture medium, back was poured enough medium to keep the explant moist and attached to the bottom of the well. The medium was changed daily until the number of attached cells was sufficient for cell culture, followed by explant transfer to another well with 3 ml of medium. The isolation cycle was stopped if on the well bottom the the cells were missing after 5 days. At the confluence of 70-80% the cells were subcultured in cell culture flasks by $4\text{-}10 \times 10^3$ cells/cm^2. The isolated cells were identified as fibroblasts by histochemical techniques with Hematoxylin-Eosin and Masson trichrome in cell culture flasks after 21 days of cell culture in overconfluence. As a control served rabbit bone marrow mesenchymal stem cells.

Results and discussions: For cell isolation 4±1 cycles were performed. The isolated cells were subcultured for 4±1 days, obtaining in a period of 26±5 days $13{,}7 \times 10^6 \pm 3.1 \times 10^6$ cells. Hematoxylin-Eosin and Masson trichrome staining allowed identification of a secreted extracellular matrix characteristic for fibrous tissue that was stained red and deep blue respectively, while staining of the matrix secreted by the control group was absent.

Conclusions: The used method of fibroblasts isolation is safe, cheap, efficient and allows isolation of a large number of cells in a short period of time.

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BIOBASED POLYFARNESENE- MOLECULAR DYNAMICS AS STUDIED BY BROADBAND DIELECTRIC SPECTROSCOPY AND OSCILLATORY SHEAR RHEOLOGY

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Abstract*: A new type-A polymer, whose normal mode relaxation is strongly dependent on molecular weight.*

Key words: Biobased polyfarnesene, Broadband dielectric spectroscopy, rheology

Introduction: Along with the rapid natural gas feedstock growth in support of chemical manufacturing, interest in creating chemicals and polymers from renewal biological sources has continued and grown in popularity. One such biobased molecule is trans-β-farnesene (7,11-dimethyl-3-methylene-1,6,10-dodecatriene), produced by yeast fermentation of sugar feedstocks. [1, 2].

Experimental and/or Modelling: Purified trans-β-farnesene (High Performance BioFene, Amyris) was anionically polymerized in heptanes using n-butyl lithium as the initiator, as described in more detail in [2]. The polyfarnesene (PFs) under investigation were acid-neutralized (leading to nonfunctional end groups), and the resulting lithium salts were filtered prior to solvent removal via steam stripping (under N_2). This synthetic procedure leads to a chain microstructure composed of primarily 1,4-(cis, trans)-addition products (i.e., C11 pendant groups) and ∼10 mol % 3,4-addition products (C13 pendant units), as determined from 1 H NMR. [2] No 1,2-addition products were detected using Fourier transform infrared spectroscopy. Broadband dielectric spectroscopy (BDS) and oscillatory shear rheology were used to investigate the molecular weight dependence of the dynamics of bulk amorphous PF.

Results and discussions: Figure 1 shows the dielectric α, β and normal mode (n) relaxations processes as a function of 1000/T. The low-temperature processes (β) coincide for all PFs with mean activation energy (Ea) = 28 kJ/mol. The origin of this relaxation is associated with PF side group motions in the glassy state. The α

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relaxations (dynamic T_g values) are observed at higher temperatures, and the relaxation frequencies (ω_α) follow Vogel−Fulcher−Tammann (VFT) temperature dependence, typical for cooperative processes. VFT fits of ω_α versus 1000/T were extrapolated to 100s to estimate T_g values from dielectric spectroscopy.

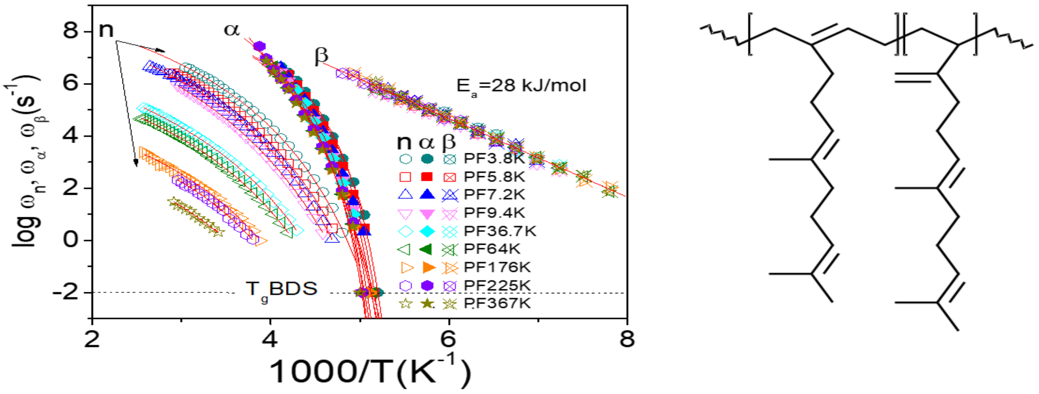

Fig. 1 Mean relaxation rates for the glassy state β relaxation, ω_β, the segmental process, ω_α, and the normal mode (NM) relaxation (ω_n) for PFs with different M_w vs. inverse temperature. The solid lines are fits using the VFT and Arrhenius equations. Polyfarnesene chemical structure: consisting primarily of 1,4 (cis, trans) addition products (C11 pendant groups) and ~10 mol% 3,4 addition products (C13 pendant units).

Unlike the α- and β- processes, the highest temperature dielectric process is very strongly dependent on PF molecular weight (Fig.1). Considering the net parallel dipole moment contribution along the PF chain backbone, we assign this process to global end-to-end chain relaxation (the dielectric normal mode). VFT dependence is observed for the normal mode, in keeping with the cooperative nature of this process.

Conclusions: BDS establish PF as a type-A polymer, whose normal mode relaxation is strongly dependent on molecular weight, providing a compliment to melt rheology for exploration of PF global chain dynamics (Fig.1). [1-4].

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GEMCITABINE-CONJUGATED IRON OXIDE NANOPARTICLES FOR *IN VITRO* POTENTIATED CYTOTOXIC EFFECTS IN HUMAN CANCER CELLS

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Abstract*:* *Iron oxide nanoparticles were conjugated in situ with Gemcitabine chemotherapy drug and the in vitro potentiated cytotoxic effects were determined in human breast cancer cells and human hepatocarcinoma cells, but not in human osteosarcoma cells.*

Key words: Gemcitabine, iron oxide nanoparticles, cancer treatment, cytotoxicity.

The purpose of this study was to increase the cytotoxic effects of Gemcitabine (GEM) chemotherapy drug in cancer cells by its conjugation to iron oxide nanoparticles (Fe_3O_4 NPs). [1]

Fe_3O_4 NPs were obtained using a modified room temperature co-precipitation method and *in situ* conjugated with GEM chemotherapy drug with no additional linkers (Fe_3O_4@GEM). The physico-chemical characterization was done using relevant methods to assess the structure and composition of the nano-conjugate: X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy, high-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED); the functionalization of the NPs was evidenced through HR-TEM and thermogravimetric analysis (TGA).

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The *in vitro* cytotoxic effects were assessed for human tumor cells of breast cancer (BT474), hepatocellular carcinoma (HepG2) and human osteosarcoma cells (MG-63) quantitatively using a tetrazolium-salt viability assay (MTT) and qualitatively through morphological investigations (fluorescence microscopy and SEM). The hemolytic potential of Fe_3O_4@GEM NPs was tested *ex vivo* on human blood from three healthy donors and the *in vivo* biocompatibility was determined in mice models. [1]

A high crystallinity and a single-phase mineralogical composition of the resulted NPs was determined through XRD and confirmed through SAED and HR-TEM. Morphological investigations showed the obtaining of core-shell-like nanoparticles with physical dimensions less than 20 nm and hydrodynamic diameters of 176.9±15 nm. These highly stable Fe_3O_4@GEM NPs (zeta potential=−32.69 mV) proved to include 6.8% GEM and to release it during 15h. [1]

GEM-conjugated Fe_3O_4 NPs are promising candidates for increasing chemotherapy drug concentrations in tumors and therefore improving its anti-tumor effects [1].

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BIOLOGICAL EVALUATION OF CHITOSAN BIO-MIMETIC ELECTROSPUN NANOFIBERS EMBEDDED WITH ARGININE AND PROPOLIS

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Abstract*:* *New nanofibrous mats derived from chitosan and PEO were subjected to biological evalution using spectrophotometric assays for proving the antioxidant activity and anti-hemolitic potential.*

Key words: electrospun nanofibers, wound healing, chitosan, arginine, propolis

Introduction: Nanotechnology offers a superlative approach to accelerate the healing of acute and chronic wounds by stimulating the various phases of healing. The aim of this paper is to develop new electrospun nanofibers based on chitosan and polyethylene oxide and to evaluate their antiradical ability as new dressing materials in the treatment of wounds [1].

Experimental and/or Modelling: The matrices' preparation was done in two stages: (i) the formation of 3 biopolymeric solutions starts by dissolving CH and PEO in 50% acetic acid by stirring at room temperature. The two solutions will be mixed in appropriate ratios, then, over the resulting mixture, the active substances (arginine and propolis) were added and stirred until a homogeneous solution is obtained; an INOVENSO nanospinner was used, a needle syringe of appropriate size filled with the polymer solution and then different values of flow-rate, applied voltage and also different distances from the tip of the syringe to the collecting plate were applied, depending on each sample [2].

Results and discussions: Following the research, new electrospun-nanofiber materials were evaluated, based on chitosan and various active substances (arginine and propolis), in terms of antioxidant activity, using 2 in vitro tests and in terms of anti-hemolytic potential, using spectrophotometric assay. After analyzing the data obtained, it was concluded that nanofibers with propolis incorporated as a solid substance and not a tincture obtained the best results.

Conclusions: The studies and results obtained justify the evaluation of the biological, antibacterial and pro-healing potential in the treatment of various

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wounds, starting from the antibacterial/antioxidant effects of chitosan and the beneficial role of topical propolis applied in the treatment of wounds.

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BOOK OF ABSTRACTS

SICHEM – 2020

C – Biomaterials and composites in chemical and biochemical applications (BCCBA)

3. Poster presentations

NEW CERIUM SUBSTITUTED HYDROXYAPATITES FOR BIOLOGICAL FLUORESCENCE LABELING

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Key words: Hydroxyapatite, Cerium, fluorescence

Introduction: Several lantanum ions, such as Eu^{3+}, Tb^{3+}. Gd^{3+}, La^{3+}, Ce^{3+}, etc., have been explored as promising candidates for biomedical applications such as imaging, immunocytochemistry, DNA detection [1-3]. Among them, Ce^{3+} ions, well recognized to exhibit good antibacterial properties and with an important role in preventing caries [4], has a special place in biomedical applications [5].

Experimental and/or Modelling: Herein, we report the new biocompatible photoluminescent ceramic materials: cerium doped hydroxyapatite (Ce^{III}Hap and Ce^{IV}HAp) obtained by co-precipitation procedure, at low temperature. Thus, were selected different Ce^{3+} and Ce^{4+} concentrations (xCe = 0.05, 0.1, 0.25, 0.5 and 1.0), starting from calcium (calcium nitrate), cerium (III) (cerium nitrate), cerium (IV) (amonium cerium nitrate) and phosphorus (diammonium acid phosphate) salts. The Ca / P atomic ratio was 1.67 and the Ce / (Ce + Ca) atomic ratio ranged from 0 to 10%.

Results and discussions: Characterization techniques like X-ray diffraction (XRD), Fourier transform infrared (FT-IR), UV-Vis spectroscopy and photoluminescence (PL) spectra, scanning electron microscopy (SEM) were used to determine structural and morphological parameters.

The emission spectra for both Cerium series are similar. As the percentage of Ce in the sample increases, the fluorescence intensity decreases. The decrease is more accentuated in the tests with Ce than in those with Ce (IV). The differences are given by the intensity of certain bands that are attributable to specific types of network faults and recombination processes of positive electron-empty pairs.

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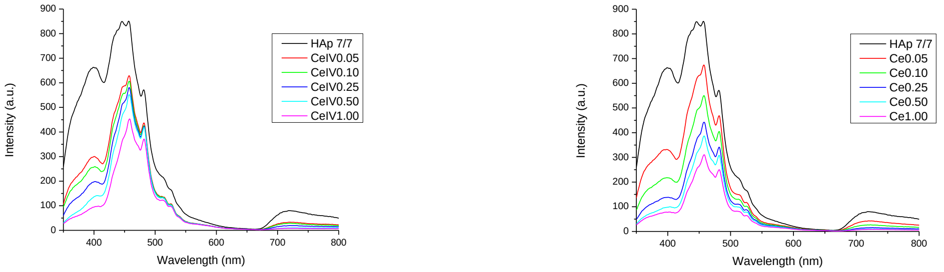

Fig. 1 Fluorescence spectra for HAp, recorded with 7/7 slots and HApCeX, X_{Ce}= 0.05, 0.1, 0.25, 0.5, 1.

Conclusions: The aim of the present study was to obtain nano-hydroxyapatite doped with Cerium by using a simple synthesis method (co-precipitation method) and, subsequently, physico-chemical characterization due to the fact that the material obtained can be used in florescence labeling.

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NOVEL MATERIALS BASED ON NATURAL POLYMERS FOR DRUG DELIVERY

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Abstract: *A new material was obtained by dissolving of cellulose, chitosan and polyurethane in 1-ethyl-3-methyl-imidazolium chloride ([EMIm$^+$Cl$^-$]).*

Key words: Cellulose, Chitosan, Polyurethane, Lignin, Ionic liquid, Ketoconazole

Introduction: Cellulose, chitosan and lignin are promising natural polymers for various applications. These polymers need further exploration as they attracted a lot of attention due to their antioxidant and antimicrobial properties [1-3]. Polyurethane is a biocompatible synthetic polymer often used for its elasticity. In this work, we synthesised and characterized new materials for potential drug delivery.

Experimental: *Reagents:* [EMIm$^+$Cl$^-$], chitosan and cellulose were purchased from Sigma Aldrich, while lignin and polyurtehane were obtained in the lab; *Preparation of composite films:* Cellulose (CEL), chitosan (CS), polyurethane (PU) in a ratio=1:0.25:0.25 were dissolved in [EMIm$^+$Cl$^-$] (IL) under magnetic stirring at 100 ^{0}C. Lignin (L) and ketoconazole (K) as fillers were added into above mentioned polymeric matrix.

Results and discussions: The obtained materials were characterized by Scanning Electron Microscopy (SEM), Fourier-transform Infrared Spectroscopy (FTIR) and mechanical testing. The recorded FTIR spectra were used to calculate Total Crystalline Index (TCI), Lateral Order Index (LOI) and Hydrogen Bounds Intensity (HBI). An increase in the degree of ordering, as well as an improvement of the HBI value for all materials, as compared to the polymeric matrix was registered (Table 1).

Tabel 1. Total Crystalline Index (TCI), Lateral Order Index (LOI) and Hydrogen Bound Intensity (HBI) values obtained from the FTIR spectra analysis of the biomaterials

Biomaterials	**TCI=A_{1376}/A_{2902}**	**LOI=A_{1437}/A_{899}**	**HBI=A_{3336}/A_{1336}**
CCP*	2.349	1.765	3.161
CCPOL*	1.159	1.959	4.511
CCP-K*	1.562	3.093	5.835
CCPOL-K*	1.134	2.523	5.946

*CCP = Cellulose-chitosan-polyurethane;
CCPOL = Cellulose-chitosan-polyurethane-organosolv lignin;
CCP-K = Cellulose-chitosan-polyurethane-ketoconazole;
CCPOL-K = Cellulose-chitosan-polyurethane-organosolv lignin-ketoconazole.

Having in mind the potential applications of the developed materials, ketoconazole as antifungal agent was used. Data from Table 2 evidence that the

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addition of organic lignin increases the inhibition rate of some microbial agents in the polymeric matrix, while samples containing ketoconazole show a 97-100% inhibition rate for all microbial agents.

Tabel 2. Growth inhibition rate against three different microbial agents performed on the developed materials

Biomaterials	CFU		Inhibition	CFU		Inhibition	CFU		Inhibiton
	100µl		*Escherichia coli*	100µl		*Candida albicans*	100µl		*Staphylococcus aureus*
	ATCC 25922 Escherichia coli			*Candida albicans 90028*			*Staphylococcus aureus 25923*		
	Control sample+ Sample initial number of colonies	24 h	%	Control sample+ Sample initial number of colonies	24 h	%	Control sample+ Sample initial number of colonies	24 h	%
Control sample	287	287	0	255	255	0	293	293	0
CCP	287	1	100	255	63	75	293	3	99
CCPOL	287	6	98	255	34	87	293	46	84
CCP-K	287	0	100	255	0	100	293	10	97
CCPOL-K	287	0	100	255	0	100	293	0	100

Also, the results of the drug release tests show that lignin addition into the polymeric matrix has a positive effect on the release of ketoconazole (Figure 1).

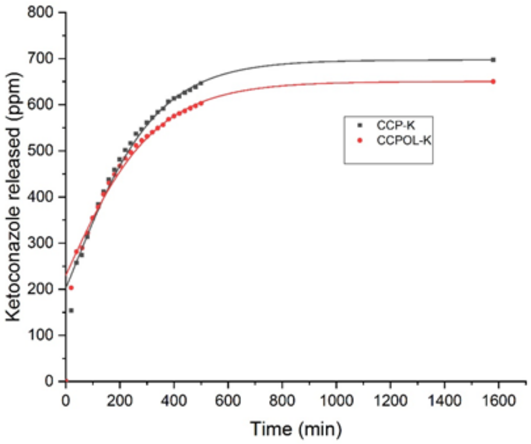

Fig. 1. The graphic of controlled release tests of ketoconazole at pH=7.2 for 30h

Conclusions: It was found that the addition of L increased the inhibition rate of some microbial agents in the polymeric matrix and improved the release of K.

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CHITOSAN/GRAPHENE OXIDE NANOCOMPOSITE MEMBRANES AS ADSORBENTS WITH APPLICATIONS IN WATER PURIFICATION

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Abstract: *The scope of this article is to develop composite membranes using chitosan (CS) and graphene oxide (GO) as adsorbents for the removal of inorganic pollutants, such as heavy metal ions, particularly* Pb^{2+}*, from aqueous solutions. GO was obtained by modified Hummers method and blended with CS solution. The introduction of EDTA compound in CS/GO suspension lead to an increased adsorption capacity of CS/GO for elimination of heavy metals by forming stable chelates with them. The synthesized membranes were examined by IR spectroscopy and SEM and the adsorption behaviour of* Pb^{2+} *from aqueous solutions using CS/EDTA/GO membranes was evaluated using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Adsorption performances were studied by monitoring the concentration of the* Pb^{2+} *against adsorption period at an initial content of the adsorbent. The maximum adsorption efficiency of* Pb^{2+} *metal ions reached 767 mg/g for CS/EDTA/GO, 0,1%, 889 mg/g for CS/EDTA/GO 0,3%, 970 mg/g for CS/EDTA, 853 mg/g for CS and 1526 mg/g for GO. These findings show promising potential for CS/EDTA/GO membranes as effective adsorbent materials for the removal of heavy metal ions in water.*

Key words: chitosan, graphene oxide, EDTA, lead, nano-adsorbent

Introduction: In the last years, the presence of toxic pollutants in wastewater has become a concerning problem affecting the ecological environment and human health [1]. Of all methods used for removing pollutants, adsorption is the most significant process [2, 3]. This study examined the adsorption process of CS/EDTA/GO membranes in the elimination of Pb^{2+} ions from wastewater.

Experimental and/or Modelling: *Preparation of CS/EDTA/GO films:* Known amounts of GO were dispersed in 10 ml CS/EDTA and treated by mild sonication for 15 min. The composite membranes were dried in the oven for 24h at 40°C; *Adsorption experiments:* The adsorption experiments were realized by taking a fixed mass of dry film (20 mg) in 15 ml of metal solution. 1 ml of each mixture was collected from time to time (10, 20, 30, 45, and 60min).

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Results and discussions: The inner structure of CS/EDTA/GO determined by SEM is much denser than the inner structure of CS which leads to an increasing in the mechanical strength of the membranes [4, 5]. Irregular, wrapped zones assigned to the presence of GO platelets can be seen, that can form during solvent evaporation [6]. Lead can form strong complexes with oxygen-based functional groups such as -COOH and -OH. The functionalization of chitosan with EDTA and loading with GO sheets can lead to an increase in the adsorption capacity against heavy metals. the adsorption capacity achieved the equilibrium state at ~20 min (Fig. 1), the films having a maximum adsorption capacity of >99% when a standard solution of Pb^{2+} is used (15ml, 100ppm) for each 20mg of adsorbent.

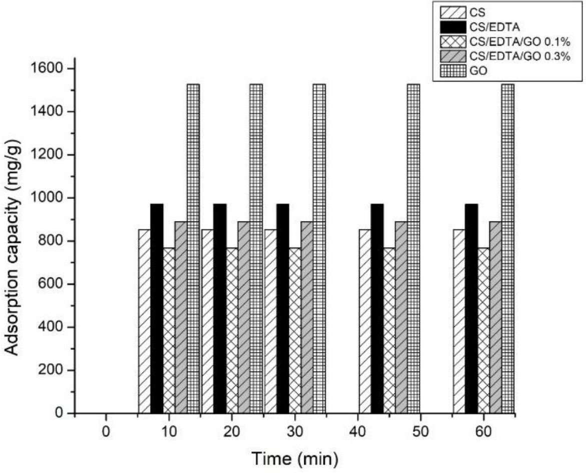

Fig. 1 Sorption capacity of the membranes: CS, CS/EDTA, CS/EDTA/GO 0.1%, CS/EDTA/GO 0.3% and GO sheets

Conclusions: Hydroxyl and carboxyl groups from both GO and EDTA can make CS/EDTA/GO ideal adsorbents for the removal of metal ions from wastewater.

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SYNTHESIS AND CHARACTERIZATION OF A MULTIFUNCTIONAL NANOCOMPOSITE MATERIAL BASED ON Fe_3O_4 AND HYDROXYAPATITE FOR BONE CANCER THERAPY

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Abstract: *The present paper aims to approach a relatively new concept regarding the combination of hyperthermia treatment with chemotherapy for bone cancer using a nanocomposite material consisting of hydroxyapatite (HAp), iron oxide (*Fe_3O_4*) and a therapeutic agent (carboplatin-CPt). The synthesized materials were characterized by way of IR spectroscopy, X-ray diffraction, scanning electronic microscopy, vibrating sample magnetometry and particle size distribution.*

Key words: nanocomposite, magnetite, hydroxyapatite

Introduction: The properties of each material used for obtaining the target antitumor system represent the basis for approaching this strategy as a feasible application for bone cancer treatment [1]. Hydroxyapatite is a versatile material with a wide variety of applications in bone related diseases, including drug delivery systems, while Fe_3O_4 is already involved in clinical trials for hyperthermia [2, 3].

Experimental and/or Modelling: In order to obtain the complex system of HAp-CPt-Fe_3O_4, we adopted a gradually synthesis. More precisely, individual syntheses of the component materials were obtained by co-precipitation method, followed by obtaining HAp-CPt systems and combining the latter one with Fe_3O_4. Carboplatin represented 10% of the total mass of the HAp / AtAg antitumor system and Fe_3O_4 represented 5% of the final composite material.

Results and discussions: SEM images show a very good homogeneity of the component phases in the final system with both acicular morphology of hydroxyapatite and spherical morphology specific to magnetite. Magnetite nanoparticles synthesized in this study have the necessary magnetic properties to be used in biomedical applications according to VSM measurements. The adsorption of carboplatin is evidenced by a decrease in intensity of the peaks corresponding to hydroxyapatite in the diffractograms related to HAp-CPt compared to a pure HAp diffractogram.

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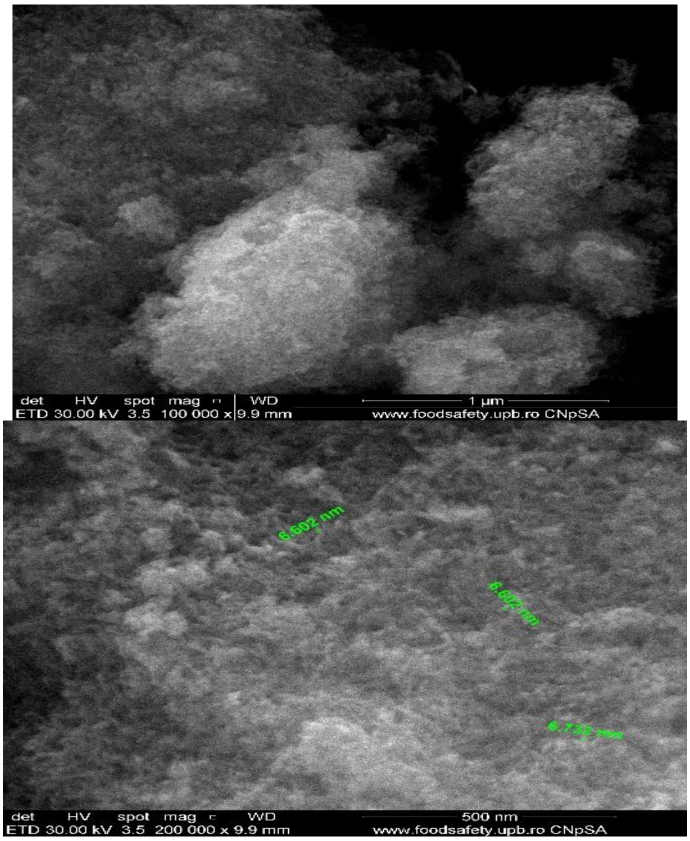

Fig. 1 SEM micrographs of HAp-CPt-Fe_3O_4

Conclusions: At present the nanocomposite system addressed in this paper has the desired physico-chemical characteristics for their application in the treatment of bone cancer.

Acknowledgement:

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BACTERIAL CELLULOSE DRESSDINGS LOADED WITH ANTIBIOTICS FOR THE TREATMENT OF WOUNDS

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Abstract: *Bacterial cellulose dressings are used in the treatment of skin wounds due to their unique characteristics. The wet environment of these dressings is an important feature that ensures an efficient healing. Bacterial cellulose has multiple characteristics for use as a dressing, but doesn't have microbial activity and to enhance these antimicrobial performance, bacterial cellulose dressings have been loaded with amoxicillin and bacitracin as antibacterial agents. Infrared characterization and thermal analysis confirmed the binding of bacterial cellulose to the drug. Hydration capacity showed good hydrophilicity, a desired property for efficient dressings. The results confirmed the presence of the drugs in the structure of bio-cellulose dressings as well as the antimicrobial efficiency against Staphylococcus aureus and Escherichia coli. The antimicrobial assessments were evaluated by contacting these dressings with the above mentioned bacterial strains and evaluating the growth inhibition of these microorganisms.*

Key words: Bacterial Cellulose; skin wounds; effect antimicrobial; drug delivery, dressings

Introduction: An ideal wound dressing should facilitate a suitable healing environment, allow rapid tissue regeneration, reduce pain and prevent infection during the healing process [1, 2]. Bacterial cellulose has attracted considerable interest in many areas, but especially in the medical field as a cure for skin wounds and burns, artificial skin, and drug delivery systems [6].

Experimental and/or Modelling: The bacterial cellulose membranes were obtained in static culture using Hestrin-Schramm medium containing 3% fructose after 7 days. Bacterial cellulose was lyophilized, loaded with active substances and lyophilized again. The solutions of bacitracin and amoxicillin were made in two different concentrations of 1% and 3% respectively.

Results and discussions: Bacterial Cellulose is a good support for the absorption of the drugs, showing a rapid and massive water absorption which may be suitable to absorb exudate and maintain a proper humidity and oxygen permeability to

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assure wound healing. The graphs presented in Fig.1 illustrate the hydration capacity for the following samples: BC-control, BC-bacitracin 1%, and BC-bacitracin 3%. The initial growth (within the first 30 min of immersion) is particularly fast for all three samples and results a water absorption of about 1000, 1150 % hydration capacity for the samples loaded with bacitracin and ~1900% for BC. These samples are stable for at least for an additional day.

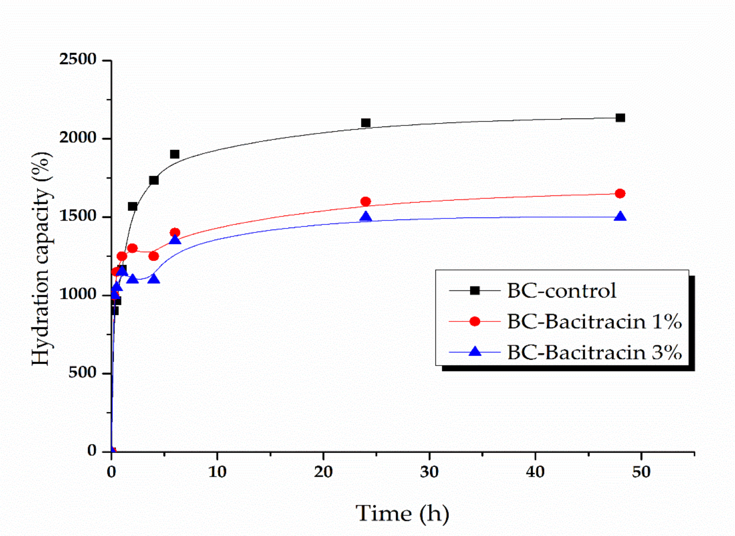

Fig. 1 Absorption kinetics of BC samples loaded with bacitracin 1% and 3%

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Conclusions: Based on the obtained results, these samples are able to adsorb a large amount of water and exudates and also to adsorb and release antibiotics.

Acknowledgments: G.M.L.P acknowledges the support of Operational Program Human Capital of the Ministry of European Funds through the Financial Agreement 51668/09.07.2019, SMIS code 124705.

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POTENTIALLY THERAPEUTIC NANOSTRUCTURES FOR BREAST CANCER TREATMENT

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Abstract*: The paper presents the synthesis and characterization of some nanostructures with therapeutic potential for breast cancer.*

Key words: Iron oxide nanoparticles, laser pyrolysis, cytotoxic evaluation

Introduction: Iron oxide nanoparticles are known for their wide range of applications, including biomedical applications due to their unique properties. Herein, we synthesized iron oxide nanoparticles and used doxorubicin as an anti-cancerous agent in order to use the nanosystem for breast cancer therapy. Furthermore, carboxymethyl cellulose was used as a stabilizer and the system, as well as the individual constituents underwent cytotoxic evaluation.

Experimental and/or Modelling: Laser pyrolysis technique was used to synthesize the iron oxide nanoparticles with iron pentacarbonyl as an iron precursor. Carboxymethyl cellulose (CMCNa) was used as a stabilized agent for the nanoparticle suspension. Cytotoxic evaluations were carried out on both healthy cells, as well as breast cancer cells (MCF7).

Results and discussions : Figure 1 shows the effect of the nanosystem on the breast cancer cells viability for 24 and 48 hours. It has been observed that there was a significant drop in cellular viability in the cells treated with nanoparticles and doxorubicin, as well nanoparticles with carboxymethyl cellulose and doxorubicin as compared to the control. The decrease in cell viability is directly proportional to the increase in doxorubicin doped particle concentration. Even though there are not significant changes for the individual constituents of the nanosystem, a decrease of almost 50% in cell viability can be observed in the case of exposure to the dose of 12.5 µg/mL iron oxide nanoparticles and 100 ng/mL doxorubicin.

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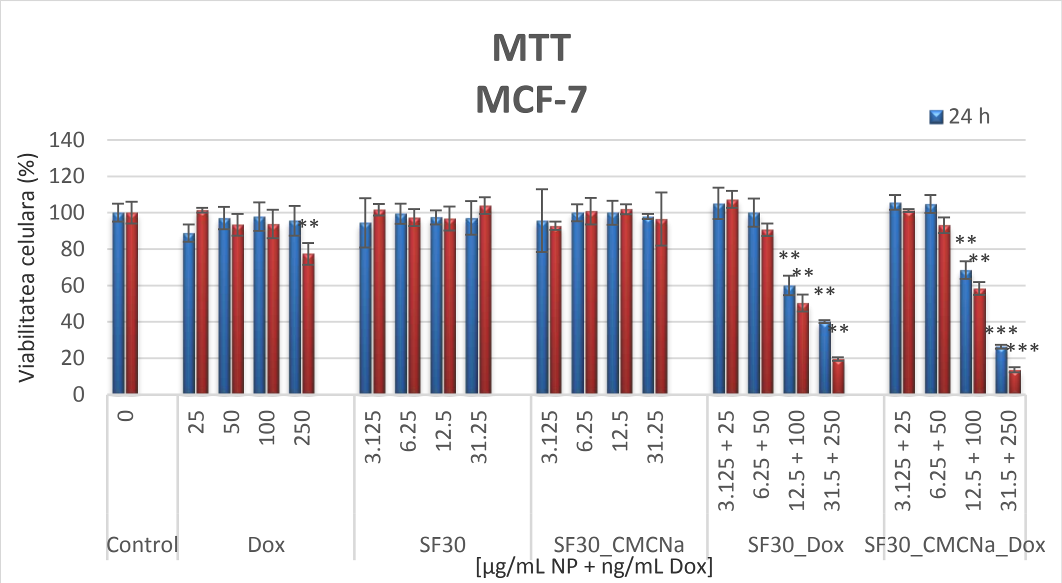

Fig. 1 Cellular viability on the cellular line MCF-7 which were exposed to different concentrations of iron oxide nanoparticles (3.125, 6.25, 12.5 and 31.12 µg/mL) and doxorubicin (25, 50, 100 and 250 ng/mL).

Conclusions: The effects of the nanosystem on cellular viability have been observed. It can be noted that the decrease in cellular viability is strictly related to the concentration of the doxorubicin doped nanoparticles and the exposure time.

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FUNCTIONALIZATION ROUTES WITH SILOXANES AND SILVER NANOPARTICLES ON THE STONE SUBSTRATE

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Short Abstract: *The antibacterial treatment used for the stone monuments, claddings, heritages, consists in the protection of their surface with specific products which are against the formation of biofilms. Based on their high antimicrobial effect silver nanoparticles can be used in the stone treatment together with siloxanes as the coupling agent which play an important characteristics.*

Key words: antibacterial effect,silver nanoparticles, surface silanization, siloxanes

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

Experimental and/or Modelling: *Reagents:* The stones surface selected were treated with various chemical products based on siloxanes, as the coupling agent with different reactive groups (sulphate, thiol, amino, ethers, esters, ethanol amide, carboxylic groups) to form bonds with the substrate and the other functional groups either they will act as detergent groups or the specific functional group react with the silver nanoparticle synthetized by various routes[4-6].

Impregnation processing of various stone substrates : The treated stone surface with functional groups able to bond the silver nanoparticle shown a relative high antibacterial activity against the microorganisms biofilm already formed or which tends to form at the surface or inside of the stone structure.

Investigation and determination the presence of the antibacterial surface: The impregnated stone were tested by FTIR, SEM EDAX and microbiological tests. All tests were done confirmed the presence of silver nanoparticles both on the stone treated surface also inside of the stone structure. The biological test confirmed the presence and activity of silver nanoparticles against the microorganisms.

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Results and discussions: The figure 1 IR spectra indicated the impregnation of the limestone confirmed by SEM EDAX test

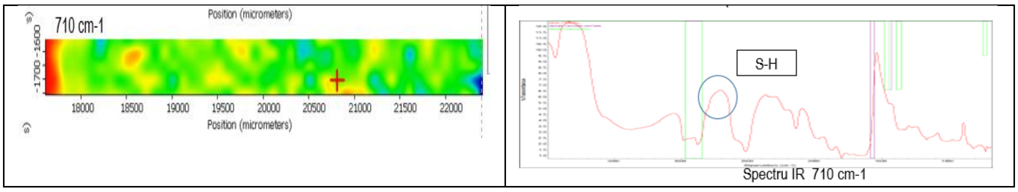

Fig. 1 Limestone impregnated with the COAT O SIL product contain thiol groups and alcohol

Conclusions: The silanization of the stone surface can drive through by the type of siloxanes used and the antibacterial component to the high antimicrobial efficiency of the surface with the protection role against the formation of biofilms.

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COMPLEX STRUCTURES PRODUCED BY TWO-PHOTON POLYMERIZATION FOR TISSUE REGENERATION

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Abstract: *By laser techniques, a complex, biocompatible structure was created with potential applications in bone regeneration.*

Key words: 3D structures, two-photon polymerization, bone

Introduction: Studies have shown that surface topography influences the spatial arrangement of cells, proliferation and functional activity. We are currently looking for the most tissue-friendly material, as well as the topography of the surface that stimulates the cells to express their functional characteristics as quickly as possible, leading to rapid tissue regeneration. [1]

Experimental: We fabricated structures by laser direct writing by two-photon polymerization, using the Photonic Professional 3D Lithography system Nanoscribe GmbH. We employed a commercially available photopolymer IP-L780 (NanoscribeGmbH), a biocompatible liquid (2-(Hydroxymethyl)-2-[[(1-oxoallyl)oxy]methyl]-1, 3-propanediyl diacrylate (>95%) and 7-(Diethylamino)-3-(2-thienylcarbonyl)-2H-1-benzopyran 2-one (<5%), formulation with optimized sensitivity for fast 3D structuring. [2] In accordance with the computer models, structures with different surface height ratios resulted. We investigated cell morphology by scanning electron microscopy, differentiation and mineralization by measuring alkaline phosphatase, osteocalcin production and mineralization. [3]

Results and discussions: Results showed that the level of cells osteogenic differentiation and mineralization was statistically higher in the structure with moderate layers separation.

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Conclusions: Structures are well defined over the entire 3D volume with submicron errors, making them suitable candidates for different types of cell differentiation.

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

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ISOLATION AND CHARACTERIZATION OF COLLAGEN FROM TAILS OF *HYPOPHTHALMICHTHYS MOLITRIX* FOR USE AS BIOMATERIAL

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Introduction - Collagen is a natural biopolymer with a broad range of applications in the cosmetic, pharmaceutical and food industries. In recent years, more attention has been focused on the isolation of collagen from aquatic sources, due to its superior properties compared to collagen from mammals raw materials [1]. Moreover, sustainable socio-economic and environmental principles promote the full use of natural resources, which reinforced the idea of valorizing of the fish by-products from fish processing. Fish by-products can be an alternative source for collagen production having the advantage of a low risk of transmitting diseases and solves the religious constraints of Hindus, Jews and Muslims who cannot consume collagen isolated from cattle, sheep and pigs, respectively [2, 3]. Starting from the idea of valorizing the fish by-products and protecting the environment, the present study aims is to isolate collagen from silver carp tails (*Hypophthalmichthys molitrix*), which is one of the three species of fish most frequently processed in Romania [3].

Experimental methods – the collagen from silver carp tails was isolated by enzymatic hydrolysis method with pepsin.

Results and discussion – The experimental results confirm the isolation of type I collagen. The highest amount of isolated collagen was obtained by using a concentration of pepsin of 1200 U / g. The structure of the triple helix and the purity of obtained collagen was proved by FTIR analysis. Moreover, the UV-Vis and EDX analyzes also revealed that the lyophilized collagen is pure. SDS-PAGE analysis showed the molecular weights of the silver carp tails collagen ranged from 100 to 250 kDa and with similar peptide fragments profile. The results of cytotoxicity and cell proliferation assays of the isolated collagen against fibroblasts cell line indicate the non-cytotoxic effect at concentrations lower than 100 µg/mL collagen.

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Conclusion – The experimental results support the successful obtaining of the type I collagen which could be used as biomaterials.

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SOL-GEL THIN FILMS PREPARED WITH SILANE PRECURSORS, DEPOSITED ON PLASTIC SUBSTRATES

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Short Abstract: *Hybrid systems have been synthesized via acid-catalyzed sol-gel process using silane precursors (tetraethoxysilane (TEOS, methyltriethoxysilane (MTES), vinyltrimethoxysilane (VTMES), octyltriethoxysilane (OTES), and/or hexadecyltrimethoxysilane (HDTMES)), and deposited onto plastic substrates. The properties of resulted materials were investigated by FTIR and UV-Vis spectroscopy, AFM analysis and contact angle measurements.*

Key words: sol-gel process, thin films, plastic substrates, wettability

Introduction: Multifunctional silica thin films/coatings are becoming very attractive due to their variety of applications from anti-icing to self-cleaning, low-adhesion, antibacterial, anti-reflection, anti-contamination and anti-fogging [1].

Experimental: *Reagents:* TEOS, MTES, VTMES, OTES, HDTMES were used as silica source. The chemicals were used as received; *Production of thin films:* Sol-gel hybrid systems based on silane precursors were deposited onto plastic substrates and dried at 25 °C.

Results and discussions: FTIR spectra were recorded in order to evaluate the functional groups present in the silica thin films. The reflectance of thin films was about 10%. AFM analysis indicated that the surface topography can be chanced as function of silica sol formulations. The surface wettability was changed from hydrophilic to hydrophobic.

Conclusions: These obtained materials can generate coatings with potential use in optical lenses, mobile phones and solar panels.

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PREPARATION AND CHARACTERIZATION OF SILVER NANOPARTICLES/ ALGINATE MEMBRANES FOR SKIN TISSUE ENGINEERING

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Keywords: alginate-based biomaterials, alginate-silver nanoparticles membrane, biocompatibility and antimicrobial activity

Introduction: Alginate is a biomaterial with excellent applications in biomedical field, drugs delivery and tissue engineering due to its favorable properties such biocompatibility, biodegradability and gelation features [1,2]. Seo *et al* [3] developed alginate-silver nanoparticles composite sponge that showed an enhanced antimicrobial activity in comparison to the simple alginate.

Experimental and/or Modelling: According to the above presented study [3] alginate-silver nanoparticles and sodium alginate sponge/ membrane were synthesized, in order to evaluate their biocompatibility on human keratinocytes. The alginate-silver nanoparticles and sodium alginate sponge/ membrane were obtained starting from 5% sodium alginate solution, afterwards stirred for 24 h and then dried through the lyophilization process, overnight.

Results and discussions: The study showed that alginate can be a potential candidate for skin tissue engineering, because the presence of stabilized silver nanoparticles provides a synergism between antimicrobial and anti-inflammatory properties. The synthesized membranes were structurally and morphologically characterized by *SEM*, *FTIR* spectroscopy and *TG* analysis followed by *in vitro* biological assessments. Various amounts of silver nanoparticles were loaded, and further antimicrobial and biocompatibility assessments were done. The figure below shows the microscopic evaluation of epidermal keratinocytes (HaCaT cells) grown 24h in the presence of these membranes was done in order to evaluate the biocompatibility of these materials.

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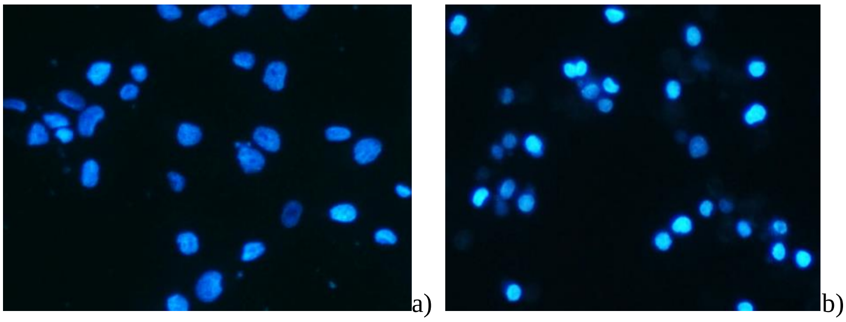
a) b)

Fig. 1 Microscopic evaluation of epidermal keratinocytes:
a) Alginate control, b) Alginate +0,1% Ag

Conclusions: The safety level of silver nanoparticles was established and the possibility to continue these studies for targeting skin healing is considered.

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

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TIO_2 NANOPARTICLES FOR WASTEWATER TREATMENT

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Keywords: TiO_2 nanoparticles, antimicrobial properties, nanostructure membranes, wastewater treatment

Introduction: Lately, nano-sized nanoparticles have gained interest in diverse technologies because of their ability to be synthesized and manipulated into smaller materials. Everyday, people are trying to overcome water pollution and using nanometric inorganic particles such as TiO_2, Ag and ZnO with antimicrobial properties [1]. Because of its interesting photocatalytic properties, TiO_2 has been used in applications such as decontamination, purification and wastewater treatments [2, 3].

Experimental and/or Modelling: According to the presented study [3], TiO_2 nanoparticles were synthesized, in order to evaluate their antimicrobial properties before incorporating them in nanocomposite membranes. The TiO_2 was synthesized through a sol-gel process, from titanium tetra-isopropoxide as a precursor then used in further synthesis for membranes.

Results and discussions: The main purpose of this study was to demonstrate that TiO_2 nanoparticles can be a potential candidate used in further synthesis for nanocomposite membranes preparation because of their excellent antimicrobial properties. The synthesized TiO_2 nanoparticles were structurally and morphologically characterized by TEM, X-ray diffraction, FTIR spectroscopy and antimicrobial assessments. Various amounts of TiO_2 nanoparticles were analyzed, and further antimicrobial assessments were done against *Enterococcus faecalis* ATCC 19433, *Escherichia coli* ATCC 25923 and *Salmonella enterica* ATCC 13076.

Conclusions: The synthesized TiO_2 nanoparticles investigated through TEM, XRD, FTIR and antimicrobial assessments were done. Based on the obtained results from antimicrobial assessments it can be concluded that the TiO_2 nanoparticles can assure the antimicrobial activity of the nanocomposite membranes and will be used in developing antimicrobial membranes based on chitosan.

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COMPUTED AIDED STUDY ON ORAL AVAILABILITY AND BIOACTIVITY SCREENING FOR LUTEOLIN DERIVATIVES

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Abstract*:* *In silico study using DFT method was carried out on several Luteolin (L) derivatives to assess their drug-likeness properties and bioactivity in order to establish their pharmacological profile. Molecular features and key descriptors for oral availability and drug-likeness properties were obtained with Spartan 18 Software. Bioactivity scores towards GPCR ligand, Ion channel modulator, Kinase inhibitor, Nuclear receptor ligand, Protease inhibitor and enzyme inhibitor are predicted with a property calculation engine (Molinspiration Cheminformatics). Results were discussed to find and optimize the lead compound for design of new therapeutically potential agents.*

Key words: Luteolin, virtual screening, *bioactivity, oral availability*

Introduction: Lipinski C.A. and co-authors [1] were establish limitations for properties assessing oral availability of drugs and pharmacokinetics. Veber and co-workers [2] add supplementary molecular restrictions to improve the predictions about drug-likeness. We evaluated such properties and bioactivity of several Luteolin derivates, to supplement our previous work [3].

Computational modelling:

The 3D structures of Luteolin (**L**), **L**-5-O-glucoside, **L**-7-O-glucoside, **L**-6-C-glucoside, **L**-8-C-glucoside, **L**-7-O-rutinoside and **L**-7,3'-di-O-glucoside were generated and optimized by energy minimization using molecular mechanics force fields (MMFF) [4] with Spartan'18 software, Wavefunction, Inc. Irvine, CA, U.S.A. [5]. Property computations were performed using Density Functional Theory (DFT) and improved ωB97X-D functional [6], 6-31G* polarization basis set [7], for equilibrium geometry at ground state. Bioactivity scores were calculated with Molinspiration miscreen engine.

Results and discussions: Figure 1 illustrates the oral bioavailability calculated parameters for the lead compound (**L**), according Lipinski's rule of five and Veber's restrictions for PSA (polar surface area). Graphical representation of calculated values of PSA *vs* molecular weight (MW) for Luteolin derivatives are given in Figure 2. All investigated structures respect limitation for MW, except Luteolin-7-O-beta-rutinoside and Luteolin-7',3-di-O-glucoside, that exhibit larger weight than 500 g$\cdot$mol^{-1}. Concerning PSA, only the lead molecule (**L**) obeys the imposed restriction of 140Å^2 (predicted PSA for **L** = 90.988Å^2). The predicted values the water-octanol partition coefficient (logP), are illustrated in Figure 3, *versus* PSA; we can observe that all compounds are strongly hydrophilic, due to their abundant hydroxyl groups, presenting negative values, ranging between -

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2.67 (**L**-7',3-di-O-glucoside) and -6.39 (**L**-6-C- and **L**-8-C-glucosides). The more flexible molecule is the one presenting two glucoside residues, with 7 rotatable bonds, followed by **L**-7-O-bteta-rutinoside, with 6 rotatable bonds. The ability of substituents to rotate influence the ligand's ability to interact with the amino acid residues of the biological target, dictating the docking score, and therefore the binding energy of ligand-protein complex and consequently, the bioactivity. Among studied molecules, the most rigid molecule is **L**, with one single rotatable bond.

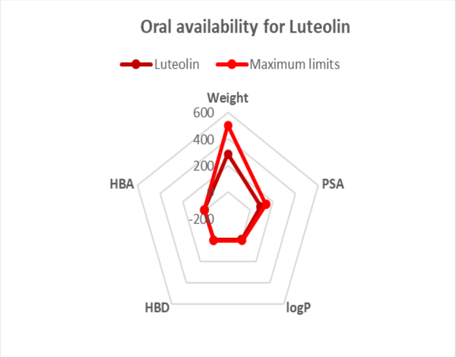

Fig. 1 Lipinski and Veber's parameters for **L**.

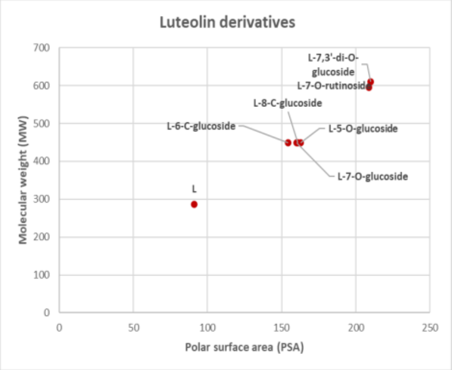

Fig. 2 MW *vs* PSA
for **L** derivatives.

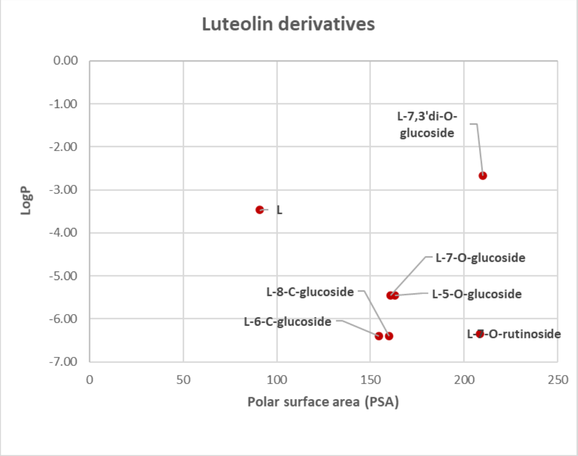

Fig. 3 logP *vs* PSA
for **L** derivatives.

Concerning the bioactivity screening towards GPCR ligand, Ion channel modulator, Kinase inhibitor, Nuclear receptor ligand, Protease inhibitor and enzyme inhibitor, given in Figure 4, we can observe that Luteolin stand out with the highest score against Nuclear receptor (0.39). Active molecules exhibit bioactivity scores > 0; moderately active - between −5.0 and 0.0, and inactive, < −5.0. Generally, all compounds are actives or moderately actives against selected human targets.

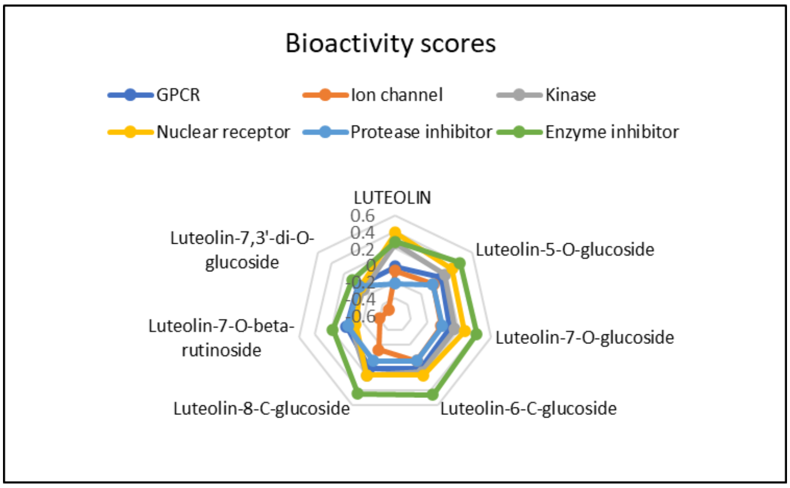

Fig. 4 Bioactivity plots for **L** derivatives.

Conclusions: As resulted from our virtual screening, Luteolin exhibits great oral availability. All investigated structures are active or moderately active against common human targets, being feasible candidates for the optimization and design of new medicines, as suggest certain inhibitory activity upon fatty acid synthase activity [8] and malignancies treatment [9, 10].

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A VERSATILE MATERIAL OF THE XXIST CENTURY: APATITIC COMPOUNDS WITH MULTIFUNCTIONAL PROPERTIES

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Introduction

In the field of materials, apatitic compounds are the most probably studied in this century, due to their multifunctional properties. They can be used in environmental applications, for air, water and soil pollution control [1], in biomedical applications [2] or cultural heritage protection [3].

Results and discussions

In order to enhance potential properties of these materials, changing its architecture can be an alternative to the use of toxic substances. For each final application the apatitic structure presents a particular importance. As previously demonstrated by our group [4], apatitic materials with Mn presented good efficiency in environmental applications and poor antimicrobial potential, meanwhile for those materials in which incorporation of silver was made post-synthesis have presented anti-microbial properties towards planktonic (free) cells, reducing the formation of monospecific biofilms and recommended them for cultural heritage applications [5]. In this context, the present work focuses on our previous results obtained in environmental domain and cultural heritage protection, in the international context. Also, this paper summarizes different aspects related to the synthesis and characterization of apatitic materials, as well as, the correlation of their morphology related to final application. The literature review was conducted using different databases (Scopus, Web of Science, ScienceDirect, SpringerLink) using as keywords “hydroxyapatite”, “apatitic materials”, “phosphatic compounds”, or multiple keywords “apatitic materials for environment”, “apatitic materials for cultural heritage protection” within the envisaged time period (2015–2020).

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BOOK OF ABSTRACTS

SICHEM – 2018

D – Green applied chemistry and agro-resources valorization (GACARV)

1. Keynotes

International Chemical Engineering and Material Symposium, SICHEM 2020, 17-18 September 2020, ISSN 2537-2254

MICROALGAL BIOPOLYMERS WITH COMPLEX INTERFACIAL AND RHEOLOGICAL PROPERTIES: STRATEGIES OF EXTRACTION-PURIFICATION AND EXAMPLES OF APPLICATION

Alina-Violeta Ursu[1,*], Gholamreza Djelveh[1], Alain Marcati[1], Anïssa Awi[1], Zaineb Trad[1], Bogdan Trica[1,2], Philippe Michaud[1], Tanase Dobre[2], Christophe Vial[1]

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Abstract: *Separation-purification-application of microalgae biomass polymers with high techno-functional properties*

Key words: Microalgae, Biopolymers, Protein, Pigment, Polysaccharide, Emulsification, Foaming

Introduction:

Microalgae (including Cyanobacteria) are unicellular photoautotrophic microorganisms which can produce biomass with a great efficiency using light, CO_2 and water. The complex biochemical composition is at the origin of numerous applications in various fields such as those of animal feed, human food, energy and texturing agents [1]. In order to enhance the utilization of this worthy biomass at industrial level, extraction-separation-purification methods need to be adapted particular and specific cell (wall) structures [2,3]. This study presents different approaches for the recovery of techno-functional agents from an eukariotic microalgae (*Chlorella sp.*) and a cyanobacteria (*Arthrospira sp.*).

Experimental and/or Modelling: The targeted biopolymers were proteins, pigment-protein complexes (such as phycocyanin) and polysaccharides. After harvesting, all biomass underwent one or several cycles of freezing (-20°C) and thawing (20°C) in order to favor cell wall permeability to aqueous solvent. *Chlorella sp.* was additionally treated with high pressure (up to 2,7 kbar) due to its rigid cell wall. This cell disruption treatment led to release the intracellular proteins with a significant extraction yield. After optimization of extraction parameters (pH, temperature and cell lysis), physical (membrane separation) or chemical (pH shifting) steps were applied. Indeed, pH shifting allows to separate proteins-chlorophyll complex from *Chlorella sp.* with potential interest as an emulsifier.

Results and discussions: High pressure cell lysis combined with isoelectric precipitation generates protein-pigment aggregates (molecular weight below 800 kDa) with high emulsion capacity and stability. Extraction at alkaline pH followed by pH shifting generates protein pellets with high foaming ability. Protein pellets

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recovered from *Arthrospira sp.* and *Chlorella sp.* with optimized process flow sheets present techno-functional properties, such as emulsion and foaming abilities higher to whey protein isolate considered as references by food industry.
The feasibility of microalgae protein extract utilization as foaming agent in high viscosity model formulations (mix of glucose, water and proteins) was proved in batch (beaker scale) and in continuous (semi-pilot scale) foaming operations.

Conclusions: Flow sheets with optimized unit operations are proposed to recover microalgae polymer aggregates as potential replacers of classical commercial ingredients as emulsifiers and foaming agents.

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BOOK OF ABSTRACTS

SICHEM – 2020

D – Green applied chemistry and agro-resources valorization (GACARV)

2. Oral presentations

ANTIOXIDANT ACTIVITY OF POLIPHENOLIC EXTRACT FROM ROSÉ WINE GRAPE MARC LOADED ON FUNCTIONALIZED MESOPOROUS SILICA

Ana-Maria Brezoiu [1,*], Laura Bajenaru [1], Mihaela Deaconu [1], Daniel Lincu [1, 2], Anicuta Stoica-Guzun [1], Raul-Augustin Mitran [2], Cristian Matei[1], Daniela Berger [1]

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Abstract*: Polyphenols-loaded silica materials showed improved stability and antioxidant activity.*

Keywords: polyphenolic extract; antioxidant activity; mesoporous silica; polyphenols release

Introduction: Grape marc is an important residue from the wine industry, with high amount of polyphenols having antioxidant and anti-inflammatory properties [1]. However, the main issues regarding their use for nutraceuticals or cosmetics is the ability to preserve their bioactivity and stability and to improve their bioavailability which could be achieved by loading onto mesoporous silica.

Experimental: The composition of polyphenolic extract was analyzed by reverse phase HPLC-PDA and through spectrophotometric determination of total polyphenols, flavonoids and anthocyanins content. The radical scavenger activity was assessed using DPPH and ABTS assays. The embedded extracts were characterized by FT-IR spectroscopy, N_2 adsorption-desorption isotherms, thermal analyses and radical scavenger activity determination on solid samples [2].

Results and discussion: The hydroalcoholic polyphenolic extracts showed high amount of polyphenols being correlated with a good radical scavenging activity (RSA). The conventional extract loaded on functionalized mesoporous silica showed better RSA in comparison with the free extract after several months of storage, while the acidic properties of functional groups led to higher amount of polyphenols released in PBS pH 5.7. The cellular viability assessment and intracellular reactive oxygen species (ROS) level on NIH3T3 fibroblast cells proved no significant toxicity for polyphenols-loaded MCM-41 silica type supports and the lowest cytosolic ROS production was observed for extract loaded on MCM-41 silica functionalized with propionic acid moieties (MM@MCM-COOH), which could be corelated with the highest amount of extract released from silica-type support in PBS pH 5.7.

Conclusion: The embedded extracts, especially MM@MCM-COOH, showed an improved stability and a better *in vitro* antioxidant effect than the extract alone.

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EXTRACTION OF BIOACTIVE COMPOUNDS FROM PROPOLIS. INFLUENCE OF OPERATING PARAMETERS

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Abstract: *The extraction of polyphenols and flavonols from propolis was studied in terms of solvent composition, liquid:solid ratio, and time. Total polyphenols concentration and antioxidant capacity quantified the process efficiency.*

Key words: extraction, propolis, bioactive components,

Introduction: Propolis contains a wealth of bioactive compounds. Polyphenols and flavonols are commonly extracted in alcoholic solutions [1]. This study evaluates the extraction capabilities of free or hydro-alcoholic solutions (the former, more desirable for certain consumers) and identifies the best operating conditions.

Experimental and Modelling: *Reagents:* water (A) and alcoholic solution (25, 50, 70%, E, EE, EEE) were used for extraction. *Operating conditions:* The liquid:solid ratios used were 2:1, 4:1, 6:1. Phases were contacted at 150 rpm for 1, 3 and 5 days. The antioxidant capacity of extracts was determined with ABTS, using Trolox as model species [2]. *Modelling:* The influence of polyphenols upon the antioxidant capacity was modelled with a asymptotic type equation, $Q_a = (K_1 \times c_p)/(K_2 + c_p)$, the parameters being regressed through the experimental data, using an in-house built MATLAB® software.

Results and discussions: Extraction in large liquid volumes is more efficient (mg active compounds/g propolis), while concentration (mg active compounds/mL extract) increases with the alcohol content and decreases with the liquid:solid ratio (fig 1). The antioxidant capacity increases with the polyphenols content (fig. 2).

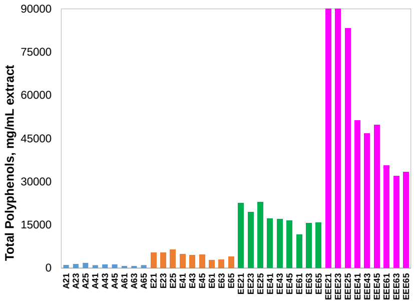

Fig. 1 Polyphenols levels in the extracts

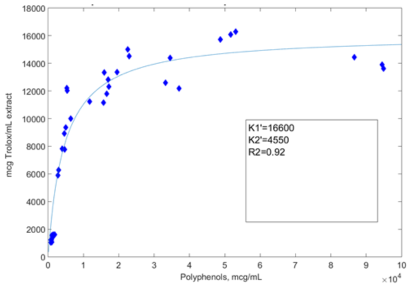

Fig. 2 Antioxidant capacity versus polyphenols content

Conclusions: The optimum operation conditions for highest antioxidant capacity correspond to 50 % alcoholic solutions and 2:1 liquid:solid ratio.

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CAROTENOIDS GREEN EXTRACTION FROM TOMATOES

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Introduction: Food industry generates high amounts of waste which can be valorized. Tomatoes are the second most produced and consumed vegetables, and during their processing 40% of the tomatoes is obtained as waste which consists in a mixture of tomato peel and seeds. Currently, this residue is underestimated, being used for animal feed production or disposed of, although it contains high nutritional quality oil and carotenoids, mainly lycopene. Carotenoids are known for their antioxidant activities and are useful in the treatment and prevention of cancer and cardiovascular diseases [1].
The extraction and identification of plant biologically active compounds, as lycopene and β-carotene from tomatoes, is very important in food and pharmaceutical industries. The extraction procedure must be efficient and environmentally friendly. Green extraction techniques involves the substitution of conventional toxic solvents, which are petrochemical based, to bio solvents that are natural and less hazardous to the environment, as ethyl acetate, bioethanol, polyether or supercritical carbon dioxide. Conventional solvent extraction is the most used method to separate desired compounds from matrices, while supercritical CO_2 extraction is a green separation technique that uses the supercritical CO_2 which exhibits the unique properties of liquid and gases above the critical point. Moreover, supercritical CO_2 fulfills almost all the ideal characteristics of a green solvent such as recyclability, biodegradability and non-toxicity [2].

Experimental: This study is focused on recovery of carotenoids, lycopene and β-carotene from two different matrices of tomatoes: as tomato slices and tomato residue (as mixture of peels and seeds). Prior to extraction, tomato samples are dehydrated at 50ºC for 48 hours. Dehydrated samples are subjected to two extraction techniques: Soxhlet extraction for 6 hours using two different green solvents as bioethanol and ethyl acetate and supercritical CO_2 extraction for 10 hours by varying process parameters as extraction pressure of 400 and 450 bar and CO_2 flow of 9 and 11 kg/h. UV-Vis spectrometry method is used to quantify carotenoids from tomato extracts. The extraction efficiency is analyzed in terms of yield and carotenoids composition.

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VALORIZATION OF ACTIVE PRINCIPLES FROM ELECAMPANE (INULA HELENIUM), IN A CONCENTRATED AND PURIFIED FORM, BY SOLVENT EXTRACTIONS AND ULTRASOUND TREATMENT

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Key words : inulin, allantolactone, GC-MS, ultrasound.

Introduction: Elecampane (*Inula helenium. L.*) also called horse-heal, sporadically cultivated as a medicinal plant, is found in the spontaneous flora trough wet places in meadows, orchards and vineyards. In folk medicine it is used for headaches, asthma, bronchitis, lung disorders, and stomach disease. The root of Elecampane (*Inula helenium. L.*) contains inulin (30-50%), about 5% volatile oils, waxes, flavones and alantolactones. Studies have showed that root extracts possess antihelminthic, antimicrobial and insecticidal activities. The leaves contains alantopicrin (bitter principle), vitamin C and mineral salts while the flowers contain helenine.

The active principles offers diuretic, anti-rheumatic, anti-inflammatory properties while the bitter principles of alantolactone/isoalantolactone offers general tonic and moderately antitumor properties.

Experimental and/or Modelling: To obtain pure extracts there were used procedures such as ultrasound treatment, ethanol extraction as well as maceration in n-hexane/methanol solvent. The physicochemical analytical measurements were performed to determine the total polyphenols content (chlorogenic acids, caffeic acids, gallic acids), flavones and carbohydrates for each concentrated extract, separately.

The total polyphenols content (expressed in gallic acid equivalent) was determined by Folin-Ciocalteu method. Total flavones (expressed in rutin equivalent) were determined by a spectrophotometrically method in the presence of aluminum chloride. The antioxidant activity was determinated by reliable methods such as CUPRAC based on a calibration curve using Trolox (antioxidant) as standard, FRAP-II and DDPH assay.

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Results and discussions: In the present study we have aimed to identify and dose the active ingredient in Elecampane (*Inula helenium. L.*), as well as concentration and purification of some active principles.

We have determined the essential oils, by steam distillation. The quantity was about 5mL/plant kg. Alantolactone and isoalantolactone, as well as the chemical composition of the oils, were identified by GC-MS, using the spectrum library NIST.

Conclusions: Applying this protocol we can determine which extraction method is more efficient for highlighting dosed compounds with application in the pharmaceutical industry, in particular for obtaining food supplements and cosmetics.

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VALORIZATION OF APPLE POMACE EXTRACT USING MESOPOROUS SILICA SUPPORT WITH ENHANCED STABILITY

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Keywords: apple pomace, polyphenolic bioactive compounds, silica mesoporous supports, characterization

Introduction: Valorization of apple pomace by extraction of valuable bioactive compounds, including pectin and polyphenols as potential ingredients for foods, nutraceuticals or cosmetics is of increasing interest [1]. This direction has become more and more applicable thanks to the eco-friendly extractions methods and the progress for the development of different supports designed to reduce the extract sensitivity and enhance its stability [2].

Experimental and/or Modelling: In this study, we report the embedding of bioactive extract obtained by microwave extraction of free pectin apple pomace, into mesoporous MCM-41-type silica matrix synthesized by the sol-gel method assisted by hydrothermal treatment according to a described procedure [3], using synthetic and natural silica sources. Polyphenolic extract was characterized for total polyphenols and antioxidant activity using UV-Vis methods and by UHPLC-MS/MS for profiling the bioactive compounds. The obtained supports were characterized by N_2 sorption measurements to evaluate their porosity, small- and wide-angle XRD to assess their structural features, as well as SEM to investigate the morphology. FTIR spectroscopy and TG analysis were used to evidence the removal of the used precursors, the functionalization of the mesoporous support with amino groups and the presence of the polyphenolic compounds.

Results and discussions: The overall hydro-alcoholic extract from apple pomace contained high polyphenolic content (28.00 mg equivalent of gallic acid/g dry pomace) and had a good antioxidant activity (1800 µmoli Trolox equivalent/mL extract). UHPLC-MS/MS profiling revealed bioactive compounds such as gallic, chlorogenic, cafeic, ferulic and p-coumaric acids, catechin, epicatechin and quercetin derivatives. The characterization results confirmed the well-ordered hexagonal mesophase of the MCM-41, functionalized or not with amino groups. Also, the embedding of the polyphenols compounds was confirmed by FTIR and SEM techniques.

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Conclusions: This study demonstrated the use of mesoporous silica as adsorbent for embedding high amounts of important bio-active principles, which can be used furthermore as dietary sources or nutraceuticals.

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CHARACTERIZATION OF BATCH BOTTOM SPRAY FLUID BED COATING OF SEEDS WITH SODIUM ALGINATE USING A MINIMUM-RUN RESOLUTION V DESIGN

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Key words: fluidized bed, seed coating, design of experiments

Introduction: Seed coating is one technology traditionally used to improve handling and protection of seeds. Nowadays, this system can be used as a carrier for ingredients promoting plant-growth and germination such as protectants or nutrients [1]. The batch fluidized bed coating of seeds is a process commonly used to get uniformly covered seeds with minimum losses and reduced process time. Sodium alginate is frequently proposed as a binder for biodegradable or edible films.

Experimental and/or Modelling: Seed mass, temperature, process time, alginate solution feed rate, nozzle pressure and alginate concentration were considered as relevant factors influencing the process. The process performance in varying conditions was evaluated in terms of yield, degree of peeling, film thickness and variability of film thickness. The experiments were run on a Mini-Glatt/ Midi-Glatt fluidized bed system. The main effects and secondary interaction effects are evaluated using a minimum-run resolution V design. This is an optimal approach considering there are 6 possibly significant factors.

Results and discussions : An optimal set of values for the 6 factors can be estimated from the results obtained. However, a better description of the proposed responses can be obtained by augmenting to a response surface experimental design for the three most impactful factors whilst fixing at a constant value factors which had a lower effect.

Conclusions: This is the first step in developing a reliable, useful understanding of the batch fluidized bed coating of seeds process. The ultimate goal is to obtain a flexible understanding of the process which will allow the quick adaptation of the process parameters for various combinations of type of seed and binder.

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REMOVAL OF HEAVY METALS FROM NICKEL-CONTAINING EFFLUENTS USING *SHEWANELLA XIAMENENSIS* BIOFILM PLACED ON ZEOLITE

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Abstract

The capacity of *Shewanella xiamenensis* biofilm placed on zeolite to remove metal ions from nickel containing effluents with the following chemical composition: Ni(II), Ni(II)-Sr(II)-Cu(II)-Zn(II), Ni(II)-Cr(VI)-Fe(III) and Ni(II)-Zn(II)-Mo(VI)-Cu(II) under different experimental conditions was tested. The highest adsorption rate for metal present in cationic form was achieved at pH was achieved at pH 6.0. The biosorption of metal ions present in anionic form none occurred. The equilibrium data were described by Langmuir, Freundlich and Temkin isotherms. The best fit for Ni(II) was obtained for Langmuir and Temkin models in all analyzed systems. The maximum adsorption capacity of biosorbent ranged from 3.6 mg/g in Ni(II)-Zn(II)-Mo(VI)-Cu(II) to 3.9 mg/g in Ni(II) system. The lowest values were obtained for Ni(II)-Zn(II)-Mo(VI)-Cu(II) system 1.98 mg/g. The kinetics of metal ions biosorption was described by pseudo-first-order, pseudo-second-order, and Elovich models. Thermodynamic calculations showed that metal biosorption was a spontaneous process and endothermic for all metal ions present in solutions in cationic forms. Different approaches for Ni(II) removal from real industrial effluent were proposed. It was proved that combination of bacteria *Shewanella xiamenensis* and zeolite results in the formation of highly efficient biosorbent for selective metal removal from industrial effluents.

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BOOK OF ABSTRACTS

SICHEM – 2020

D – Green applied chemistry and agro-resources valorization (GACARV)

3. Poster presentations

EXPERIMENTAL INVESTIGATION METHODS OF POLYMER DEGRADADTION

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Abstract*: The present work purpose is to present a review of the curent experimental investigation methods of polymer degradation towards microplastics formation.*

Key words: Polymer degradation, Pollution, Microplastics, Environment

Introduction: Despite the fact that the presence of plastic products in our lives is a necessity, this synthetic materials are the newest form of pollution and a real danger to all ecosystems. Microplastics are fragments of plastic smaller than 5 mm, developed in the polymer degradation process and whose main source of abundance is a consequence of anthropic actions [1].

Types of polymers degradation: Once on market, with time, due to various external factors, plastic materials start to undergo a series of structural and compositional changes and degradate. This processes are slow and take place over long periods of time given the fact that plastics are materials constisting of long chain molecules. Thus, depending the type of polymer and its specific properties, polymer degradation can follow two type of degradation: biotic and abiotic [2].

Experimental methods of polymer degradation: The dynamic of every transformation in nature is governed by an initiator factor and afterwards by a model mecanism of the process. Thereby, this paper will present a series of experimental models of polymer degradation based on the nature of the process.

Biodegradation is a natural or artificial process of degradation caused by the actions of microorganisms. Although this process is quite complex, many studies indicate that some insects, fungi and other microorganisms have the ability to degradate numerous types of plastics [2],[3],[4].

Abiotic degradation refers to environmental factors as: mechanical forces, temperature, chemicals, light and water which acts on the structure of the material until it yields and disintegrates [2],[5],[6],[7].

The consequence of this degradation processes is represented by the most difficult to control pollution form: microplastics pollution.

Conclusions: Contrary to the many benefits, plastic materials can become a major concern due to the poor waste management strategy.

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POTENTIAL MEDICINAL VALUE OF HEMP SELECTIVE FRACTIONS

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Abstract: *Cannabis sativa is a species with valuable but underused pharmacological properties. Even its by-products such as the grist, could have medicinal value. This study proved the anticancer potential of some selective fractions, but further analytical studies are essential to identify the responsible compounds.*

Key words: *Cannabis sativa, anticancer, grist, seeds* (TNR 10)

Introduction: *Cannabis sativa* L. (hemp) has the highest industrialization capacity of all technical plants. The resulted products are diverse, from the medicinal or cosmetic substances, to automotive or construction materials. The aim of this study was to fractionate the peeled seeds and grist hydroalcoholic extracts and to evaluate the cytotoxic potential against a normal and a cancer cell line.

Experimental: *Plant material:* Hemp raw material (peeled seeds and grist) was gifted by a grower from North-Eastern area of Romania. *Preparation of extracts:* The total extracts were prepared by soaking 20 g of hemp peeled seeds or grist in 200 mL 50% alcohol (1:10 w/v) and further partitioned with chloroform (C fractions), ethyl acetate (EA fractions) and butilic alcohol (B fractions). Each selective fraction (including the exhausted waters - W fractions), was further diluted according to *in vitro* assay protocol. *Cell lines and viability assay :* Caco-2 (human colorectal adenocarcinoma), SC (normal human monocytes) were cultured according to manufacturers instructions (ATCC, USA). Cell viability was evaluated by MTS assay (CellTiter 96-Aqueous One Solution Cell Proliferation Assay®, Promega).

Results and discussions: We conducted a screening of cytotoxic potential of selective fractions (15 - 500 μg/mL) isolated from crude extracts of hemp peeled seeds and grist against a normal and a cancer cell line after exposure for 24 hours. It can be observed that most of the hemp selective fractions are not cytotoxic to SC cells, except for the highest concentration of butanol and aqueous fractions (500μg/mL) that induce a cell viability below 30% (Fig. 1).

At the same concentration, butanol fractions but not the aqueous one, exhibit cytotoxic effect on Caco2 cells, similar to the positive control, 5-fluorouracil. Interestingly, hemp total extracts did not exhibited any cytotoxic effect on Caco2 cells (Fig. 2). Previously, *C. sativa* compounds, mainly cannabidiol, were found to interact synergistically for cytotoxic activity against colon cancer cells [1, 2].

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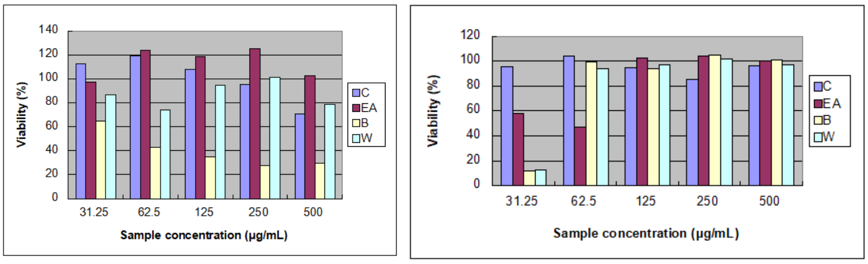
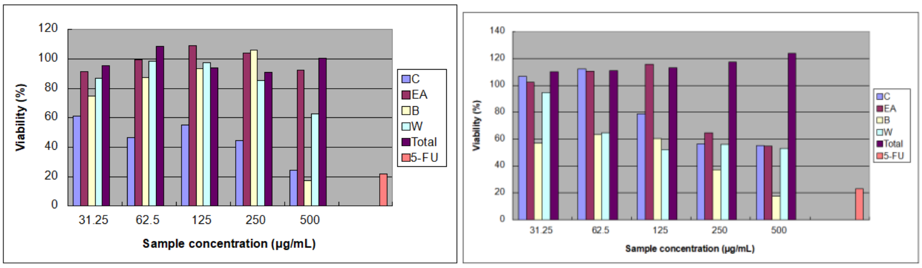
In our case, analytical studies to identify responsible compounds for exerting anticancer effects are a must.



a) b)

Fig. 1. SC cells viability after exposure to various concentrations of peeled seeds (a) and grist (b) selective extracts



a) b)

Fig. 2. Caco2 cells viability after exposure to various concentrations of peeled seeds (a) and grist (b) selective extracts

Conclusions: *Cannabis sativa* is a species with valuable but underused pharmacological properties. Even its by-products such as the grist, could have medicinal value. This study proved the anticancer potential of some selective fractions, but further analytical studies are essential to identify the responsible compounds.

Acknowledgements

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LALLEMANTIA IBERICA SEEDS OIL EXTRACTION

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Abstract: *The aim of this study is to present the oil extraction from dragon's head (lallemantia iberica) seeds using different extraction methods. For this purpose, the working conditions have been varied in a series of experiments in order to determine the optimum extraction conditions and finally the verification of these conditions. The experiments were conducted using ultrasound-assisted extraction (UAE) and batch extraction.*

Key words: *Lallemantia iberica* seeds, ultrasound assisted extraction, Box-Behnken design

Introduction: *Lallemantia iberica* (Bieb.) Fischer & C.A. Meyer is an annual oil plant cultivated in the past in Ukraine and Russia. *Lallemantia iberica* seeds contain in excess of 30% (up to 38%) siccative oil with an iodine index between 163 and 203, this oil being superior to the linseed oil, which is the standard commercially available highly unsaturated oil, with an iodine index of 170-185, in most cases. Because *Lallemantia* oil is rich in unsaturated fatty acids it offers an interesting potential for use in foods and also in the dye and varnish industry.

Experimental The initial oil content of *Lallemantia* seeds was determined using a laboratory Soxhlet extractor and three organic solvents. Batch extraction was performed in a glass extractor under mechanical stirring to ensure a good contact between phases. Ultrasound assisted extraction was carried out using a 500 W Ultrasonic Processors – VCX Series (Sonics & Materials, Inc., USA). The response variable was oil yield calculated using equation Eq.1, where M_{oil} is the mass of the extracted oil (g/100g seeds) and M_{ds} is the mass of the dried seeds.

$$Y_{oil} = \frac{M_{oil}}{M_{ds}} \times 100 \qquad (1)$$

A series of extraction experiments, varying the following parameters, were conducted: different solvents, solid/liquid ratio (S/L ratio), time and temperature. For the UAE, the ultrasound intensity was another parameter taken into consideration.

Results and discussions: Lallemantia iberica seeds oil contain both linolenic acid (60%) and linoleic acid (13.66%). In batch extraction the most important operating factors were temperature and extraction time. For ultrasound extraction the most important factors were solid/liquid ratio and ultrasound intensity.

Conclusions: Ultrsound assisted extraction technique and batch extraction were applied for the extraction of Lallemantia seed oil. As compared with conventional extraction methods, the extraction yield was higher using ultrasounds.

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BLACKBERRIES SEED OIL EXTRACTION

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Abstract*: The aim of this experimental study is to optimize the extraction conditions for blackberries seed oil obtaining. Batch extraction and ultrasound assisted extraction were used as extraction methods. A comparison of extraction yield obtained was done using a factorial experiment 2^3.*

Key words: Blackberries seeds, ultrasound assisted extraction, factorial experiment

Introduction:

Blackberries and other berries are among the most widely consumed fruits not only fresh but also in processed forms such as gems, jellies, beverages and other products. They have a high content of phytochemicals such as flavonoids, tannins, and phenolic acids recognized as having beneficial health effects in humans. During processing, in the fruit and beverage industry, a large amount of pomace, consisting mostly of seeds, is produced. This pomace could be considered a raw material for blackberries seed oil manufacturing [1].

Experimental The initial oil content in blackberries seeds was determined using a laboratory Soxhlet extractor using n-hexane as solvent. Batch extraction was performed in a glass extractor under mechanical stirring to ensure a good contact between phases. Ultrasound assisted extraction was carried out using a 500 W Ultrasonic Processors – VCX Series (Sonics & Materials, Inc., USA). The effect of process variables were studied and optimized using a 2^3 factorial experiment.
A desirability function was used for optimization of extraction process in both cases. The response variable was the extraction efficiency calculated using equation Eq.1, where $M_{oil\ ef.}$ is the mass of the extracted oil (g/100g seeds), $M_{oil\ Sox.}$ is the mass of the oil obtained by Soxhlet extraction.

$$Y = \frac{M_{oil\,ef.}}{M_{oil\,Sox.}} \times 100 \qquad (1)$$

Results and discussions: In case of blackberries seed oil extraction using ultrasound assisted extraction, the main process factors (ultrsound amplitude, extraction time, and temperature) were investigated using a 2^3factorial experiment. A regression model presented by Eq.2 was obtained.

$$Y = 0.8158 + 0.00425 \cdot X_1 - 0.041 \cdot X_2 + 0.003 \cdot X_3 + 0.0255 \cdot X_1X_2 - 0.026 \cdot X_1X_3 - 0.00175 \cdot X_2X_3 + 0.01675 \cdot X_1X_2X_3 \qquad (2)$$

The statistical significance of the regression model was checked by F-test and p-value, the model being significant. The highest extraction yield was obtained at

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30^0C, 30% US amplitude and 20 minutes extraction time. For these values the extraction efficiency was Y=0.930.

Conclusions: Blackberries seed oil was extracted with high extraction efficiency using ultrasound assisted extraction. In comparison with batch extraction US assisted extraction needs less time and a lower temperature, the extraction efficiency being higher.

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USING BACTERIA TO ENHANCE THE PHYTOREMEDIATION PROCESS APPLIED TO SOILS POLLUTED WITH INORGANIC POLLUTANTS

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Abstract*:* *In our study, three bacteria - Azotobacter chroococcum, Bacillus subtilis and Pseudomonas fluorescens were isolated from soil to study their interaction with Linum usitatissimum (flax), Panicum miliaceum (millet) and Rumex patientia (patience dock) plants in soils as Plant Growth Promoting Bacteria (PGPB). Therefore, the main objective of this paper was to establish if the selected bacteria may enhance the growth of each of the three selected plants, followed by proper selection of PGPB for application in phytoremediation of soils polluted with heavy metal.*

Key words*:* *Linum usitatissimum*, *Panicum miliaceum*, plant growth promoting bacteria (PGPB), *Rumex patientia*, sterile soil, non-sterile soil

Introduction: The PGPB can enhance plant growth directly by facilitating nutrients acquisition (e.g. nitrogen, phosphorus) and phytohormone content (e.g. auxin, cytokinins and gibberellins), or indirectly acting as biocontrol bacteria (protect the plants against patogens) [1, 2].

Experimental and/or Modelling: In order to establish the effects of *A. chroococcum*, *B. subtilis* and *P. fluorescens* on the development of plants, the experiments were carried out in polypropylene pots with 15 g of soil (sterilized and non-sterilized soil) and 2 seeds inoculated with or without microorganisms. The plants were grown for 25 days in the period September 9 - October 3, 2019, under laboratory conditions.

Results and discussions: The results showed that the selected microorganisms produce positive effects on the growth of flax, millet and patience dock, compared to the plants grown in the absence of the microorganisms. Also, there were observed some differences between plants growth in sterilized soil and plants growth in non-sterilized soil. For example, the roots of *Linum usitatissimum* and *Rumex patientia* grown in sterile soil are more branched compared to the plants grown in non-sterilized soil.

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Conclusions: The selected microorganisms were improved the growth of flax, millet and patience dock and can be considered as PGPB. So, based on this study the further work will be focused on the identification of PGPB mechanisms involved in bioremediation of soils polluted with heavy metals.

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CHARACTERIZATION OF WHITE WILLOW BY HPLC AND SPECTROPHOTOMETRIC METHODS

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Introduction: White willow (*Salix alba*) extracts have been used for longer than a century as antipyretic agents and as treatment for many rheumatic disorders. To the present day, extracts of willow are well-known as containing precursors of aspirin that have inhibitory effects upon the activity of enzymes that generate inflammation and pain.

White willow represents the main source of salicin and other salicylic derivatives (e.g. salicortin, 2'-O-acetyl-salicortin), compounds that share a similar structure to aspirin (acetyl salicylic acid), therefore it is also known as “nature’s aspirin”. Salicin can be cleaved (by enzymatic hydrolysis induced by emulsion and diastase) into glucose and saligenin (also known as 2-hydroxybenzyl alcohol or saligenol). Saligenin, in turn, produces salicylic acid via oxidation which has notable analgesic, antipyretic and antirheumatic properties, thus generating, stepwise, a prolonged effect.

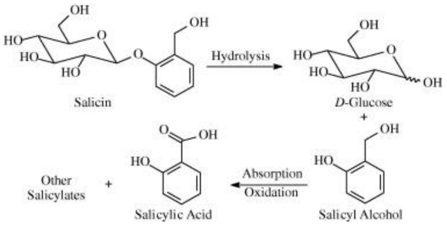

Figure 1. Conversion of Salicin→Saligenin→Salicylic Acid

Likewise, tannins present in white willow have a tonic, astringent, coagulant and mildly haemostatic effect.

This paper presents the studies made to investigate the composition of different parts of white willow by HPLC and spectrophotometric methods.

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Materials and methods: The selected plant for this purpose is white willow. The research was carried out on young and mature willow from different parts of the plant: bark, tree branch, leaves.
Their chemical composition was studied using HPLC – total salicylic derivatives expressed as salicin[1] and UV-Vis spectrophotometric methods – total polyphenols expressed as gallic acid (Folin–Ciocalteu method)[2], total flavones expressed as rutin and total tannins expressed as pyrogallol. Knowing that these classes of compounds also have antioxidant activity, the authors also set out to correlate the results obtained for polyphenols, flavones and tannins with antioxidant activity. For the determination of the antioxidant activity the CUPRAC (cupric-reducing antioxidant capacity) method was used.

Results and conclusions: Results show a higher content of salicylic derivatives in the willow bark and the tree branch than in the leaves. Polyphenols and flavones were determined in all samples with notable results for the leaves (67,2 mg/g in comparison with 21,3 mg/g for the tree branch). Also the results for the antioxidant activity correlate with the results obtained for polyphenols and flavones.

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PLANT OILS USED IN THE DEVELOPMENT OF LIPID NANOTRASPORTER (NLC) - BASED HYDROGELS FOR VARICOSE VEINS TREATMENT – COMPOSITION STUDY

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Introduction: In recent years, the importance of plant oils obtained by cold pressing has increased not only for their fat content but also for their frequent use in the pharmaceutical and cosmetic industry. The purpose of the paper consisted in carrying out a composition study for a series of plant oils in order to correlate it with their antioxidant activity, following their use in the development of hydrogels based on lipid nanotransporters (NLC) which have a therapeutic effect on varicose veins.

Experimental: Plant oils were obtained by cold pressing the seeds of pumpkin, castor, evening primrose, wheat germ, organically grown grape seeds, imported jojoba oil. The determination of fatty acids was performed by gas chromatography coupled with mass spectrometry (GC-MS). In order to identify the peaks corresponding to the analyzed compounds, the NIST spectrum library was used. Antioxidant activity was established by the FRAP (Ferric Ability Reducing of Plasma) method.

Results and discussions: The chromatograms obtained highlight the richness of saturated and unsaturated fatty acids present in the selected plant oils, the table showing the percentages of saturated and unsaturated fatty acids and the antioxidant activity of each type of plant oil studied.

No.	Oil Name	Total saturated fatty acids [%]	Total unsaturated fatty acids [%]	Antioxidant activity [mg Fe/g sample]
1.	Pumpkin seed	21,0	78,0	1100,3
2.	Castor oil	2,5	97,0	890,5
3.	Evening Primrose	6,8	93,0	560,7
4.	Wheat germs	18,7	80,3	950,4
5.	Grape seed	11,0	88,0	780,9
6.	Jojoba	0,5	75,0	690,5

Due to the disadvantages of conventional therapy, there is an obvious requirement for the development of new alternatives based on nanostructured topical formulations containing natural active principles and leading to a coupled action

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of high therapeutic performance and improved safety profile for the treatment of varicose veins.
Fatty acids in plant oils are contained in cellular and neuronal membranes, being useful for supplementing and normalizing unbalanced diets in adults and children and frequently used in pharmaceutical and cosmetic techniques as carriers of various active substances.

Conclusions: From the plant oils studied we ended up choosing to develop hydrogels based on lipid nanotransporters (NLC) from pumpkin oils and wheat germ oils which besides their high percentage of unsaturated fatty acids, also have high antioxidant activity. These oils will be used in cosmetic products which have a therapeutic effect on varicose veins.

Acknowledgment:
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OPTIMIZATION OF OLIVE OIL MILL WASTEWATER TREATMENT BY MEANS OF ELECTROCOAGULATION

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Abstract*:* *Pollutant removal from olive oil mill wastewater by electrocoagulation (Fe electrodes)*

Key words: olive mill wastewater, electrocoagulation, iron electrodes, chemical oxygen demand, phenols.

Introduction: Olive mill wastewater (OMWW) generated by the olive oil extraction process is the main waste product of this industry. These effluents are saline, very acidic, rich in organic matter, and contain poorly biodegradable polyphenols [1-2]. Electrocoagulation (EC) is an efficient technology for OMWW decontamination, the resulting sludge, rich in iron oxide (in our case), has a good potential as a substrate for dark fermentation or anaerobic digestion.

Experimental and Modelling: The experimental set-up consisted of a glass electrolytic cell (1 L) and two iron electrode spaced 2 cm apart and immersed during each experiment in 400 mL of liquid effluent. The chemical oxygen demand (COD) and polyphenolic compounds (PC) removal efficiency were determined after the EC treatment followed by sludge elimination by settling (24 hours, 20°C). The variables were the electrolysis time (up to 60 minutes) and the current density (up to 3 A).

Results and discussions: The EC treatment of crude OMWW (pH 4.47, COD 82.65 g.L^{-1}, electrical conductivity 7.8 mS.cm^{-1}), even at low current density, generates high quantities of gas which accumulate at the liquid/air surface, which forms stable foams and entails negative effects on the removal efficiency. This drawback can be corrected by a dilution of initial media with process wastewater.
As expected, it was found that an increase in electrolysis time and current density improves significantly the effectiveness of the treatment, but at the expense of higher power input (Fig. 1a and 1b). Thus, COD and PC can be effectively removed by EC, but energy requirements become excessive when COD removal is higher than 60% (Fig. 1a), whereas the oxidation of polyphenols require electric potential achieved only when current is at least 3 A (Fig. 1b).

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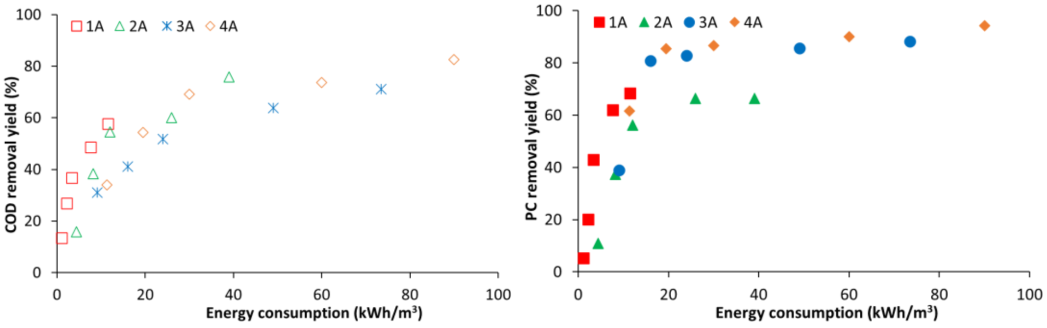

(a) (b)

Fig. 1 Removal efficiency of COD (a) and PC (b) against energy consumption

Conclusions: EC is a useful tool for COD and polyphenols elimination from OMWW. Moreover, the sludge rich in iron oxide has good potential as additional substrate for energy vector production by dark fermentation.

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AFFORESTATION A MOST EFFICIENT METHOD TO REDUCE CO_2

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Abstract*: This work presents a comparative study of mains NET in terms of technical-economic impacts.*

Key words: climate change, greenhouse gases, Negative Emissions Technologies, CO_2 emisions, afforestation, economic efficiency.

Introduction: Climate change is caused by modifications in Earth's energy balance because of natural factor: changes in Earth's orbit, changes in solar activity (solar explosion, or volcanic eruptions); and anthropic factors: greenhouse gases emission resulting by burning of fossil fuels, change in land use (forest surface decreasing and agricultural land surface increasing) [1]. Global warming and climate change concerns have released global efforts to reducing the concentration of atmospheric carbon dioxide [2]. Today are emitted approximately 30 GT of GHG and in 2050 are expected to be emitted 62 Gt GHG [3]. The global CO_2 emissions in 2050 would have to be reduced by 50-80% of the emission levels in the year 2000, where was emitted the 23 GT of GHG [4].

Experimental: The methods used for decreasing of atmospheric CO_2 known as Negative Emissions Technologies, NET, are numerous, such as: storage in biomass (primary production - algae growth, afforestation/reforestation, etc.), direct air capture (artificial trees and storage), geological carbon capture and storage, chemical storage (lime soda process), methanation, slow pyrolysis, ocean alkalinity addition (ocean liming), energy from biomass production (biogas, biofuel) etc [5, 6]. This work presents a comparative study of mains NET in terms of technical-economic impacts.

Results: The cost for the most used NET varied between 60 to 700 \$/t CO_2 storage [5]. The cheapest method to CO_2 storage is forestation/afforestation with cost range between 20 -100 \$/t CO_2 emitted. The capacity of CO_2 storage on hectare of land varies with type of tree, age and climatic conditions.

Conclusions: The largest amount of CO_2 (about 30 t CO_2/year/ha) is stored in old (over 70 years) hardwood trees. A case study afforestation in Romania showed

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that the excess of CO_2 that will be emitted until 2050 can storage in trees if the annual afforestation rate is 10 thousand ha.

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TOXICITY OF SINGLE AND COMBINED IONS OF LEAD AND CADMIUM FOR LETTUCE (*LACTUCA SATIVA ATTRACTION*)

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Abstract: *The toxicity of heavy metals to the plant and animal kingdom has been studied over time, finding that some heavy metals, although necessary for the growth of plants and animals at low concentrations, can generate negative effects when they exceed certain concentration limits, specific to each heavy metal. Other important factors that determine the magnitude of toxic effects in plants, for example, are the concentration of metal and plant species. Heavy metals can inhibit the photosynthetic activity of plants. Heavy metals easily accumulate in the human body through ingestion, inhalation or dermal contact, creating a major risk to human health even at low levels of exposure. In this context, the aim of the paper was to investigate the effects of the toxic action of lead and cadmium ions, single and as mixture on seed germination and growth of root length, shoots of lettuce (Lactuca sativa Attraction). Lettuce tolerance to heavy metal toxicity was investigated in laboratory conditions, analyzing the degree of deterioration of physiological processes of plants. Exposure of plants to these heavy metals by increasing the concentration of metals from 10 mg/L to 500 mg/L has resulted in a decrease in seed germination efficiency and plant growth dynamics. Cadmium ions have been shown to be more toxic than lead ions. The results showed that in the binary mixture of heavy metals (Cd and Pb), the growth and development of lettuce are affected to a greater extent compared to the individual heavy metals. The most severe toxicity was observed in the case of root growth, compared to the other components of the plant. Future studies will focus on assessing the risks to human health posed by the consumption of salad contaminated with heavy metals.*

Key words: heavy metals, *Lactuca sativa Attraction*, phytotoxicity, toxicity index, tolerance index

Introduction: Heavy metal pollution is usually the result of the activity of certain industries, such as mining, extraction of ores containing metals, ore processing activities, production of pigments, pesticides, galvanizing or metal plating of surfaces. , plastics manufacturing etc. [1].

Phytotoxicity tests are very important for the assessment of the ecological risks of pollutants, and various studies have shown that the most common effects of heavy metals on plants that have been clearly observed have been manifested by inhibiting seed germination and plant root growth [2,3]. In this context, the main objective of the paper is to assess the degree of deterioration of the physiological processes of lettuce (*Lactuca sativa L.* Attraction) under the individual influence of heavy metals Pb (II) and Cd (II) and the binary mixture of Pb(II) + Cd(II)

Experimental: *Solutions and reagents:* stock solution of $PbCl_2$ and $CdCl_2$ of 1000 mg/L, distilled water; *Procedure:* The tests were performed in triplicate, with 10 lettuce seeds being deposited in each sample, in Petri dishes, on Whatman

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filter paper. The seeds were moistened with 3 mL of Pb(II) solution of known concentration (10-500 mg/L), 3 mL of Cd(II) solution (10-500 mg/L, and for the toxicity of combined ions Pb(II)+Cd(II), the same volume of 3 mL was used by making a mixture of 1.5 mL Pb(II) + 1.5 mL Cd(II) of concentration 10-250 mg/L. At the same time, control tests were performed where the paper was moistened with distilled water; *Determination of optimal germination conditions:* the seeds were left for 7 days at a temperature of 18±2^{o}C, in alternating light/dark conditions to start the germination process and seedling growth.

Results and discussions: The results obtained on the toxicity of Pb (II) and Cd (II) on the root, stem and leaves of lettuce (*Lactuca sativa* L. Attraction) are represented graphically in Figure 1, and show that, when using concentrations of 250 and 500 mg/L in a solution of Cd(II), the seeds are unable to germinate.

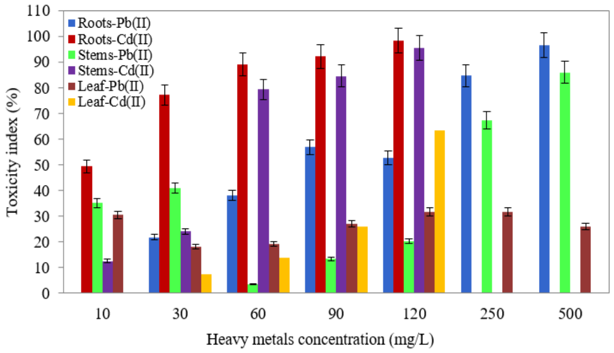

Fig. 1. Toxicity index for roots, stems and leaf of *L. sativa Attraction* under Pb (II) and Cd(II) stress

Conclusions: The results showed a decrease in seed germination and plant growth, by increasing the concentration of metals, and the increase in lettuce was more affected in the presence of Cd (II) compared to Pb (II).

Acknowledgments: 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-2019-5239, Contract no. 269PED/2020, within PNCDI III.

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LEAD-INHIBITORY EFFECTS IN TOLERANCE AND EARLY GROWTH OF CEREALS

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Abstract***:*** *In this paper we have investigated the toxicity of lead in wheat ((Triticum aestivum L.) hybrids (specifically, Glossa genotype). The study examined the effect of different concentrations of Pb(II) on the germination degree of wheat seeds, the elongation rate for roots, stems and the elongation inhibition rates for roots and stems. A number of 10 seeds, previously sterilized with NaOCl were placed in Petri dishes containing one layer of Whatman filter paper moistened with 10 mL of* $PbCl_2$ *solution of known concentration, to generate the metallic stress. In parallel, a similar sample but wetted with 10 mL of distilled was prepared as control. The number of germinated seeds were determined and these seeds were retained on the Petri dishes. The seedlings were analyzed in terms of roots and stems lengths and biomass. The results showed that the seed germination rate was affected by the presence of* $PbCl_2$ *ions, while the roots and stems length decreased as the concentration of metal increased. In conclusion, the toxic effect of Pb(II) depends on metal concentrations and the specific parts of the plant.*

Key words: germination, lead, phytoremediation, toxicity, wheat seeds

Introduction: Heavy metal pollution is a serious problem for both the environment and human health. Agricultural soils contaminated with heavy metals cause large losses of production worldwide, due to their toxicity, non-biodegradability and mobility [1]. Lead is among the most toxic heavy metals, which once in the soil, can be transported to plant, animal and human tissues through the food chain and can affect the activity of vital cellular components [2]. Therefore, it is a vital need to find long-lasting and safe methods for remedying the environment. For this purpose phytoremediation is often the most efficient and advantageous method [3].

Experimental and/or Modelling: *Solutions and reagents:* lead ion solution - concentration range 50-400 mg/L, distilled water, sodium hypochlorite (20%), ethyl alcohol (99%), nitric acid and hydrochloric acid, 4-(2-pyridylazo)-resorcinol or PAR, ammonia (25%), acetone; *Procedure:* 10 wheat seeds were evenly distributed in Petri dishes containing a layer of Whatman filter paper with 10 mL $PbCl_2$ solution of known concentration (50-400 mg/L) to create metal stress, and 10 mL of distilled water for control samples. After 5 days of germination, growth indicators were determined, and then the roots and stems were collected separately to determine the fresh and dry biomass; *Determination of optimal germination conditions:* Wheat seeds and glassware should be sterilized and left

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for a period of 5 days to germinate in conditions of intense light and temperature between 15-20^{o}C.

Results and discussions: By performing phytotoxicity tests, it was observed that the germination of wheat seeds took place in the presence of lead ions, but with the increase of metal concentrations, the growth rate of roots and stems decreased. Greater damage to the roots has been observed, as these are the first organs of the plant exposed to lead ions.

Conclusions: It was found that the toxicity of Pb(II) in wheat seeds, roots and stems depends on the values of metal concentrations. The wheat hybrid *Glossa* can be considered, if necessary a potential phytoremediating agent of lead, but for relatively low Pb(II) concentrations.

Acknowledgments:

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ASSESING AN ADVANCED PRETREATMENT METHOD ON THE BIODEGRADABILITY OF SUNFLOWER SEED CAKE TO BIOGAS

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Abstract*: Lignocellulosic biomass is a renewable and abundantly available substrate for anaerobic digestion. Yet, for a cost-effective biogas production using lignocellulosic materials, pretreatment methods are usually required to enhance solubilisation by lignin removal and for cellulose crystallinity reduction. In this paper, the influence of γ-ray irradiation on the digestibility of sunflower seed cake in batch mesophilic anaerobic digestion was investigated.*

Key words: Biogas, gamma irradiation, mathematical modelling, pretreatment, sunflower

Introduction: Anaerobic digestion (AD) is generally a suitable and efficient way to treat various types of organic wastes for energy and nutrient recovery. However, some specific substrates can show low biodegradability during the hydrolysis step of AD which may be due to their recalcitrant structure hampering the activity of microbial enzymes [1]. In this paper, the effect of gamma irradiation pretreatment on the biomethane production of sunflower seed cake (SuSC) was evaluated.

Experimental and Modelling: *Materials:* SuSC, which is an agro-industrial by-product of the sunflower oil production, and irradiated SuSC samples were used as substrate for the biochemical methane (BMP) tests; *BMP tests:* The experimental set-up for BMP tests is shown in figure 1. Batch AD tests were carried out at mesophilic temperature for 74 days. The methane content in biogas was determined by GC-MS, while the biogas volume was measured by the water displacement method. *Pretreatment method:* The exposure of SuSC samples to γ-rays was carried out using a ^{60}Co source at a dose rate of 1.0 kGy/h, for a total irradiation dose of 0, 50, 100 and 150 kG, corresponding to samples S1, S2, S3 and S4, respectively. *Modelling:* Results of BMP tests were used to predict the dynamic of biomethane yield using Cone and modified Gompertz kinetic models.
Results and discussions: Time variations of experimental biomethane yields for untreated (S1) and pretreated (S2-S4) substrates, which are presented in figure 2, show a decrease in the biomethane yield with increasing irradiation dose. The biomethane production of the irradiated samples decreased by up to 2.4 times in comparison with that of the untreated sample. Biomethane yields predicted using Cone and modified Gompertz kinetic models were similar and in a good agreement with experimental results. Over-acidification of the AD broth or some competing processes occurring simultaneously in the lignocellulosic material

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might be responsible for irradiation failure to increase the methane production of SuSC [2, 3].

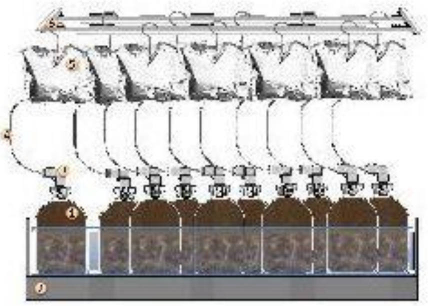

Fig. 1 Experimental set-up:
(1) brown glass serum bottles;
(2) thermostatic water bath;
(3) connection system;
(4) connection tube;
(5) gas collecting bag;
(6) hanging system for gas bags

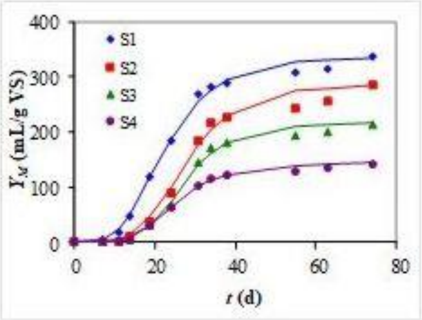

Fig. 2 Time variation of biomethane (M) yields for untreated (S1) and pretreated (S2-S4) substrates (bullets: experimental data, lines: data predicted by Cone model).

Conclusions: Results indicate that SuSC might be a valuable substrate for AD. The high irradiation pretreatment does not however bring value to the biomethane production of samples. Further investigation is needed to establish the exact mechanisms underlying the decrease in biomethane production with increasing irradiation dose.

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