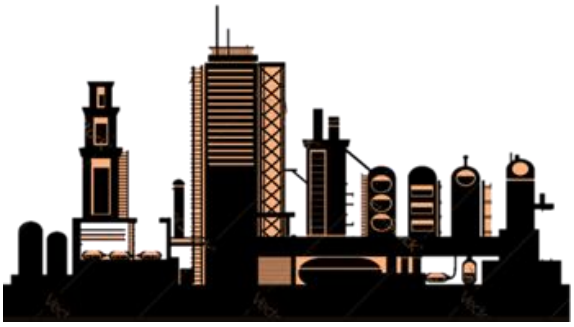
ICCE 2020

International Conference on Chemical Engineering

5th International Conference on Chemical Engineering

Romania, Iași, October 28 – 30, 2020

Book of Abstracts



"Gheorghe Asachi" Technical University of Iași	"Cristofor Simionescu" Faculty Of Chemical Engineering and Environmental Protection

Innovative Materials and Processes for a Sustainable Development

5th International Conference on Chemical Engineering

Romania, Iași, October 28 – 30, 2020

ICCE 2020

Celebrating 100 years since the birth of Prof. Cristofor I. Simionescu

BOOK OF ABSTRACTS

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BOOK OF ABSTRACTS

Section 1 Advanced Materials, Manufacturing and Processes

DISPERSION IN A TWO-PHASE FLOW SULZER COLUMN

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Axial mixing in the case of a single liquid phase flow and two-phase (gas-liquid) flow in a Sulzer packed-bed column has been studied. Tap water and respectively, air have been counter-currently circulated. The pulse response technique consisting of an inert salt solution injected at the column entrance, followed by its concentration measurement at the column exit was used.in order to establish the residence time distribution, $E(\theta)_{exp}$, and the normalized dispersion, σ_θ^2, at different liquid and gas flow rates. All the residence time distributions were relatively symmetrical, with an increase in the experimental data dispersion, as the gas flow rate increased.

From the normalized dispersion values calculated based on the obtained data, the distribution functions corresponding to the axial dispersion model and the cellular model were determined and compared to the experimental distributions. Depending on the gas and liquid flow rates, good similarity with one model or another was obtained.

Furthermore, the axial dispersion coefficient and its dependence on the gas-load factor have been established. Additionally, the liquid hold-up in the column, calculated as a ratio of the liquid superficial velocity to the liquid real velocity, was determined at different gas and liquid flow rates and was correlated also to the gas load factor.

For the nine Sulzer packages inserted in the column, the pressure drop, measured with a differential manometer connected to the bottom and top of the column packing, increased with the gas load factor, for different liquid flow rates. Comparisons with some literature correlations are included.

Chemical recycling of wastepaper to valuable products

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One of the most daunting issues facing the world is the mounting waste problem that is not only an environmental problem but an economic loss as well because almost all wastes are considered to be a useful resource. The paper recycling is of practical interest since this is a cellulose-containing raw material that can be used to produce valuable cellulosic materials.

In our previous paper, we described the preparation of the super-swollen hydrogels from hardwood pulp, flax fibers and cotton cellulose regenerated from the solutions of DMAA/LiCl (Kotelnikova et al., 2017). In another paper, we isolated powder celluloses from waste newsprint paper and cardboard wrapper using acid hydrolysis. The prepared samples were used as adsorbents for a dye (Mikhailidi et al., 2019). The aim of this study was to develop an effective and low-cost method for producing cellulose-based functional hydrogels (HGs) directly from the paper wastes. Characterization of the properties of the HGs was the second goal of this study.

Two types of paper wastes were processed, namely, packaging and filter cardboard (CB) and newsprint paper (P) with or without ink. The wastes were subjected to dissolving in solvent system DMAc/LiCl, according to the method described elsewhere (Kotelnikova et al., 2017). The dissolving ability (DA) of the P and B samples mostly depended on the type of paper/cardboard and the temperature during the dissolving. The DA varied in wide range, i.e. from 25% to 99 mass.%. The P sample exhibited the least DA (25 - 42 mass.%), while the CB samples had higher DA (50 - 99 mass.%). The filter CB had the highest DA that was similar to the solubility of the hardwood pulp.

The solutions of waste paper and cardboard in DMAc/LiCl were coloured to a different extent from slight-yellow to brown depending on the temperature of the dissolving and type of the pristine paper. After dissolving and filtration, the solutions were disposed into shallow flat containers. Over time, spontaneous gelation occurred due to the self-assembly of cellulose chains in the solutions. The stable gels formed without changing temperature and any nonsolvents. The solvent was replaced with water by rinsing and the super-swollen HGs from P and CB were obtained (below, P-HG, CB-HG, respectively). The HGs were transparent or opaque and some of them were slightly coloured. They were kept in water and were stable so long as needed. To study the properties of the HGs, they were freeze-dried and then characterized using chemical methods, WAXS, FTIR, and SEM.

The swelling degree and the equilibrium water content were very high for all studied samples of HGs and these values were higher for the CB-HGs (3890 - 4005 mass.% for packaging and filter CB, correspondingly) than for the P-HG (3720 mass.%). This fact is all the more surprising as the X-ray crystallinity of the pristine CB samples (Cryst. = 33.2%) was higher than that of the P (Cryst. = 22.6%). However, the CBs contained some impurities and this diminished the dissolving ability.

Due to high equilibrium water content, we proposed that the hydrogels should have a developed pore system. Surface and bulk morphology and micro-architecture of the freeze-dried HGs were studied with SEM. The surface of the pristine CB sample had densely packed structure at the micron length-scale with no indication of preferred orientation, while the CB-HG revealed a random network with evenly distributed through pores of different sizes. Evidently, it's the porosity that largely determines the high sorption properties of the HGs.

According to the FTIR analysis, both pristine P and CB had absorption bands characteristic to cellulose I and revealed a high content of cellulose. However, they contained lignin and hemicelluloses. The spectra of the HGs revealed a higher chemical purity and a sharp resolution of absorption bands. The overall spectra of the regenerated samples corresponded largely to the cellulose I polymorph.

In conclusion, the low-cost and effective method was developed for the preparation of the hydrogels from waste papers. The physico-chemical properties of the hydrogels seem to be promising for practical application.

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New equations for gas phase pressure drop in expanded metal sheet packings for transfer processes in packed columns

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The horizontal expanded metal sheet packing (called also Holpack) is designed and investigated for carrying out mass and heat transfer processes in column apparatuses (Kolev, 2006). The packing is made of expanded metal sheets, placed horizontally on certain distance from one another along the column height. To avoid the one-sided direction of the fluids by the lamellae forming each sheet, the sheets are arranged consequently by rotating of 90^0 in the same direction – the so called "crosswise" arrangement. This construction leads to low specific weight and creates condition for highly effective heat and mass transfer at comparatively low gas pressure drop, as well as large specific effective surface area. As a result, the packing was successfully implemented in many processes in the chemical and power industry, as well as in the environmental protection (Kolev et al., 1987; Kolev et al., 1996; Semkov and Zhelev, 2001). A thorough research was needed to be accomplished with a view of the most appropriate cases for its use as well as for collecting data and working out equations for determination of its main characteristics, included in the corresponding mathematical models. Such are the equations for pressure drop (dry and wet), loading point, effective area, axial mixing of the phases, and coefficients of mass transfer, controlled by gas and liquid boundary layer, etc.

The earlier models and equations for determination of the pressure drop of dry and irrigated Holpack packing as well as for loading point gas velocity were proposed by (Kolev and Darakchiev, 1973; Kolev, 2006). Subsequently, after many years of practical (incl. industrial) experience (Semkov, 2006), three new improved dependences were developed, firstly presented in this work. It is necessary to underline that in the new equations the same experimental data are used as in the old ones; the principal differences evolve from the structure of the new equations and the better estimation of the geometric dimensions.

The proposed new equations are derived using the dimensional analysis and the least squire approach regression. For each equation the main statistic parameters (the mean arithmetic error and the standard deviation) are given. The confidence intervals of the constants based on Student distribution at 95% confidence level are presented as well. The comparison with the experimental data is illustrated in appropriate diagrams.

The accuracy of the new equations is substantially improved, in particular for the loading point – 4.56% mean arithmetic error and 7.67% standard deviation, offering a stable base for industrial design and applications.

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Investigation of the influence of chitosan on the properties of bleached cellulose papers

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Polymers which are produced naturally or genetically from microorganisms have a great potential as fillers, coatings or films used in paper and packaging field. At polysaccharides mostly used are chitosan, starches and alginates. They have great properties such as nontoxicity, can be used in many fields of material science and are available in the market also as waste materials. Because of their hydrophilic nature, polysaccharides exhibit poor water vapour barrier. Chitosan is one of the most biodegradable, non-toxic and commonly used polysaccharide, which is derived from the deacetylation of chitin. It has also attracted interest in packaging, especially in food packaging as edible films and coatings. It has high crystallinity and a hydrogen bonds between molecular chains, which exhibit great oxygen properties. Due to the positive charge on the amino group under acidic conditions, chitosan binds negatively charged molecules and therefore represents a greater barrier against grease. Due to its good barrier properties, chitosan coatings can be used also as barriers in packaging (Brodnjak, 2017).

In the production of different paper grades either printing or packaging, bleached celluloses of different wood species are used, in different proportions and have to have different hydrophobicity, which is done with the help of various sizing agents such as rosin size and aluminium sulphate and other synthetic sizing agents. These synthetic sizing agents can be replaced by some natural polymers; such natural biopolymer is chitosan.

The aim of the present work is to study the influence of chitosan biopolymer solutions on the properties of papers with different composition with bleached celluloses as fibre material. The chitosan solution is added during the formation of the paper sheets in various consumption - 0.2%; 1%; and 2% of o.d.f. Paper samples are made of different fibrous compositions from bleached sulphate softwood pulp (BSWP) and bleached sulphate hardwood pulp (BHWP) in the ratio - 50% BSWP:50% BHWP, 80% BSWP:20% BHWP, 100% BSWP and 100% BHWP. It was found out that the use of chitosan additive in the composition of bleached cellulose paper samples leads to improved strength and hygroscopic properties. $Cobb_{60,}$ (g/m2) water absorption studies, shows that the addition of chitosan solution reduces it values. In paper samples from 100% BSWP, the addition of 0.2% chitosan solution is sufficient to impart hydrophobicity. The addition of rosin size and aluminium sulphate to the paper samples after the addition of chitosan further reduces the water absorption capacity of the paper.

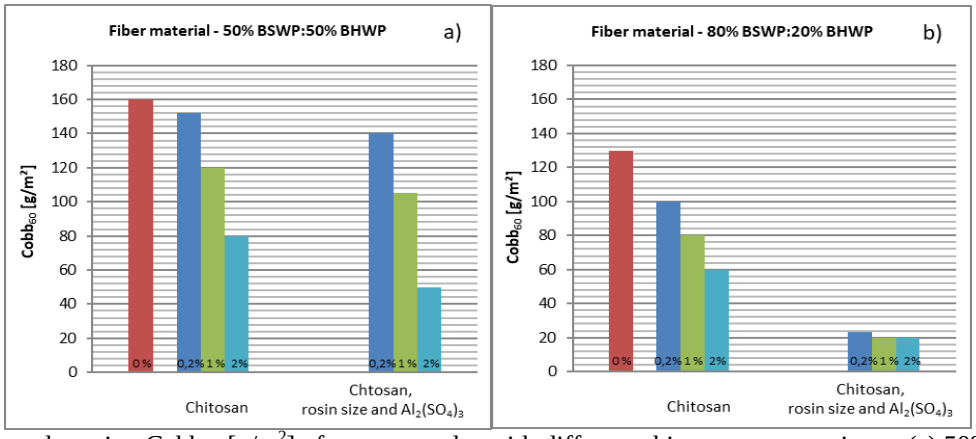

Figure 1. Water adsorption $Cobb_{60}$ [g/m^2] of paper samples with different chitosan consumption at (a) 50% BSWP:50% BHWP and (b) 80% BSWP:20% BHWP

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Thiourea-chitosan hydrogels: preparation and sorption of heavy metal ions

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Novel sorbents based on chitosan and its derivatives are continuously developed to remove heavy metal ions and organic pollutants from contaminated waters (Dragan et al., 2018). In this study, porous hydrogels based on chitosan functionalized with thiourea groups (CHITU) were prepared through cryogelation technique and were evaluated for the sorption of Cu^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} from simulated contaminated waters. The CHITU hydrogels were characterized by SEM, EDX, TGA and rheology measurements, while their heavy metal ions sorption capacity was determined using ICP-OES. The maximum experimental sorption capacities of CHITU hydrogels towards Cu^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} were 129.8 mg/g, 134 mg/g, 83.4 mg/g and 132.5 mg/g (experimental conditions: temperature = 25 ^{o}C, contact time = 24 h and pH = 5), respectively. The fitting of equilibrium and kinetics sorption data with various empirical models gave evidence that the sorption process of all metal ions was best described by the Sips and pseudo-second order models, respectively. Reutilization of CHITU hydrogels in three consecutive sorption/desorption/regeneration cycles showed that they possess completely renewable sorption properties.

In comparison with other literature available on CHI-based sorbents (Petrova et al., 2014; Mende et al., 2016), the CHITU hydrogels designed herein have similar sorption properties for Cu^{2+}, but net superior sorption properties for Co^{2+}, Cd^{2+} and Ni^{2+}. Hence, CHITU hydrogels can be considered as promising matrices for the removal of heavy metal ions from contaminated waters.

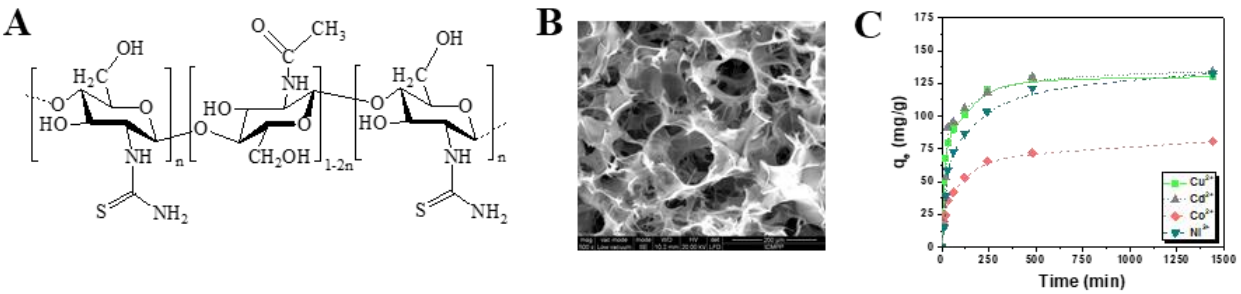

Figure 1. The structure of CHITU polymer (A), the SEM image of the CHITU hydrogel (B) and kinetics of Cu^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+}sorption by the CHITU hydrogel (C).

Acknowledgements
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Chitosan copolymers with improved solubility by Ring-Opening Polymerization technique

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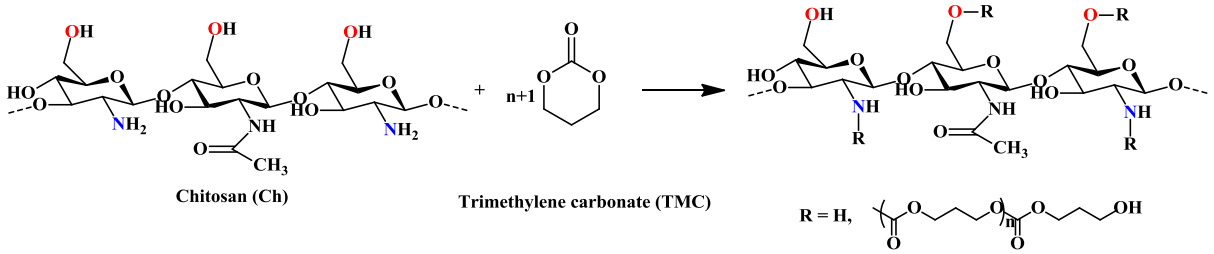
Polysaccharides are one of the classes of high interest in biomedical field due to their properties, such as the ability to retain water, rheology, the ability to form inter- and intramolecular bonds. In addition, the structural diversity together with the possibility of forming numerous derivatives from biopolymers are benefits that strengthen the motivation for their use and development. Particular attention was paid to chitosan (Ch), the completely or partially deacetylated form of chitin, obtained by treatment with strong alkali. Sources of chitin and chitosan include fungi as part of their cell wall and insect exoskeletons, but the most abundant source is shellfish waste (Niaounakis et al., 2014).
Although its properties recommend chitosan as a promising polymer for a wide range of applications, its main limitation is its low solubility in media with a pH above ~ 6.5. This parameter is difficult to manage because it is related to the degree of deacetylation (DD), the distribution of acetyl groups, pH, type of acid used and ionic concentration (Rinaudo et al., 2006). In order to improve the solubility of chitosan both at neutral pH and in a basic media, the point of interest of the researchers was its chemical modification, in order to extend its applicability in different fields, especially in the biomedical field.
The goal of this study was the synthesis and characterization of novel chitosan derivatives, by Ring-Opening Polymerization technique of a 6-membered cyclic carbonate ester, when chitosan acts as an initiator. The reactions were performed in heterogeneous system using different molar ratios between chitosan and monomer, in melt bulk or in solution, in presence of a swelling agent for chitosan (Liu et al., 2005).



Scheme 1. Synthetic pathway for obtaining of the chitosan derivatives

The obtained derivatives were characterized from the structural point of view, using ^{1}H-NMR and FTIR spectroscopy. The supramolecular changes induced by grafting the side chains on the chitosan backbones, along with the morphology of the films casted from solution were investigated using polarized light microscopy (POM), atomic force microscopy (AFM) and fluorescence microscopy (FM).
The solubility of the chitosan grafted copolymers was evaluated by varying different parameters, including the solvent, pH and temperature. Some derivatives presented the property of being water soluble, in comparison to the pristine chitosan that presents solubility only in acidic media, this being the first step for the upcoming research.

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Iminoboronate chitosan hydrogels – a promising tool in the treatment of Candida infections

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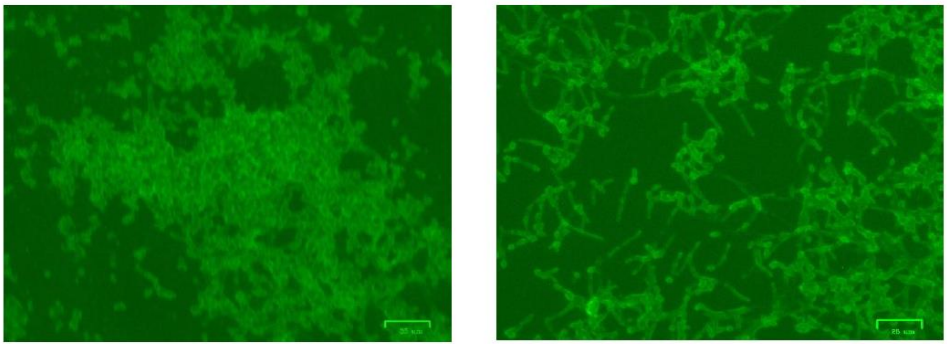
Hydrogels are an important class of biomaterials with applicability in many areas of medicine: from drug delivery to tissue engineering and not only. There are plenty of polymers which proved to be able to form hydrogels, by chemical or physical processes[1,2]. Among them, chitosan is by far one of the most intensely used because of its therapeutic properties, being biocompatible and biodegradable, presenting also hypoglycemic, hypolipidemic, antitumoral and antifungal properties[3].

Therefore, this study had as main objective the obtaining of biocompatible hydrogels based on chitosan and 2-formyl phenyl boronic acid (2-FPBA) - a monoaldehyde with strong antifungal properties. By varying the molar ratio between the NH_2 group of chitosan and the CHO functional group of 2-FPBA, a series of hydrogels based on imino-boronate motif was prepared and characterized. FTIR and NMR demonstrated the formation of the imine linkage between the reagents, while Wide Angle X-ray diffraction revealed the three-dimensional nanostructuring of the iminoboronate-chitosan network, consequence of both the reversibility of the imine linkage and of the hydrophilic/hydrophobic segregation. The xerogels presented a highly porous morphology as demonstrated by scanning electron microscopy and a mass equilibrium ratio between 10 and 60, depending on the ration between NH_2 and CHO functional groups. The antifungal activity of the obtained hydrogels was evaluated on two Candida strains, glabrata and albicans on both planktonic yeast and biofilm and the obtained results recommend these materials as a promising tool for the treatment of Candida infections.



a) **b)**

Figure 1. (a) Biofilm of C. albicans in a control well (without hydrogel) after 48 h; (b) Biofilm of C. albicans after being in contact with the hydrogel based on chitosan and 2-FPBA.

Acknowledgments

This work was supported by the Romanian National Authority for Scientific Research MEN – UEFISCDI (grant number PN-III-P1-1.2-PCCDI2017-0569, no. 10PCCDI/2018 and by the project H2020-MSCA-RISE-2019: Smart Wound Monitoring Restorative Dress-ings (SWORD) (no. 873123).

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Ionic composites based on chitosan and poly(amidoxime) grafted on starch as beads for binding metal ions

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The pollution of the waters with metal ions is becoming a huge environmental problem because of the large variety used in different human activities. Among the conventional technologies used for the heavy metal removal, such as chemical treatment, evaporation, electrolysis, membrane separation, ion exchange, separation/enrichment by sorption, and biological processes, adsorption is considered superior to the other techniques in terms of low costs and operation. Other advantages of adsorption include the flexibility in the selection of the adequate sorbent, and the possibility of enriching the trace metal amounts.
Recently, the use of natural materials such as polysaccharides for applications has attracted the attention of many investigators due to their non-toxic, low cost, ease of availability and biodegradability characteristics (Pal et al., 2006; Dragan et al., 2015; Wu at al., 2017). As a functional biological polymer, starch offers an interesting set of characteristics, including biodegradability, biocompatibility, and bioactivity. Native and modified starches have been used as row materials in the preparation of novel sorbents (Loghin et al., 2012, Dragan et al., 2014).
In this context, this study aims to obtain ionic composites based on cross-linked chitosan, as matrix, and poly(amidoxime) grafted on starch, as entrapped chelating resin, prepared as beads. The beads are obtain by ionotropic gelation/covalent cross-linking of a mixture of composed of chitosan and amidoximated starch. The obtained beads are used for binding metal ions (such as Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+}) as a function of sorbent composition, synthesis strategy, pH, sorbent dose, contact time, initial concentration of metal ions, and temperature, respectively. The resulted beads show reusability of sorption/desorption cycles with no significant decrease in sorption capacity.

Acknowledgments
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Microparticulate systems based on polysaccharides and methacrylic monomers for wastewater treatment

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Nowadays, various types of natural and synthetic polymers can be used for the preparation of graft copolymers with different architectures and tailored properties for different application fields (Mahanta et al., 2015; Mittal et al., 2016). Among natural polymers, we chose chitosan and gellan gum. Chitosan is one of the most studied biopolymer due to its well-known properties in terms of biodegradability, biocompatibility, bioadhesion, bioactivity, non-toxicity, haemostatic behavior and wound healing properties while gellan gum draw much attention from the scientific community even since its discovery in 1980 because it has the ability to form transparent gels at low concentrations (Rinaudo, 2006; Siqueria et al., 2011). As synthetic materials, much attention has been drawn by various acrylates and methacrylates polymers due to their low toxicity and versatile applicability. From the great variety of synthetic monomers, glycidyl methacrylate is an attractive vinyl monomer because of its low toxicity, lower cost compared with other acrylic monomers and was chosen due to its two important functional groups: the methacrylic group capable of polymerization and the epoxy group which can be functionalized very easily (Vasiliu et al, 2019). Also, dimethacrylic monomers contain two methacrylic groups which are capable to form crosslinked networks.
Combining the properties of polysaccharides and synthetic polymers in a single compound this study aimed to obtain new composite polymeric materials as sorbents of metal ions from wastewaters. The preparation method of composite grafted microparticles consisted in achieving the crosslinking and grafting reactions in a single step. This was possible by using the suspension polymerization technique with some improvements consisting in modifying the aqueous phase by adding both a polysaccharide together with the stabilizing agent as well as a water-soluble initiator in order to determine the appearance of radicals on the polysaccharide chain (Lungan et al., 2014). The successful of polysaccharides grafting onto the synthetic polymer network was highlighted by different modern techniques such as, infrared spectroscopy, scanning electron microscopy, atomic force microscopy, dimensional analysis, thermogravimetric analysis. Also, the epoxy group content and porous structure of microparticles have been studied. The porous nature of grafted and un-grafted microparticles has been followed by the following parameters: porosity (P, %), pore volume (PV, mL/g) and specific surface area (S_{sp}, m^2/g). Grafting of polysaccharide onto crosslinked networks has led to the preparation of polymeric materials with high specific surface area (50-160 m^2/g) and better swelling capacities (101-106%) compared to microparticles based on glycidyl methacrylate and dimethacrylic monomers [(31-69 m^2/g) and (39-57%), respectively]. Furthermore, the sorption properties of grafted and un-grafted microparticles were tested using Cu(II) and Ni(II) solutions. Two-parameter isotherm models were used to evaluate the adsorption equilibrium. The kinetics were fitted with the pseudo-first order, pseudo-second order and intraparticle diffusion models. The results showed that the grafted microparticles have a higher adsorption capacity, making it suitable for use as sorbents in wastewater treatment.

Acknowledgements
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New urea delivery systems based on salicyl-imine-chitosan hydrogels

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The demographic and technological evolution imposes the necessity to improve the agricultural production, especially in the arid areas. A realistic solution to do this is the development of novel multifunctional formulations based on renewable resources, which are capable to release nutrients in a controlled manner and also to control the moisture of the soil (Abobatta, 2018). Chitosan based hydrogels are proper materials for this purpose, as they are able to encapsulate nutrients and to adsorb a large amount of water (Pereira et al., 2017). In line with these premises we designed and prepared soil conditioner systems originating from renewable resources by *in situ* hydrogelation of chitosan with salicylaldehyde in the presence of urea, the oldest soil nutrient used in agriculture (Iftime et al., 2017; Iftime et al., 2019).

The urea delivery systems were characterized from the structural and supramolecular points of view by FTIR spectroscopy, X-ray diffraction, SEM and polarized light microscopy.

The FTIR spectroscopy demonstrated the formation of the imine linkage between chitosan and salicylaldehyde and confirmed the presence of urea in the resulted systems. Wide Angle X-ray diffraction and optical polarized microscopy revealed the formation of organized supramolecular 3D systems, while SEM showed highly porous morphologies. Both X-ray and SEM techniques proved that the urea encapsulation was realized in form of submicrometric and micrometric crystals distributed in the pores walls and pores when the salicylaldehyde crosslinker amount was high, while in the other cases, the urea had a more homogenous, fine distribution, mainly in the pore walls.

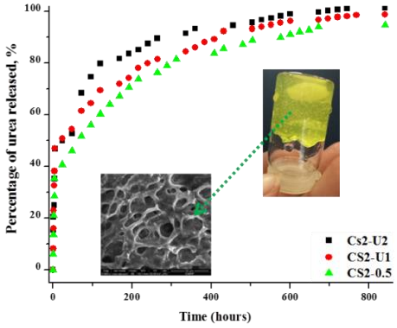

Figure 1. The percentage of urea release during 35 days from the salicyl-imine-chitosan systems

The *in vitro* release kinetics of urea in distillated water was evaluated by NMR spectroscopy, revealing that the salicyl-imine-chitosan hydrogels are able to provide a sustained release of the encapsulated urea during 35 days. The ability of the systems to act as plant regulators was assessed by germination tests and measurements of the nitrogen dynamics in soil. Also, the ability of the systems to retain water in soil was evaluated by measuring the water absorbency and largest water-holding ratio. The formulations demonstrated excellent water retention in soil and better growth of the plants compared to reference, demonstrating a high potential for application as eco- soil conditioners.

Acknowledgments This work was supported by the Romanian National Authority forScientific Research MEN–UEFISCDI (grant number PN-III-P1-1.2-PCCDI2017-0569, no. 10PCCDI/2018) and by the projectH2020-MSCA-RISE-2019: Smart Wound Monitoring Restorative Dress-ings (SWORD) (no. 873123).

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Effect of metal doped ZnO ceramic nanostructures on photocatalytic properties

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Nowadays, the ceramic nanostructures based on pure ZnO and doped with various metals (La, Er, Sm, Ag, Mo, Sn, and so on) with one dimensional shape are intensively studied due to their remarkable performances in photocatalysis, optics, electronics, semiconductor materials, etc [1-3]. It is known that ZnO is a semiconductor material with a band gap energy of 3–3.37 eV and a large exciton binding energy of 60 meV. Likewise, undoped/doped ZnO materials are often used in waste water treatments by degradation of the organic dyes. Therefore, in this work we proposed to obtain ZnO doped with La, Er, Sm, Ag, Mo in various concentrations (from 0 to 4%) using electrospinning-calcination method. Polyvinylpyrrolidone (PVP) was utilized as a matrix in the electrospinning process. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used for morphological and structural characterization of resulting materials. SEM and TEM analysis show the formation of uniform, long and continuous fibers with diameters in the range 0.39 to 1.19 μm and major differences in the size and shape of the crystalline grains. Optical band gaps of these ceramic nanostructures were estimated from reflectance data using Kubelka-Munk theory and were found to vary between 2.5 and 3.5 eV, depending on the type of dopant and doping concentration (0 to 4%). The photocatalytic activity of ZnO:Me products was investigated by using different dyes (Methylene blue, Congo-Red, Rhodamine B, Amaranth) under UV and visible light irradiation. Good performance and significant improvements were observed for all doped materials with maximum efficiency values of up to 98%. Figure 1 shows some examples of photocatalysts based on ZnO doped with Ag, Sn, Sm obtained by electrospinning-calcination method, and their photocatalytic testing for degradation of organic dyes (Congo-Red and Amaranth).

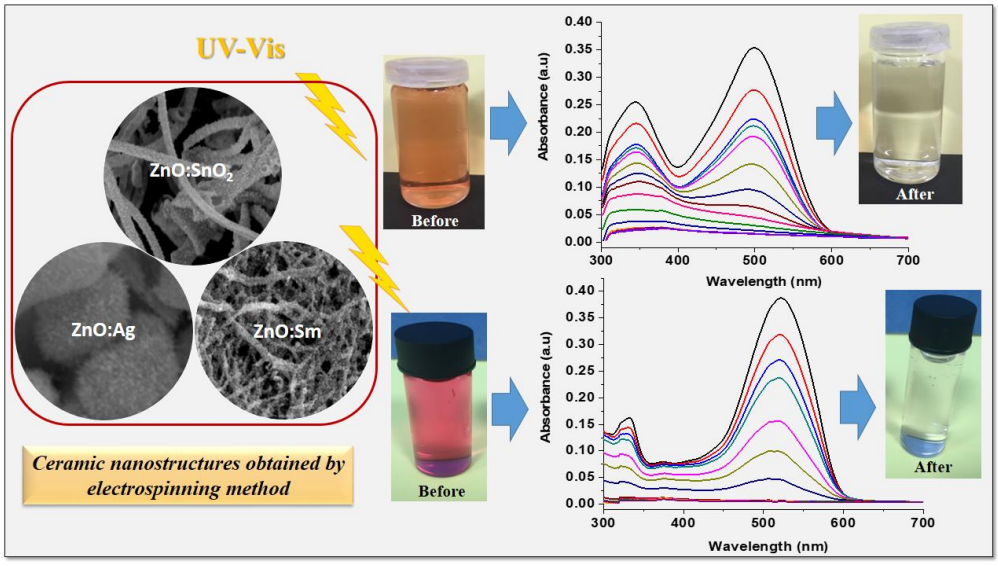

Figure 1. SEM images of $ZnO:SnO_2$, Ag, Sm; profiles of UV-Vis absorbtion spectra recorded after degradation under UV-light irradiation of Congo Red and Amaranth dyes.

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Novel chitosan-based nanofibers for wound healing applications

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Aim

The classical method of producing nanofibers is via electrospinning technique, which offers the possibility of working at a nano-scale with a high yield (Sarhan, W., 2015, Rieger, K. A., 2016). The aim of this study is to encapsulate and characterise new chitosan-based nanofibers for medical applications.

Matherials and methods

Propolis extract (7.5% v/v), L-arginine HCl (7.5% wt/v) and Manuka Honey (7.5% wt/v), propolis-*Calendula officinalis* extract respectively were dissolved in a mixture (1:1 volume ratio) of polyethylene-oxide (2% wt/v) and chitosan (3% wt/v) acetic acid solution (50% v/v).

The viscosity of the solutions was measured using a parallel-plate measuring system. Fiber morphology and average diameters were observed by a scanning electron microscope. Four antioxidant tests (DPPH, ABTS, FRAP, phosphomolybdate assay) were performed in order to assess the best antioxidant matrix. Haemocompatibility was performed to assess *in vitro* properties.

Results

A good correlation between viscosity, superficial tension and obtaining of proper, smooth nanofibers was established. The chitosan-based nanofibers loaded with propolis-*Calendula officinalis* (Figure 1) extract showed the best antioxidant potential in all four antioxidant tests. *Calendula officinalis* has also been used in dermatological issues traditionally and has proven beneficial in modern applications, too and provided best haemocompatibility score.

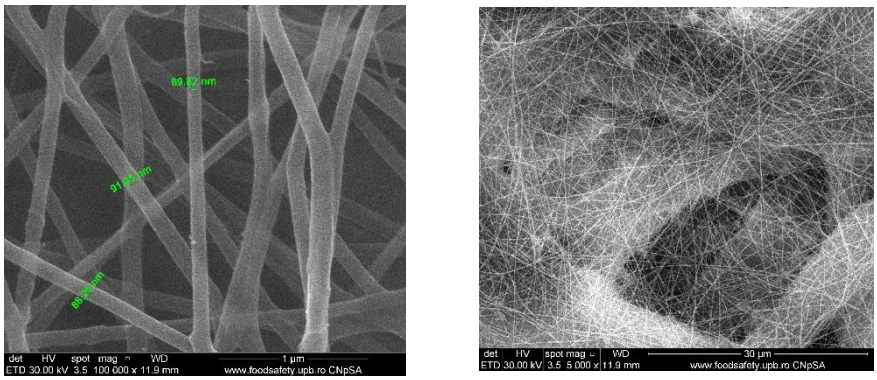

Figure 1. SEM micrograph of propolis/*Calendula officinalis* nanofibers and mean diameter

Conclusion

In this work, we successfully developed smooth, continuous, randomly oriented L-arginine/Manuka honey/Propolis/*Calendula officinalis* nanofibers providing a new option for developing wound dressings.

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A new sponge-type hydrogel as a 3D support for tumoral cell culture

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Sponge-type hydrogels are promising materials for drug delivery or other biomedical engineering applications due to their physical similarity to biological soft tissues (Ye et al., 2012). In addition, they represent appropriate three-dimensional tissue surrogate models for *in vitro* testing of the effectiveness of drugs. Glycosaminoglycans (GAGs) are long un-branched polysaccharides consisting of repeating disaccharide units. One of the most used GAGs as biomaterial is hyaluronic acid (HA), consisting of alternating units of D-glucuronic acid and D-N-acetylglucosamine, linked together via β-1,4 and β-1,3 glycosidic bonds. HA is one of the major components of the extracellular matrix of skin, cartilage, and the vitreous humor (Vlierberghe et al., 2011), having the ability to promote healing (Matsumoto et al., 2010).

In the present work, a new sponge-type hydrogel was obtained by cross-linking hyaluronic acid (HA) and poly(methylvinylether-alt-maleic acid) P(MVE-alt-MA) through a solvent-free thermal method (Larrañeta et al., 2018). The sponge-type hydrogel was characterized and checked as a support for cell growth. The influence of concentration and weight ratio of polymers on the morphology and hydrogel stability was investigated. The total polymers concentration of 3 % (w/w) and the weight ratio of 1:1 were optimal for the synthesis of a stable hydrogel and to promote cell proliferation. The swelling measurements revealed a high-water absorption capacity of the hydrogel in basic medium. Diphenhydramine (DPH) was loaded within the hydrogel as a model drug to investigate the ability of drug transport and release. In vitro studies revealed that the hydrogel promoted the adhesion and proliferation of human hepatocellular carcinoma cell line HepG2, providing a good 3D support for cell culture to obtain tumor scaffold surrogates (figure 1).

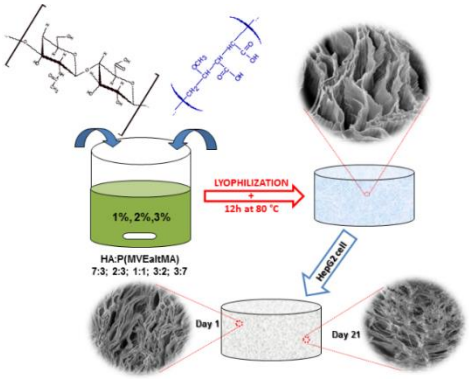

Figure 1. Scheme for design and application of sponge-type hydrogels as 3D support for tumoral cell culture

Acknowledgments
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Effect of metal synergy and loading on binary W-Mo/HZSM-5 catalyst systems for non-oxidative conversion of methane into carbon and petrochemicals.

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Abstract

Currently, oil, natural gas, and coal are relied on as primary energy sources [1]. However, these primary energy sources are of fossil origin. Processing of energy from fossil fuels is associated with emission of carbonaceous compounds into the atmosphere [2]. Therefore, non-oxidative conversion of methane into carbon, and valuable petrochemicals remediates emission of this greenhouse gas into the atmosphere [3] .

In this study, we demonstrate the development of a series of stable, durable and tuneable binary catalyst systems comprising of W, &Mo supported on HZSM-5 which were synthesized and tested for quantitative determination of product distribution in non-oxidative conversion of methane into carbon and petrochemicals. The catalyst systems were synthesized by incipient wetness impregnation, dried, calcined, and characterized by BET, SEM, XRD, FT-IR, TGA, and TEM for surface area, shape and size, crystallinity, acidity and presence of functional OH groups, quantity and type of deposited coke, and morphology of deposited carbon nanomaterial respectively. The prepared catalysts were tested for non-oxidative methane conversion in a custom-made stainless-steel packed bed reactor at different metal loading and process conditions. Gaseous and liquid products from the reactor were analyzed using an online gas chromatograph equipped with TCD column for analysis of gaseous products and FID column for analysis of liquid hydrocarbons. From the results obtained, competing reactions between different species of W and Mo played a significant role in determining methane conversion and product distribution.

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Intelligent Micro-vehicles for Drug Transport and Controlled Release to Cancer Cells

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The idea that pH decreases significantly in tumours is widespread, however recent progress in the measurement of pH in cancer tissues has revealed that the intracellular pH of cancer cells is neutral or even mildly alkaline compared to normal tissues (Hao et al., 2018). However, in both cancer and normal cells the pH drops from 6.0-5.5 in endosomes to 5.0 in lysosomes after particle internalization by EPR effect. Here, the design of "intelligent" delivery systems able to exploit these pH variations is reported.

Poly(*N*-isopropylacrylamide-co-4-vinylpyridine) (poly(NIPAAm-co-4-VP)) was synthesized and characterized as an exciting pH/temperature sensitive copolymer with a pK_a value of 5.05. The lower critical solution temperature (LCST) of the copolymer was determined at physiological conditions (phosphate buffer (PB) at pH = 7.4 and 36 °C), and at acidic pH values similarly to those of cell compartments. Values of LCST of the copolymer with the co-monomer molar ratio of 86:14 (NIPAAm:4-VP) are 22.1 and 36.8 °C in PB at pH = 7.4 and pH = 5.0, respectively. Therefore, the drug loaded microspheres synthesized from this copolymer are insoluble at physiological conditions (PB at pH = 7.4 and 36 °C) and keep the drug inside, but quickly solubilize at lysosomal conditions (pH = 5.0) releasing the cargo. The wettability of the copolymer films with the same composition was also determined under conditions similar to those used for release studies. It was proven that the copolymer has a certain degree of wettability even at temperatures situated above the LCST, favouring a slight leakage of the drug.

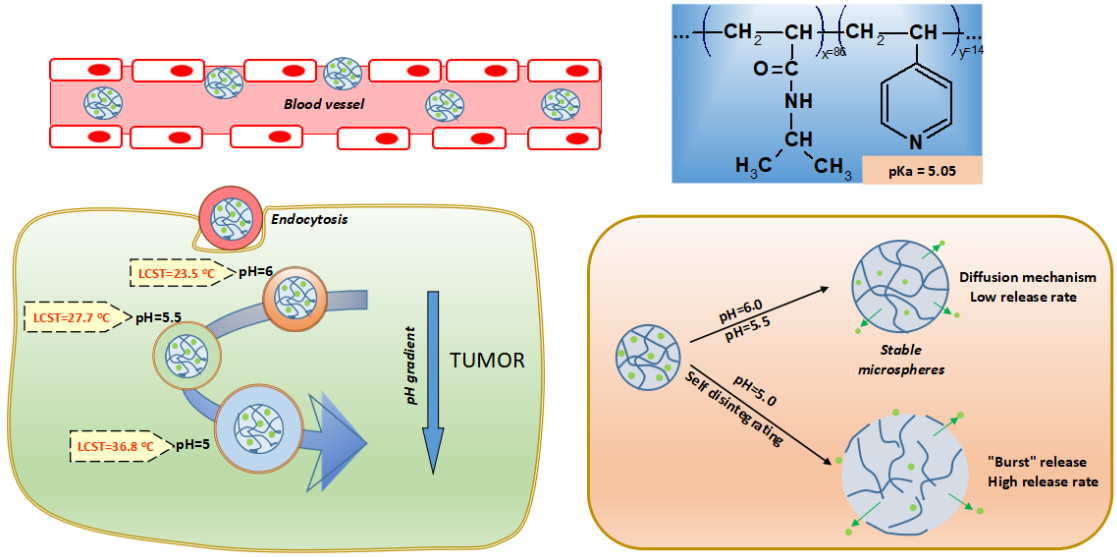

Figure 1. Schematic representation of intelligent micro-vehicles action

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Development and characterization of new polymeric systems for sustained release of hypoglycemic sulfonylureas

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Background: In recent years, the interest in using natural polymers as drug delivery systems significantly increased. Consequently, a wide range of studies are focused on the development of systems type polymeric matrix-drug, in order to improve the pharmacokinetic and pharmacological profile of some drugs. Chitosan is a natural polymer obtained by alkaline deacetylation of chitin, presenting some important properties as biocompatibility, biodegradability, lack of toxicity and low immunogenicity. In addition to this, chitosan presents some pharmacological effects including hypoglycemic, cholesterol-lowering, antihypertensive, antioxidant, antimicrobial and favorable effects in reducing obesity, making it suitable for the development of different multi-target drug-polymer systems. The aim of this study was the development and *in vitro* characterization of new polymeric systems based on chitosan, in whose matrix was included gliclazide, a hypoglycaemic sulfonylurea extensively used in diabetes treatment. **Materials and methods:** The new polymeric systems were prepared as microparticles, through inotropic gelation method, using pentasodium tripolyphosphate (TPP) as cross-linking agent. Medium molecular weight chitosan in concentration of 1.5% was used, the concentration of cross-linking agent was 2% and the chitosan: gliclazide ratio ranged between 1:0.5, 1:0.75, 1:1. The microparticles obtained were characterized in terms of size, structure and morphology using IR Spectroscopy and Scanning Electronic Microscopy (SEM). The hydration ability was studied in distilled water and simulated gastric fluid. The encapsulation efficiency and the release of the drug from the polymeric matrix in conditions that simulate gastric and intestinal media, were determined using a HPLC method. **Results:** It were obtained stable systems, the most favorable ratio between chitosan and gliclazide being 1:1. The size of the microparticles obtained ranged between 528.8 and 563 µm. The IR analyses proved the drug encapsulation and the SEM analyses showed the surface morphology. The encapsulation efficiency was 62.17%; the systems obtained showed good hydration ability and the percentage of drug release from the polymeric matrix was 79.28%. **Conclusions:** The chitosan-gliclazide developed systems represent a step in the attempt to modulate the pharmacokinetic and pharmacotoxicological profile of some consecrated antidiabetic drugs.

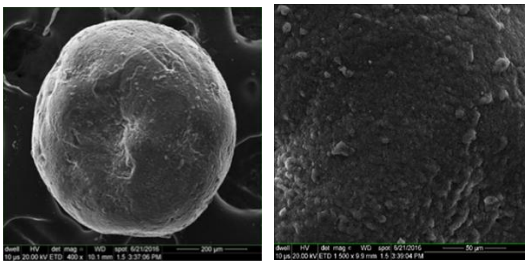

Figure 1. Microparticles type chitosan-gliclazide

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Dual silicone-based elastomeric networks as electromechanical transducers

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Ocean Energy Harvesting using Dielectric Elastomers (DE) as power take-off (PTO) systems is a relatively new technology with great potential [1-6] aiming to reduce the main drawbacks of classic technologies. Basically, it aims to replace the wave energy converters (WEC) PTO (classic air turbine) system with a polymer-based one. The polymeric-based PTO system is a stretchable dielectric elastomer coated on both sides with compliant electrodes, thus forming a variable capacitor capable to convert mechanical energy into electric energy [7]. Recently (2019) a polymeric-based PTO with two polymeric layers (approximately 20 cm in diameter) gave a remarkable average performance in realistically scaled sea states of up to 3.8 W (corresponding to hundreds of kilowatts at full-scale) exceeding a solar panel with comparable dimensions [8]. The obtained results demonstrated the possibility of designing dielectric elastomer-based WEC devices that are conceived for large-scale electrical energy production.

Silicone-based elastomers are the most studied class, due to their properties: high flexibility, low toxicity, resistance to weathering, good dielectric strength and operating on various temperatures (-120 to 200 ^{0} C). The polar nature of the siloxane bond is a premise for good dielectric properties, but the methyl groups hinder the Si-O dipoles to approach one each other, thus they possess a low dielectric permittivity, which is still the main disadvantage along with tear strength. The main aim is to increase the conversion efficiency of silicone-based PTO by increasing the tear strength and the dielectric permittivity of silicone elastomers in an original approach which consists in obtaining new interpenetrated polymer networks (IPNs) mimicking at a molecular level the spider webs due to the versatile chemistry of silicones. The remarkable mechanical resistance of the spider web lies not only in the chemistry of the intertwined strands but also in its unique geometry [9], architecture adapted by the proposed polymeric networks.

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New Multitarget Polymer Systems For The Treatment Of Diabetes Mellitus

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Diabetes mellitus (DM) is a one of the major diseases in the world that affects more than 8% of adults meaning approximately 380 million people. For this reason, improving the antidiabetic agents bioavailability is a major concern of researchers.

Aims. The aims of this study were to develop new polymeric systems, as chitosan microparticles, to improve the pharmacological and pharmacokinetic profile of two oral antidiabetic agents: metformin (M) and glibenclamide (G). Another one was to investigate the hypoglycemic effects of these new polymeric systems on diabetes mellitus induced with streptozotocin to rats.

Material and methods. Chitosan microparticles, chitosan-drugs were obtained by ionic gelation method using pentasodium tripolyphosphate (TPP) as crosslinking agent. In order to optimize the method for obtaining chitosan microparticles, the chitosan concentration (1%, 0.75%, 0.5%), TPP (1%, 2%) and the concentration of the active drug (30 mg, 22.5 mg and 15 mg) was varied. The particle size, structure and morphology was studied by scanning electron microscopy; the swelling degree was evaluated in distilled water and in simulated gastric fluid (SGF). The drugs loading efficiency was evaluated using UV spectrophotometric method (Chellappan et al 2019; Raghavendra and Kumar 2017). Type 2 diabetes mellitus was induced by streptozotocin on Wistar rats. The antidiabetic drugs (M, G) and chitosan-antidiabetic drug microparticles (CS-M, CS-G, CS-MG) were orally administered, once per day, for a period of 45 days. During the experiment it were investigated the biochemical parameters such as glycaemia and glycosylated haemoglobin (Avram et al 2017).

Results. Following the optimization process, it has been established the optimal formula for loading the two active substances in the polymer matrix. For glibenclamide, the percentage varied depending on the ratio of drug: polymer used, and it has been at the same time proved higher than that registered for metformin. In combination of the two substances, similar levels of individual loaded were obtained. The swelling degree of polymeric systems developed in SGF was higher compared in distilled water. Oral administration of these new polymeric systems significantly reduced the blood glucose levels in reference with the diabetic rats. The best hypoglycaemic effect was recorded for CS-MG formulation.

Conclusions. In this study, it was obtained three polymer-drug systems: CS-M, CS-G, CS-MG, which were physico-chemical, morphological and spectral characterized. Also was tested in vivo hypoglycemic activity of these new polymeric systems.

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Antioxidant and anti-hemolytic evaluation of nanofibrous mats derived from chitosan/PEO blend embedded with active biomolecules for wound healing application

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As nanotechnology develops rapidly in recent years, incorporating bioactive agents into polymer materials for controlled drug release has become an attractive area of research (Feng et al., 2019). The **aim** of this paper is to develop new electrospun nanofibers based on chitosan and polyethylene oxide (CS/PEO) and to evaluate their antiradical ability as new dressing materials in the treatment of wounds.

Materials and methods: The preparation of CS/PEO matrices was performed in two stages: (i) the formation of biopolymeric solutions by dissolving CS and PEO in 50% acetic acid stirring at r.t. The two solutions will be mixed in appropriate ratios, then, over the resulting mixture, the active substances: arginine (Arg) and propolis (Pr) 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, in depending on each sample (Ajmal et al., 2019). The evaluation of the antiradical ability was performed using the free radical DPPH and the cation radical $ABTS^{+\cdot}$. The antiradical capacity was calculated as a percentage of inhibition (I%) using the formula: $I\%=(A_0 - A_s/A_0) \times 100$ where, A_0 = the absorbance value of the 0.1 mM DPPH methanolic solution /$ABTS^{+\cdot}$ ethanolic solution and A_s = the absorbance value of the formulation, read at 30 minutes and 60 minutes after the addition of the DPPH methanol solution/read at 6 minutes after the addition of the ABTS solution^{+} (**Fig. 1a, b**) (Daemi et al., 2018). The evaluation of the anti-hemolytic potential was also performed by a spectrophotometric method, by the ability to stabilize erythrocyte membranes at lysis induced by hypotonicity (**Fig.1c**).

Results and discussions: Following the research, new electrospun-nanofiber scaffold based on chitosan were evaluated in terms of antioxidant activity, using 2 in vitro tests and in terms of anti-hemolytic potential.

Conclusions: After analyzing the data obtained, it was concluded that nanofibers with propolis incorporated in solid state obtained the best results. The studies and results obtained justify the evaluation of the biological, antibacterial and pro-healing potential in the treatment of various wounds, starting from the antibacterial/antioxidant effects of chitosan and the beneficial role of topical propolis applied in the treatment of wounds.

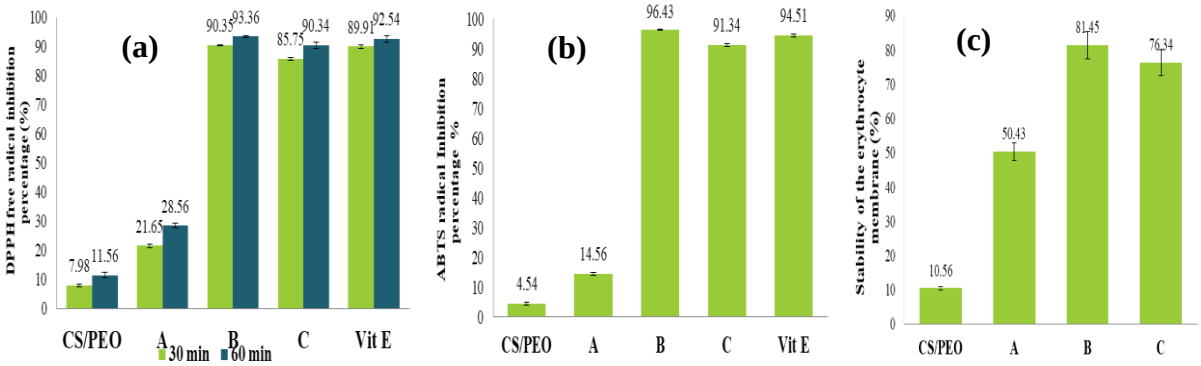

Fig. 1. Determination of **(a)** DPPH antiradical ability **(b)** ABTS antiradical capacity **(c)** anti-hemolytic potential, where PEO/CS/Arg (A); PEO/CS/Arg-dry Pr (B); PEO/CS-Arg-alcoholic solution Pr (C).

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Treatment of Pesticides in Wastewater by Heterogeneous and Homogeneous Photocatalysis

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Abstract. Heterogeneous photocatalysis leads to the mineralization of organic carbon through a slurry or thin film semiconductor catalyst in the presence of solar or artificial radiation and oxygen or a free radical acting as an oxidizing agent. Currently, it has many applications, from medicine, where it is used for disinfection and destruction of cancer cells, to water treatment for potable water and wastewater treatment. This study follows the behavior of an organo-persistent pesticide in various photochemical irradiation conditions. The obtained results have shown that the best behavior in the degradation of the pesticide was found for the TiO2 P-25 catalyst, which was considered a reference catalyst. Also, the most advanced pesticide degradation occurs when heterogeneous photocatalysis is performed with the aid of a higher concentration of catalyst (TiO2 P-25) and it has been observed the beneficial effect of acid pH on pesticide degradation. In conclusion, we can say that the almost complete degradation of pesticide is achieved after approx. 180 minutes in the presence of an acidic medium (pH = 3), using UV-A radiation and a TiO2-P25 type catalyst of 0.5 g/L for an initial pesticide concentration of 10 ppm.

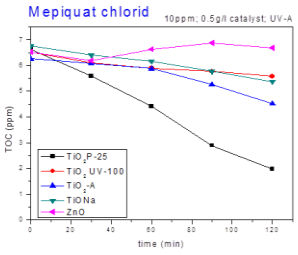

Fig.1. Pesticide degradation by heterogeneous photocatalysisusing different catalysts

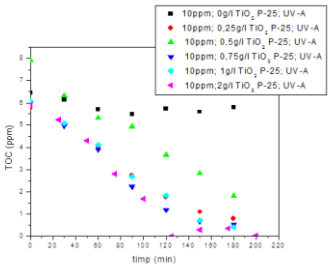

Fig.2. The TiO_2 P-25 concentration influence on the degradation of mepiquat chloride

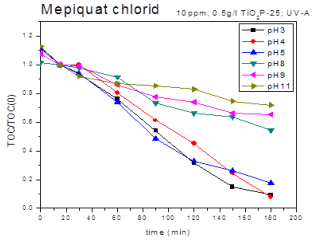

Fig. 5. Pesticide degradation in time at different pH values of the initial solution

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Quantum efficiency and band-gap assessment of various TiZr oxide nanostrucutres

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Solar energy is a virtually infinite energy source that can easily be converted into thermal, electric or chemical energy. Among various photocatalysts, TiO2, and other valve metal oxides have been widely studied due to their low costs and favorable properties. For an efficient photoexcitation of Ti and Zr oxides, it is necessary the application of light with energy higher than their band-gap energy, resulting in the formation of electron-hole pairs. The excited electrons and holes can either recombine in the material and dissipate as heat or combine with suitable electron/hole acceptors in photocatalytic reactions (Guo et al., 2019). Other aspects that influence the efficiency of the reactions are the surface architecture and chemistry of the material. Nanostructuring provides a high surface to volume ratio for the material, rendering it the possibility to absorb light more efficiently and doping is usually employed to reduce the band-gap (Ge et al., 2016). This works aim and originality is to compare the quantum efficiency and band-gap reduction of different oxide nanostructures (nanopores, nanotubes and nanochannels) obtained on TiZr by anodizing. The TiZr nanostructures were doped with nitrogen by annealing the samples in ammonia gas. The morphologies of the samples were characterized by scanning electron microscopy and photochemical experiments were performed in 0.1M Na2SO4 solution in the range of 300–800 nm. The results show that the quantum efficiency and band-gaps are dependent on both the architecture and the nitration conditions.

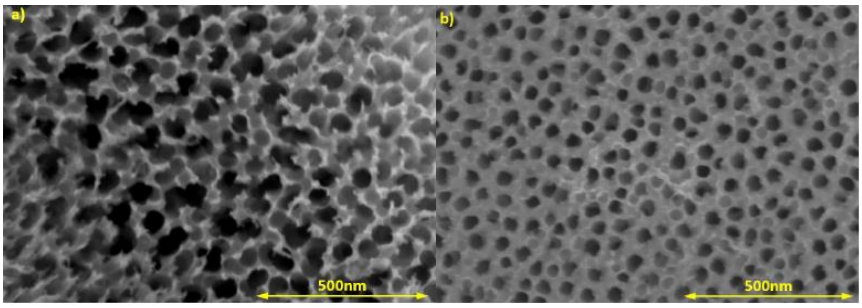

Figure 1. SEM micrographies of a) TiZr nanochannels, b) TiZr nanotubes

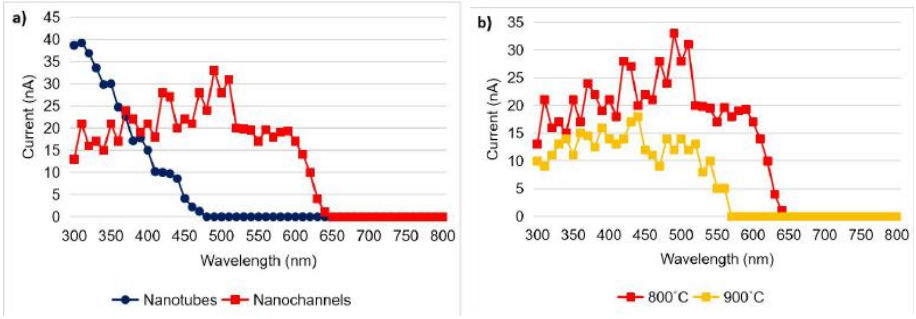

Figure 2. Quantum efficiency (ICPE ratio) for a) nitrogen doped TiZr nanotubes and nanochannels, b) nitrogen doped TiZr nanochannels at different temperatures.

Acknowledgments
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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The correlation between structural parameters and electromechanical performance of silicone elastomers

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Silicone elastomers are one of the most promising materials for dielectric elastomer transducers (DETs). In the simplest form, a DET consists of thin elastomeric membranes coated on both sides with compliant electrodes being able to deform under the action of an electrical stimulus. To enhance the electromechanical performance of silicones, the academic research has primarily been directed on improving the dielectric permittivity, Young's modulus and dielectric strength. Many of these studies include sophisticate approaches such as incorporation of different filler or chemical modifying commercial polysiloxanes by attaching polar groups while, the simple way of optimizing the elastomer have remained less explored. However, the properties of silicone elastomers can be significantly modified within certain appreciable limits by properly designing the elastomeric network. To demonstrate this, multiple series of silicone elastomer films differing by crosslinking pattern and molecular weight were prepared. The obtained results revealed that the mechanical and electromechanical behavior of silicone-based elastomers can be easily optimized by choosing the right molecular mass of the polymer and the cross-linking pattern.

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Comparative assessment of different dielectric elastomer actuators (DEAs)

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Dielectric elastomer actuators (DEAs) are electromechanical transducers that convert electrical energy to mechanical work. Compared with other actuators, DEAs have a series of advantages such as flexibility, large actuation strain, fast response, high energy density and high reliability.
Currently, DEAs are being studied extensively due to their ability to be used in a wide range of applications.
To obtained the best electromechanical results, was designed an elastomer based on high molecular weight polydimethylsiloxane-α,ω-diol. Furthermore, for comparison, was tested in same conditions two commercial elastomers and the results were compared with those obtained for the in-house prepared elastomer. To better understand the electromechanical behaviour in terms of microstructure of polymer network, it was determined the gel fraction for all elastomers. Further, stack actuators based on the three types of elastomer each of them having 30 active layers, were fabricated and evaluated. All experimental results were deeply analyzed in a correlative manner to identify the best actuator configuration.

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Considerations on the evaluation of the tribological and mechanical behavior for samples made by additive technology

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Abstract. In the last period of time there has been experimented with a new technique of making parts, known as Additive manufacturing (AM). Instead of taking a block of raw material and applying some milling or/and turning processes, the piece is built from the base, depositing layer by layer in the thinnest slices, whose shape is determined by an IT program. The process is also known as "3D printing" and represents the inverse of substrate processing. In this paper the authors analyzes samples made by additive technology both from the point of view of tribological performances (determining the coefficient of friction and wear resistance), and from the point of view of the mechanical characteristics correlated with the structure of the infill type from the inside of the samples. In this study we evaluate the tribological behavior of the 3D printed samples held in different environments (12/24/48 hours in water and respectively in lubricating oil) and the mechanical performance (fatigue resistance) in terms of infill % (10/30/60/90 percentage of the sample volume that is filled with PLA material), layer height (thickness of each PLA layer of the resulting sample) and infill pattern (array pattern type used to fill the sample).

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A NEW METHOD TO OBTAIN O/W AND W/O EMULSIONS

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Emulsions, containing two immiscible liquids, one dispersed in another, with one or two added hydrophilic-lipophilic surfactants, have been largely used in different areas such as food industry, pharmaceutics and cosmetics. Emulsions and especially, nanoemulsions, have gained popularity over the past years due to their excellent properties such as stability in time and adjustable rheological properties. One of the recent interests focuses on their use for thermal energy storage or new cooling systems.

Some of the well-known preparation techniques used can be classified in low and high energy methods and include: phase inversion temperature (PIT) and emulsion inversion point (EIP) and also, high pressure homogenization (HPH) and ultrasonication. One of the latest techniques considers aqueous phase condensation on an oily liquid film. Water droplets nucleate at the oil/air interface, disperse within the oil, the droplet size, the polydispersity and the stability of the emulsion being influenced by the oil-surfactant concentration. Despite the discussions related to the emulsion formation mechanism, the major parameters thought to influence the emulsion stability, have not been explored. Thus, this experimental study focuses on some preliminary tests intended to establish the main parameters influencing the emulsion stability, namely: the system initial temperature, the feeding vapour flow rate, the condensation time period, the emulgators : oil ratio, the water : oil ratio. The investigated system consisted of a sunflower oil layer treated with a mixture of Span 80 and Tween 80 emulgators, in different ratios, exposed to different water vapour flowrates, for several time intervals in oreder to obtain oil in water (O/W) or water in oil (W/O) emulsions. The stability of the obtained emulsions was established visually for several days after their preparation and also, by pH measurements.

Tartrazine dye decolouration and chromate reduction simultaneously in acid medium

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The continuous progress of human society has led to a development of technology in all fields.Food products are also obtained today with the help of modern technologies and processes, and the growing demand that is recorded leads to an overproduction and a varied offer from food producers. In the second half of the twentieth century, due to the development of processed foods, many additives were introduced, either of natural origin or synthetically obtained.An example of this synthetic class is the Tartrazine dye. It can be used as dye for wool, silk, paper, plastics, wood stains, leather tanning and processing. Also, in the above mentioned fields, it is used as well or even with much better results as ligand being complexed with different metal cations.
This domain has beenin our attention in previous studies and in various papers. Its use areas are extended for foods drugs and textile industry, too. Due to these multiple uses, we have found it useful to study its behavior in an acidic medium, in the presence of an oxidizing agent.Chromate [Cr(VI)]ions and azo dyes like Tartrazineare common pollutants which may co-exist in some industrial effluents.
The degradation kinetics of the oxidation process of Tartrazine dye using inorganic oxidizing agent (K_2CrO_4) have been investigated under various experimental conditions: different concentrations of H_2SO_4[10^{-2} -$5\cdot10^{-1}$ M] and temperatures [296 and 308 K].
Based on experimental results, a kinetic model for Tartrazine dye oxidation with chromate was developed.
The thermodynamic parameter, activation energy, was calculated from the rate constants of the oxidation process of the dye, measured at two different temperatures, 296 and 308 K.We concluded that the negative value for activation entropies indicate that the reaction occurs between ions of similar charge.
Based on our experimental data and literature investigations, we conclude that the destruction of azo-chromophore group by the inorganic oxidizing agent (K_2CrO_4) is explained by the highest oxidation state of this dye.

Photocatalytic degradation of organic contaminants using mesoporous ZnS

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Reducing contaminants in water is still a priority on the agenda of many research groups. Among the multitude of semiconductor materials with photocatalytic properties, Zn-based materials (oxides, sulfides, simple or doped mixtures) have the advantages of low cost and low toxicity. This study has as main objective the testing of the photocatalytic properties of some ZnS samples synthesized by the hydrothermal method. ZnS samples were prepared varying the reaction parameters, especially the amount of directing agent of the structure, presenting only the most relevant results.

$$(NH_2)_2CS + Zn(CH_3COO)_2 + H_2O \rightarrow ZnS + 2CH_3COOH + (NH_2)_2CO$$

Photocatalytic studies showed that the maximum degree of discoloration obtained was 97% for 50 minutes of irradiation. The influence of parameters such as catalyst dose, dye concentration or pH of the reaction medium was also studied.

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The kinetics of the drying process of spent coffee grounds

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Drying process of spent coffee grounds involves high energy consumption and it is an important step in using spent coffee grounds as green energy. The biodiesel, bioethanol, bio-oil and pellets can be obtained from spent coffee grounds (Gomez-de la Cruz et al., 2015). There are few studies in the literature that refers to this topic, but those use pilot-scale dryers (Gomez-de la Cruz et al., 2015; Haluschak et al., 2019; Gomez-de la Cruz et al., 2020). This study analyzes the drying process using thermogravimetric analysis. This method was chosen due to the high degree of accuracy in performing three measurements: mass change, temperature and temperature change. The Mettler Toledo TGA-SDTA851^e derivatograph oven can be used to stimulate conditions in industrial tubular dryers. The kinetics of the drying process of spent coffee grounds were analyzed using samples containing equal proportions of Arabica and Robusta coffee, in isothermal conditions at different temperatures: 50, 60, 70 and 80°C and thicknesses of the sample layer of: 0.6, 1.2, 1.8 and 2.4 mm. The thermogravimetric curves obtained for the spent coffee ground samples in constant temperature conditions allowed to represented the drying curves (moisture content – drying time) shown in figure 1 for a layer thickness of 1.2 mm. The experimental data on the time dependence of the moisture content (MR) were verified by applying different models (Erbay et al., 2009), in order to determine the most suitable one. It was found that the best results can be obtained with the modified Henderson and Pabis model (MR= a + b exp(-kt) + ct, where t – the time expressed in seconds and k – the drying rate constant). In order to highlight the periods of the drying process, based on the experimental data obtained at the four temperatures, the drying rate (kg moisture/m^2·s) was calculated. The values obtained were represented graphically in figure 2 as a function of moisture content – u (kg moisture/kg initial sample), for a layer thickness of 2.4 mm. The drying rate with constant rate (AB) and decreasing rate (BC and CD) can be observed. The calculated effective diffusion coefficients vary between $0.37 \cdot 10^{-10}$ and $9.99 \cdot 10^{-10}$ m^2/s. The activation energy is influenced by the thickness of the spent coffee ground subjected to the drying process and has values between 8.2 kJ/mol and 10.4 kJ/mol. The values obtained are comparable to what other researchers have reported in the literature (Gomez-de la Cruz et al., 2015).

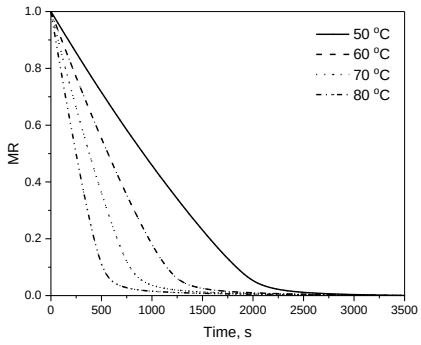

Figure 1. Experimental value for MR variation

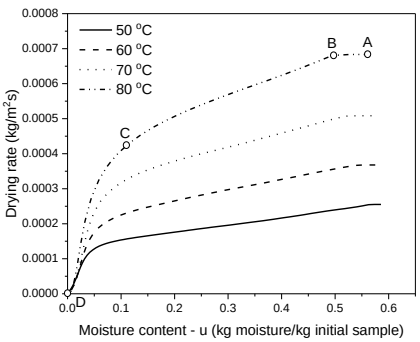

Figure 2. Moisture-dependant drying rate

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Thiolated chitosan for biomedical applications

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The chitosan is synthesized from chitin.It is cationic polysaccharide obtained from the shells of crustaceans, in particular crabs and shrimps, by the alkaline partially de-acetylation of chitin. The biodegradability, non-toxicity, bacteriostatic and biocompatibility proprieties represent the reasons why it is promising in different applications. The solubility of the polymer is influenced by the degree of de-acetylation.
The free amino groups are very important in chitosan chemical modifications. Among all chitosan derivatives, thiolated chitosan is a promising candidate for various biomedical applications due to mucoadhesive properties. In addition thiolated chitosan open the possibility for thiol-ene reaction with other polymers obtaining interesting networks without use supplementary crosslinking agents which are sometime toxic. The chitosan functionalization with thiol groups using homocysteine thiolactone was realized after a slightly modified method reported by Juntapram et al. The amount of thiol groups immobilized on chitosan was determined spectrophotometrically at UV-Vis using Ellman's reagent: 5, 5'-dithiobis (2-nitrobenzoic acid). A calibration curve for cysteine is established. Then, the calibration curve for the thiolated chitosan was performed and used to determine the amount of thiol groups including those of disulfide bonds. Compared with chitosan, the Fourier Transform Infrared (FTIR) spectrum of thiolated chitosan displayed new characteristic absorption bands, which corresponded to stretching vibration of carbonyl groups and thiol groups.
Preliminary tests of using thiolated chitosan have been performed: the potential of forming micro and nanoparticles by double crosslinking method and the formation of interpenetrated network by thiolene reaction with cyclodextrin.

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Chemical and structural characterization of carbon rich material from hydrothermal conversion of spruce bark

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In order to obtain biofuels or value-added bio-based products biomass have to be subjected to conversion. To convert biomass into a solid carbon rich material different thermochemical processes such pyrolysis and hydrothermal carbonization (HTC) are available. These processes are divergent considering the environment in which the conversion is performed as well as the absence/or not of water in system (Krylova and Zaitchenko 2018). Thus, pyrolysis is conducted in dry condition, while hydrothermal carbonization occurs in the presence of water. The main advantages of the wet process (HTC) is the possibility to use wet biomass, which leads to a reduction in production costs. Moreover, in HTC process the conversion of biomass is occurred at low temperatures (180° C – 300°C) with self-generated pressure (Evcil et al. 2020). The final solid product, named hydrochar is a porous carbon rich matrix with a very wide range of applications as solid fuel, catalyst, filler for thermoset materials, environmental remediation agent (Khan et al. 2019, Volf et al., 2020).
This work was focused on hydrothermal carbonization of spruce bark and on physic, chemical and structural changes that occurred after thermochemical treatment. Several characterization methods Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray (EDX), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller Surface Area Analysis (BET) were applied in order to highlight the new chemical and structural properties of the solid phase resulted from HTC.
For the thermochemical conversion of spruce bark into hydrochar a stainless steel autoclave, with a glass vessel inside was used. The optimal parameters were: temperature 280° C, time 1 h, solid to liquid ratio at 1:5.
The resulted solid phase had a small BET surface area, at around 13 m^2/g, and a poor porosity with a total pore volume of 0.0899 cm^3/g. However, it is important to highlight the high carbon content of hydrochar, confirmed by ultimate analysis (table 1) and a wide variety of functional groups revealed by FT-IR spectres.

Table 1. Characterization of hydrochar

Analysis		Hydrochar				
Proximate analysis	Moisture, %	1.98				
	Ash, %	0.66				
Ultimate analysis	Macroelements, %	C	O	N	Si	Fe
		77.2	20.2	1.1	1.0	0.5
Physical characterizations	Specific surface area (m2/g)	13				
	Particle size, μm	400				

Through TGA analysis the combustion behaviour of hydrochar was investigated. The combustion process took place in three steps. The first step at 68 °C was characteristic for moisture loss, the second step (276 °C) was attributed to decomposition of hemicellulose and cellulose still presented in hydrochar, while the final one (425 °C) is specific for degradation of lignin. SEM and EDX complete the information on structural properties of hydrochar.
Considering the structural, physic and chemical properties of hydrochar some innovative application will be proposed.

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Epoxidized vegetable oil for anti-corrosion coatings

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Vegetable oil represents one of the most important renewable resources to replace the petroleum-based compound. The objective of this research is to obtain new composite materials based on epoxidized vegetable oil and lignin by crosslinking them in varying proportions, under specific reaction conditions, as potential anticorrosion coatings. Highly unsaturated vegetable oils as those extracted from linseed are important raw materials for various organic compounds via epoxidation (J. Chen et al., 2019). Conversion of the unsaturated vegetable oils in more reactive epoxides, represents an important intermediary step to produce polymeric and composite materials suitable for different applications. Due to the special reactivity of the oxirane rings, epoxidized vegetable oils have a valuable potential for new classes of organic compounds (polyols, polyamines), but also for polymeric materials (polymerization or polycondensation products).
The major problem related to the anti-corrosion coatings consists in the low resistance to water vapor diffusion; the water penetrates the interface between the metal and the protective layer, thus reducing the adhesion of the coating (S. Pan et al., 2016). The current research study aims to obtain super-hydrophobic polymeric composites using vegetable oil and kraft lignin. Beside this, using lignin as filler for epoxidized vegetable oils-derived systems could improve general material performances as corrosion resistance, mechanical strength, and thermal stability.
Thermo gravimetric analysis showed a similar thermal degradation for all the synthesized composites starting at temperatures higher than 230 ° C.
The potentiodynamic polarization measurements (Figure 1) indicate that the studied coatings have a corrosion inhibition effect, significantly reducing the density of the corrosion current.

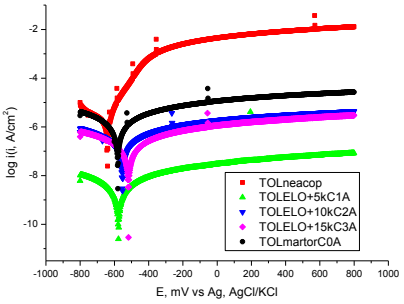

Figure 1. Tafel polarization curves in 3.5% NaCl solution.

The optimization of the synthesis pathway to produce epoxidized vegetable oil, characterization of the obtained compounds, as well as the materials performances will be presented.

Acknowledgments
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Synthesis of chitosan-based nanoparticles

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Introduction. Nanotechnology is one of the most studied field for researchers due to important applications in the area of drug delivery. Using nanotechnology principles, some features of the drugs such as solubility, bioavailability, biological effects and toxicity degree could be improved. One of the intensely studied nanosystems are the nanoparticles (NPs), which are frequently used due to their important advantages such as small particle size (1 - 1000 nm), large ratio active surface area/volume, high stability, feasibility of different drugs encapsulation, high carrier capacity and efficacy. The NPs proved to reduce the doses frequency, to provide the controlled and targeted release of loaded drugs and to improve the tolerability of the active substances (Al-Nemrawi et al., 2018).
Materials and methods. The chitosan-based nanoparticles (CSNPs) were obtained using the ionic gelation method that is based on ionic interactions between the positively charged amino groups of CS and the negatively charged groups of pentasodium tripolyphosphate (TPP). The influence of the concentration on CSNPs formation was determined using several concentrations (w/v) of TPP (0.1%, 0.15%, 0.2%) and CS (0.05%, 0.1%, 0.133%, 0.167%,0.2%). Also, other factors such as pH of CS solution (that was adjusted to 4.7 - 4.8), stirring speed (700 - 1400 rpm), reticulation time (0 min - 2 h) and surfactant role (0.5 - 1.5% Tween 80) were studied (Fan et al., 2012). Different volumes of TPP soluțion were dropped into different volumes of chitosan solutions (CS_{LMW}=low-molecular weight chitosan and CS_{MMW}=medium-molecular weight chitosan), under magnetic stirring, for 60 min, at room temperature (Sreekumar et al., 2018). The particle size (hydrodynamic diameter) and poly-dispersity index (PDI) were measured by a dynamic light scattering technique (DLS).
Results and discussions.
The increase of molecular weight is associated with the increase of particle size, in the same range of pH. The analysis of data revealed that the smallest size was obtained for CSLMW at pH of 4.7 - 4.8. The size of CSNPs was slightly higher (245 ± 10.2 nm) at pH = 5.5 and the precipitation was observed at pH = 7. The best NPs were obtained using CS and TPP in concentration of 0.1% and CS/TPP ratio of 3:1. Related to the reticulation time the results revealed that the particle size decreases from 0 min to the critical point of 1 h, after which an aggregation was observed. The increase of the speed from 700 rpm to 1000 rpm was associated with a reducing of the CSNPs size.
Conclusions. The optimized CSNPs were obtained using the following parameters: 0.1% CSLMW (pH = 4.7 - 4.8), 0.1% TPP, stirring for 1 h at 1000 rpm. Based on this optimized method, the synthesized CSNPs will be used in the next applications, as drug delivery systems for various types of drugs.

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Approaches to increase the electromechanical performance of silicone elastomers

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The low Young's modulus and softness of silicone elastomers make these materials first choice for dielectric elastomer transducers (DETs). These are well-known devices able to convert electrical energy to mechanical one or vice versa with different applications, which range from valves, pumps, wave generators, pressure sensors, to muscle replacements [1]. DETs consist of thin electrically insulating elastomeric membranes having compliant electrodes on each surface. Also, silicone-based materials are biocompatible, resistant to weathering, with stable properties over a wide range of temperatures and frequencies, good dielectric strength and maintain their specific energy over a wide frequency domain. Despite these great properties, increased electrical breakdown strength is an important requirement and strategy for optimization of the silicone DEs with respect to large achievable actuation strains, being obtained by incorporation of metals, metal oxides, coordination compounds, organic nanoparticles or additives with a voltage-stabilizing effect. The optimum material is however hard to find. Some of the group's own attempts in this regard are as follow:

•Attaching polar entities (like trifluoropropyl units, CF_3) by chemical modification. Polysiloxanes with high molecular weight containing different mol% of CF_3 groups and reactive vinyl end-groups were cross-linked in thin homogenous films. The dielectric, mechanical, and electromechanical properties were investigated in dependence of CF_3 content [2].

•Introduction of inorganic particles with high permittivity, represent another approach to enhance the permittivity of silicone elastomers. Silver nanoparticles as spheres or nanowires were incorporated in silicone matrices, the resulted material being processed as films and crosslinked. To prevent percolation, the metallic nanoparticles were coated with a thin silica shell (<4 nm). To increase their compatibility with the silicone matrix, these coated silver nanoparticles were passivated with a silane reagent or with hexamethyldisilazane. Because of the increased ε' and high strain at break, these materials might find application as dielectric in energy harvesting devices operated at low electric fields [3].

•Starting from the demonstrated ability of phenyl nuclei and the silsesquioxane cage to scavenge electrons [4,5], *octakis(phenyl)-T8-silsesquioxane* was used as voltage stabilizer filler for dielectric silicone elastomers in order to improve the dielectric strength. The incorporation and homogeneous dispersion of crystalline *phenyl-T8* into the amorphous matrix was successfully achieved by mixing the polymer and filler in solution, followed by crosslinking and solvent removal. The matured films were characterized in terms of morphology, mechanical, dielectric and actuation tests. In spite of structural incompatibility between the filler and the matrix, the obtained materials are soft elastomers showing high strain (~800%) and low Young's modulus of 50-100 kPa. The use of *phenyl-T8* in a silicone matrix led to increased electric breakdown strengths, resulting in electroactive films with fast response specific to dielectric elastomers.

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Interplay of electronic structure in ground and excited states of new di-iminopyrene-di-benzo-18-crown-6-ether derivative by TD-DFT studies

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The pyrene and its derivatives have interesting photophysical properties depicted by a strong absorption in UV-Vis range as well as specific emission spectra [1, 2]. The absorption and the fluorescence spectra are sensitive to solvent polarity, this fact suggests the use of this class of compounds as a test to determine environment behavior.

Survey of literature indicates that the pyrene moiety presented a strong electron donor effect which can be combined in several materials in order to design the electron donor-acceptor systems which can be used in energy conversion and light harvesting applications.

The presence of a double bond (-HC=N-) in the structure of the pyrene derivatives determines the formation both their trans and cis conformations. In this context, the main goal of the present study was to investigate, by DFT and TD-DFT studies, the conformational effect in the ground and excited states to predict the theoretical electronic absorption spectra and $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions of di-iminopyrene-di-benzo-18-crown-6-ether compound. Also, these studies help us in the identification of the intramolecular interactions, such as charge transfer, π- extended conjugation effect.

Our results obtained by theoretical simulations are in line with the experimental determinations |(Table 1).

Table 1. Theoretical values of the the oscillator strength (f), calculated at the TD-DFT/6-311++G(d,p) level of theory and experimental absorption wavelengths (λabs, nm) for the target compounds (trans isomers).

Solvent	TD-CAMB3LYP		TD-PBE0		Exp.
	λ_{abs}	*f*	λ_{abs}	*f*	λ_{abs}
toluene	388	1.6324	437	1.7386	396
	382	0.8391	433	0.2384	377
	330	0.0601	389	0.0001	345
ethanol	385	1.7130	433	1.7582	390
	380	0.6972	429	0.2082	380
	316	0.1111	367	0.0284	289

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Novel carbon/ZnO hybrid materials with high efficient removal of azo dyes

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Recently, the composites materials based on the combination of metal oxide semiconductor nanomaterials and different types of carbon species have been intensively used as photocatalysts due to the interesting physico-chemical properties and potential applications in water purification and environmental protection [1]. A new type of materials based on carbon/ZnO nanostructures that possess both adsorption and photocatalytic properties was obtained in three-stage: cellulose acetate butyrate (CAB) microfiber mats by electrospinning method, ZnO nanostructures growth by dipping and hydrothermal method, and finally thermal calcination at 600 ºC in N_2 for 30 min. X-ray diffraction (XRD) was used to confirm the structural characteristics, and it was found that ZnO possesses a hexagonal wurtzite crystalline structure. Also, the presence of carbon with (002) lattice planes was highlighted. The ZnO nanocrystals with a star-like and nanorod shapes were evidenced by SEM measurements. Optical properties were obtained by using UV-VIS reflectance spectra and the band gap values were determined with the Kubelka–Munk function (KM) by plotting $[F(R_\infty)h\nu]^2$ vs. hυ. A significant decrease in Eg value was found for carbon/ZnO hybrid materials, namely Eg=2.51 eV compared to ZnO nanostructures (Eg=3.21 eV) [2]. The photocatalytic activity was evaluated by studying the degradation of three dyes (Methylene Blue (MB), Rhodamine B (RhB) and Congo Red (CR)) under visible-light irradiation, obtaining very good results. The values of maximum color removal efficiency (adsorption/photocatalytic process) were the following: 97.97 % of MB (C_0=10 mg/L), 98.34 % of RhB (C_0=5 mg/L), and 91.93 % of CR (C_0=10 mg/L), under visible light irradiation with low power (a 100 W tungsten with a power of 102.74 $kJ \cdot m^{-2} \cdot h^{-1}$) and at a moderate amount of catalyst (0.5 g/L). Besides, the value of the rate constant for this material was found to be k=0.29*10^{-2} min^{-1}. The novelty of this study relies on obtaining new photocatalysts based on carbon/ZnO using cheap and accessible raw materials, and low-cost preparation techniques. Also, to our knowledge, the development of carbon/ZnO nanostructures obtained by these precursor materials, and then their testing for adsorption/degradation of organic dyes have not been reported in the literature so far

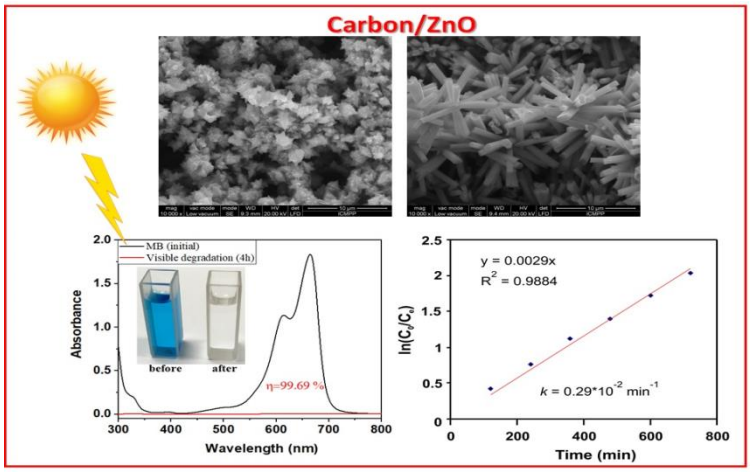

Figure 1. SEM images of carbon/ZnO with a star-like and nanorod shapes; profiles of electronic absorption spectra after degradation under UV-light irradiation of MB; Kinetics of dye concentration decay against reaction time during photodegradation processes under visible light in the presence of carbon/ZnO..

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Metallized polyimide films as blood-contacting devices

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Due to their excellent properties such as great thermal stability or environmental resistance, polyimides are widely used in high performance engineering fields. Surface properties of polymer films, which were prepared on the basis of polyimides and metallized by gold were investigated by contact angle and X-ray photoelectron spectroscopy (XPS). In this work, a fully aromatic polyimide, Kapton, and a semialiphatic one, based on 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride (DOCDA), were studied. Prior metallization of the polymer surfaces nitrogen plasma was involved.
The occurrence of polar groups on the surface of polyimide films as the resulted plasma exposure affects polar component of surface free energy. Molecular mechanics simulations were employed to investigate the structure-properties relationship of the polyimide films. Blood interactions with polymer samples were investigated from theoretical point of view.

Testing of sorption capacity of quaternized polysulfones-based membranes: Perspectives for environmental applications*

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* This paper is dedicated to the memory of Prof. Cristofor I. Simionescu (1920-2007) and to the commemorative celebration of the centenary of his birth.

With the growth of the worldwide population, the demand for new fresh water resources has become increasingly urgent, so that water treatment is truly essential to improve environmental and life quality. In recent years, the membrane technology appears to govern the field of wastewater reuse and this trend will continue in the future, towards meeting sustainability criteria in terms of environmental impacts, ease of use, and low energy costs, flexibility, and adaptability. The solution to these problems is to develop new materials which possess multifunctionality and sustainability as a result of membrane technology requirements. In this context, solutions of quaternized polysulfones (PSFQ) with a tunable content of cellulose acetate phthalate (CAP) and polyvinyl alcohol (PVA) have been processed to obtain new membrane materials explored for wastewater treatment. The cumulative effects generated by the CAP and PVA versatile nature along with molecular functionalization of polysulfone were responsible for improving the workability, surface properties, and membranes performance.
As an initial attempt to explore the filtration behavior of the hybrid membranes based on quaternized polysulfones in practical applications, the water vapors sorption capacity in dynamic regime was evaluated. Taking into account the shape of the water sorption curves presented in Figure 1, these types of isotherms with hysteresis can be interpreted as being characteristic to the porous surfaces.

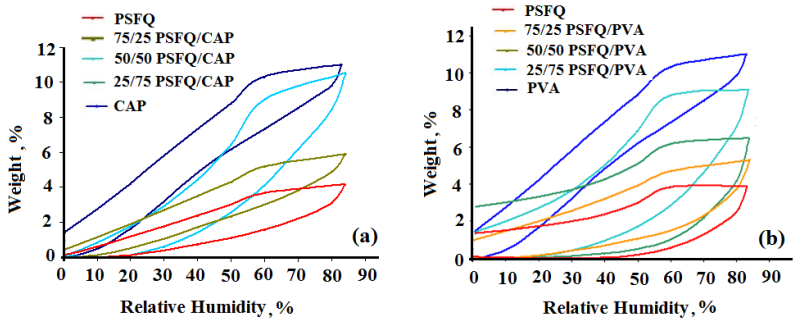

Figure 1. Sorption/desorption isotherms for the studied systems: (a) PSFQ/CAP and (b) PSFQ/PVA

By analyzing the results, the values of water vapors sorption capacities increase in the following order: PSFQ < PSFQ/CAP or PSFQ/PVA blends with different compositions < CAP or PVA. Investigations on hybrid membranes surface, based on the water vapor sorption data, have demonstrated that on their surface exist nano-sized pores whose number varies from sample to sample, depending on the structural peculiarity of polymers and composition of polymers in the blend. It is distinguished the porogen effect of the CAP and PVA that generates structures with a high specific surface area and small pore size into the polysulfone matrix. Therefore, according to our results, to obtain an ultrafiltration membrane with excellent characteristics for water treatment, it is necessary to ensure a high pore density and consequently, a high permeability.

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Bioinspired elastomer nanocomposites for dynamic harvesting and control of infrared energy flow

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Thermal management is a critical factor for the operation of modern technologies, including electronic circuits (Moore et al., 2014) and building environment control systems (Ürge-Vorsatz et al., 2015). For efficient thermal management, a key goal is to have an efficient platform that brings together desired characteristics of passive strategies for thermal control (low cost, straightforward implementation, and energy efficiency) with the on-demand active control capability. In the context of bioinspired materials, the skin of cephalopods is a powerful source of inspiration due to their dynamic optical functionality, since it has specific organelles which show impressive color changing capabilities with excellent actuation speed (milliseconds) and complete accuracy of background matching. Thus, research has been focused on emulating the ability of cephalopod skin to modulate color, with application in the infrared radiation wavelength range.
We addressed the unresolved scientific challenge of building an efficient platform for thermal control by developing a new nanocomposite material with tunable thermal infrared properties, inspired from rapid mechanical actuation and color changing ability of squid skin. We prepared nanocomposite materials which possess the ability to regulate a heat flow as large as 40 W/m^2 with a one-time mechanical input of 2-3 W/m^2 and we used as reference material the static infrared-reflecting space blanket developed by NASA in 1960.
The bioinspired materials modulate transmission and reflection of infrared radiation in a large range from near infrared to far infrared (i.e. 2-25 microns wavelength), harvesting the energy of radiation in this wavelength range. The materials are scalable so the functionality of the materials can be applied for large surfaces (square meters). After integration into clothing, the new nanocomposites manage 60-70 % of the metabolic heat flux from sedentary individuals and modulate localized changes in the individual body temperature within a setpoint temperature range of 8 °C. This functionality for the new nanomaterials could reduce global energy consumption by 3 % upon large scale use in thermoregulatory systems, including clothing.

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Characterization of silicon quantum dots' properties and hepatic toxicity in mice

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The use of quantum dots (QDs) represents a promising tool for *in vivo* imaging, tumor biology investigation and cancer treatment due to their multiple optical and electronic properties that offer advantages for medical purposes compared to conventional nanoparticles. However, QDs can also trigger toxicity effects in healthy cells as it was previously reviewed by Zhu et al. [1]. In this context, the present study aimed to characterize the silicon-based QDs obtained by laser ablation and to evaluate the *in vivo* hepatic toxicity induced by these semiconductor nanocrystals. The studied nanoparticles showed a core-shell structure with a crystalline silicon core and an amorphous silica shell, having a diameter range between 6 and 10 nm. Their tendency to aggregate provided the formation of aggregates with sizes of hundreds of nanometers. The dispersion in water of QDs revealed a hydrodynamic diameter around 200 nm and a negative zeta potential of -14 mV. In order to test their *in vivo* toxicity, different doses of QDs (0, 1 10 and 100 mg QDs/ kg body weight) prepared in 0.9% saline were injected intraperitoneally in Swiss mice. After 1, 6, 24 and 72 hours, the animals were sacrificed and the hepatic tissue was harvested. The effects of silicon QDs on antioxidant defense of hepatocytes were investigated throughout the measurement of antioxidant enzymes' activities (catalase, superoxide dismutase, glutathione peroxidase, glutathione reductase and glutathione S-transferase). The administration of the highest dose of QDs induced a significant reduction in the activity of catalase, the level being half of the control after all periods of exposure. A time-dependent decrease in the activity of glutathione reductase was noticed for all doses administered compared to control animals. After 24 and 72 h, the activities of glutathione peroxidase and glutathione S-transferase diminished in the hepatocytes of mice that received 10 and 100 mg/kg b.w. compared to control, revealing that these enzymes were vulnerable to oxidative damage of high doses of silicon QDs. However, no significant changes were observed regarding the activity of superoxide dismutase in the liver of treated mice in comparison with control, suggesting that the QDs administration would not generate superoxide anions inside hepatocytes. This study revealed the possible damaging effects on hepatocytes of high doses of silicon-based QDs (>10 mg QDs/kg b.w.) providing useful information for further clinical studies on humans.

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Preparation of polybenzoxazine-based graphene oxide nanocomposites

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The influence of graphene oxide (GO) functionalized with different organic moieties on ring-opening polymerization of benzoxazine monomer (BZ) was studied. Polybenzoxazine nanocomposites (PBZ) reinforced with four types of graphene oxide were synthesized. The polymerization behavior of all GO/PBZ nanocomposites was monitored by both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Thermal stability of nanocomposites was investigated by thermogravimetric analysis (TGA) showing a slight increase of temperature at which mass loss is 3% (Td3%) even if only 1% of graphene oxide is added as reinforcing agent.

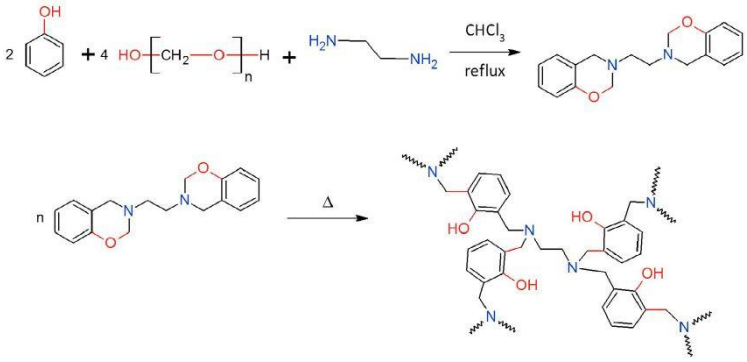

Figure 1: Synthesis of polybenzoxazine resin

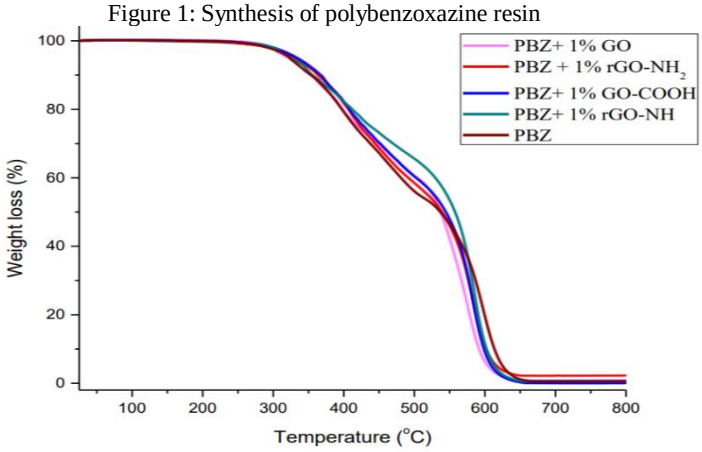

Fig. 2. TGA curves of GO-reinforced polybenzoxazine

Compared to the neat polybenzoxazine, the incorporation of only 1% functionalized GO show better thermal stability. For all the studied GO/PBZ nanocomposites the TGA curves showed a similar behavior except rGO-NH/PBZ which exhibit a higher thermal stability than all other composites due to the more crosslinked structure obtained in this case.

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Development of novel multitarget NSAID, indomethacin associated with 1,3,4-oxadiazole moiety and a nitric oxide releasing group

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Inflammation is a defense reaction (non-specific and local) of advanced living organisms to any injury that is caused by trauma, microbial toxins or harmful chemicals. In essence, the inflammation remains a crucial physiological response for the human body to any kind of aggression (Korbut, 2011).
The inhibition of the arachidonic acid cascade is one of the most used strategies for the treatment of the inflammatory diseases. Nonsteroidal anti-inflammatory drugs (NSAIDs) are the most common medications in the treatment of various inflammatory conditions like rheumatologic disorders, neurodegenerative diseases (Alzheimer, Parkinson), psoriasis, irritable bowel syndrome, asthma (Elgazzar, 2014).
The synthesis of Nitric oxide-releasing non-steroidal anti-inflammatory drugs (NO-NSAIDs) represents a novel approach to reduce the side effects of NSAIDs, especially their gastric toxicity. NO-NSAIDs consist of a known NSAID molecule and a NO-releasing group (typically $–NO_2$) linked to it via a chemical spacer (Abdelall, 2017).
Nitric oxide (NO) is a biologically active molecule involved in modulating of several physiological responses including maintenance of blood pressure in the cardiovascular system, stimulating host defenses in the immune system, regulating neural transmission in the brain, platelet aggregation, learning and memory, male sexual function, cytotoxicity and cytoprotection, development of arteriosclerosis among others, inflammation, gastroprotection.
The rationale for NO-NSAIDs development was based on the observation that NO has some of similar properties as PGs within the gastric mucosa. NO increases mucosal blood flow, mucous release, and repair of the mucosa, whereas it inhibits neutrophil activation and adherence. These effects can theoretically compensate for gastric PG reduction. Coupling a NO-releasing moiety to a NSAID might deliver NO to the site of NSAID-induced damage and thus decrease gastric toxicity (Lancaster, 2017; Kim-Shapiro,2017).
The objective of this study is the synthesis of a new molecules containing a NSAIDs as indomethacin associated with 1,3,4-oxadiazole moiety containing a nitric ester group (Fig1). The synthesis and the NO release capacity are presents in this paper. The synthesis was preceded by molecular docking study in order to support the design of suitable chemical structures able to release NO. The molecular docking study results are also presented in this paper.

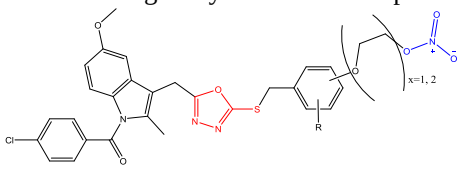

Figure 1. Chemical structure of new nitic-oxide-indomethacin drugs

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The issue of single-value glass transition temperature of polymers as it is determined from DMA

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Dynamic mechanical analysis is a suitable method that is able to determine the load bearing properties of a polymeric material over large range of temperatures. Thus, from the variation of any viscoelastic characteristic (E', E'' and tan δ) as a function of temperature, one of the most important characteristic of polymers can be determined: the glass transition temperature. As many other techniques, DMA instruments were optimized and updated to the digital age, making them approachable after a basic training. Nevertheless, thanks to the facilities offered by the computer, a tendency for oversimplification is noticed in the DMA data published in the literature. This means that from the large number of information obtained in a time-consuming DMA experiment only a temperature value is reported as the glass transition temperature.
This short presentation include DMA results obtained on three different classes of polymers (polyimide, polyurethane, poly(lactic acid)). Peculiar aspects that appear in the glass transition region of them are comparatively discussed.

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Design of functionalized hybrid PLGA-vegetable oils nanoparticles for targeted delivery of lipophilic drugs

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The hybridization process of poly (D,L-lactide-co-glycolide) (PLGA) nanoparticles is one of the most promising tools for obtaining carriers with tailored characteristics in drug delivery applications[1]. Hybrid formulations obtained by physical association of PLGA nanoparticles and different vegetable oils (HPONP) is a new trend in designing noninvasive, versatile nanocarriers for lipophilic drugs delivery. Moreover, the surface functionalization of hybrid formulation with various types of specific ligands (e.g. PEG) can increase not only the biocompatibility and their systemic circulation time but also the cellular uptake, respectively the therapeutic efficiency of the system can be improved.

The aim of the current research study is to design hybrid nanoparticles based on PLGA - vegetable oils with functionalized surface, as nanocarriers for targeted high lipophilic drug delivery and controlled release. The formulations were obtained by solvent evaporation method, employing Indomethacin (IMC) as lipophilic drug references. The performances of new hybrid carriers with standard and functionalized surface were evaluated through multiple advanced techniques (DLS, TEM, FTIR, UV-VIS, DSC and biological assessment).

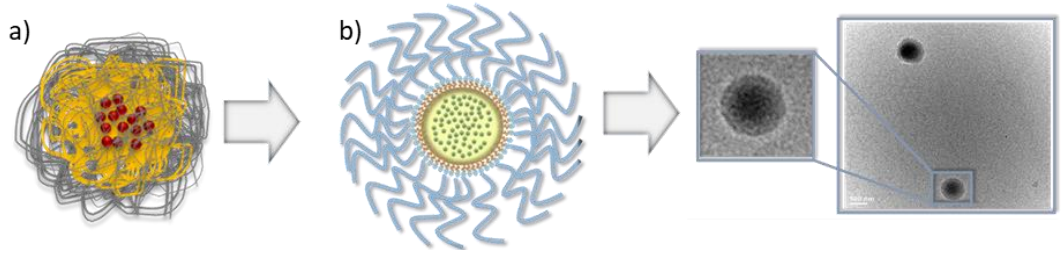

Figure 1. Schematic representation of (a)-standard and (b)-functionalized hybrid PLGA-vegetable oils nanoparticles with TEM micrographs

The TEM micrographs emphasize hybrid colloids with well-defined core-sell type structures and narrowed size distribution (DLS). The encapsulation efficiency (EE) results highlight a notable increase in the drug loading capacity of hybrid polymer–oil based nanoparticles as compared to standard ones. The cytotoxic investigation highlighted that the oil dispersion increased the cell viability by ~2.4 times as compared to standard nanocarriers, while the surface functionalization of the formulations further improve the cellular viability by ~1.5 times as compared to uncoated formulations.

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Green synthesis of metallic nanoparticles from Helichrysum arenarium: kinetics, antioxidant activity and catalytic degradation of azoic dyes

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Nanotechnology is the science that studies extremely small thigs and successfully brings together elements from physics, chemistry (organic and inorganic), material science, chemical engineering, biology, medicine [1]. Metallic nanoparticles, because of their high surface area, are versatile and can be tailored with a multitude of different molecules that give them good antibacterial, magnetic or catalytic properties. Metallic nanoparticles can be synthesized by applying conventional methods, using two approaches: "top down" or "bottom up" processes [2]. These methods are, in most cases, expensive, time consuming, use toxic chemicals and produce hazardous secondary products. Viable and feasible alternatives are environmentally – friendly methods that use microorganisms, fungi, enzymes or plants [3] and, among them, aqueous plant extract mediated biosynthesis of silver (AgNPs) and gold (AuNPs) nanoparticles are intensively studied since silver and gold are two noble metals widely known for their strong antibacterial properties. The different phytochemical compounds found in the plants act as catalysts in the reduction mechanism of silver and gold salts to corresponding nanoparticles.
This paper presents the green synthesis of silver (AgNPs), gold (AuNPs) and iron oxide (FeONPs) nanoparticles from Dwarf everlast (*Helichrysum arenarium*), a plant packet with vitamins and nutrients that, among other pharmacological benefits, regenerates the lives, helps in lowering the cholesterol levels, etc. The green synthesis of the three metallic nanoparticles was carried out using two different temperature conditions: room temperature, no stirring, no heating and at 50^0C under a constant stirring of 600 rpm for 30 minutes. The as-prepared green metallic nanoparticles were characterized using UV-Vis and FTIR recordings and dynamic light scattering determinations were used to determine the size of the metallic nanoparticles. The UV – Vis spectra were recorded at different time intervals (0 s, 30 min, 60 min, 90 min and 24 h) in order to evaluate the time-dependent evolution and stability of the green synthesized metallic nanoparticles. The antioxidant activity of AgNPs and AuNPs was recorded using DPPH (2,2 – diphenyl – 1 – picryl – hydrazyl – hydrate) assay and the values were higher for the green synthesized metallic nanoparticles compared to the aqueous extracts. Also, the potential capacity of AgNPs and FeONPs to catalytic degrade azoic dyes (e.g.: Direct Orange 26, Direct Brown 2, Direct Black 38) was spectroscopically investigated.

Acknowledgments
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Development of textile materials with antimicrobial activity using Ag/chitosan and ZnO/polyvinyl alcohol nanoparticles and gamma irradiation

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Advancements in the production and development of new textile technologies are continuously demanded because of the varied uses from clothing to medical, to industrial applications (Samayanan, Mahalingam., 2012; Jagadheesan, 2013).
By combining different methods and nanoparticles it's hoped to achieve higher properties materials and with this scope gamma irradiation has been employed being previously used as a green textile functionalization technology. Several studies demonstrated positive result of using gamma irradiation on textile dyeing and antimicrobial functionalization (L. Chirila, et al., 2016, 2018, R. Mervat, et al., 2016).
In the current study two types of nanoparticle Ag/chitosan and ZnO/polyvinyl alcohol were used to obtain cotton textiles with antibacterial properties. Gamma irradiation of textile was done with a Co-60 source at a dose rate of 1kGy/h for a total absorbed dose of 5 kGy. Three textile treatment procedures have been used: first one consisted in padding, the second one consisted in padding followed by a 2 minute drying at 100°C and finishing with a 3 minute condensation at 150°C and the third one was padding followed by gamma irradiation. The functionalized textiles characterization was done by ATR-FTIR and TG/DSC analysis as well as antimicrobial properties evaluation. By using gamma irradiation step materials with better nanoparticles fixation and antimicrobial activity were obtained.

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Host guest complexes of polychlorinated dibenzo-p-dioxins with cyclodextrins

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Polychlorinated dibenzo-p-dioxins (PCDD) are persistent organic pollutants that induce toxicity in both wildlife and humans (White, SS, 2009). The cyclodextrins (CD) are complexing agents. Inclusion complexes are formed based on the "guest – host" interaction, where the CD's cavity acts as host for a molecule. The outer sphere of CD is hydrophilic, while its cavity is hydrophobic. This means that the cavity can act as a host for compounds with poor solubility in polar solvents (Saokham P, 2018).

In this study we analyzed the molecular interactions between tetrachlorinated dibenzo-p-dioxin (TCDD), pentachlorinated dibenzo-p-dioxin (PCDD), hexachlorinated dibenzo-p-dioxin (H_6CDD), heptachlorinated dibenzo-p-dioxin (H_7CDD), and octachlorinated dibenzo-p-dioxin (OCDD) and β-cyclodextrin and γ-cyclodextrin, taking into account the different starting geometries with the aim to estimate their adsorbent potential in environmental remediation. The simulation of interaction between the seven PCDD compounds and the two CDs was conducted using the molecular mechanics (MM+), and optimized potential for liquid simulations (OPLS) force fields, both included in the Hyperchem program (Mindrila G, et al 2012). The starting geometry of CDs was obtained from the Protein Data Bank using the X-ray structures 1VFO (β-CD) and 1D3C (γ-CD) (http://www.rcsb.org/pdb/home/home.do).

The complexation and the binding energy, and their components were calculated for all of the 40 inclusion complexes. Both MM+ and OPLS calculus resulted in close values for the complexation and binding energies. It was observed an interaction difference between the inclusion complexes formed with β-CD, and those formed with γ-CD that may be attributed to the higher flexibility of the γ-CD, which may provide a better inclusion of the PCDDs molecules.

This study showed from molecular modelling calculations that recognition of the PCDD pollutants by the CDs may be possible through the formation of inclusion complexes PCDD:CD.

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Aspects encountered in TGA analysis of polymers performed under different heating schedules

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Thermogravimetric analysis is a basic and crucial investigation for polymers. On a regular basis, it is used for the determination of degradation temperatures, values that are considered further on in establishing the experimental conditions for other thermal investigations (differential scanning calorimetry and dynamic mechanical analysis).
As any thermal method the results depend on the heating rate.
The presentation aims to exemplify how the heating schedule influences the results obtained by using polymer blends based on poly(lactic acid).
Moreover, another dynamic approach is applied to the investigated polymers that is based on the adjustment of the heating rate during a run in order to improve the separation between closely occuring mass loss events.
The obtained results are comparatively discussed, attempting to evaluate qualitatively whether the degradation mechanisms are similar.

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UV protective abilities of cotton fabrics pre-treated with plasma at atmospheric pressure and coated with TiO_2-SiO_2 and TiO_2-SiO_2/reduced graphene oxide composites

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Textile materials with UV protection are attractive for manufacturing of high value-added products. The aim of this study was to evaluate the UV-protection properties of cotton fabrics pre-treated with plasma at atmospheric pressure and coated with TiO_2-SiO_2 and TiO_2-SiO_2/graphene oxide composites. A homemade model of Portable Plasma Generator was used for pre-treatment of cotton fabric-modified surfaces, under specific experimental conditions (process gas: He/air, *gas* flow rate: 5 l / min, input power: 50 W, plasma treatment time: 30 sec and 3 min). TiO_2-SiO_2 composites were prepared by two methods: (M1) the physical method by mixing TiO_2 and SiO_2 nanopowers and (M2) the chemical method (sol-gel) using titanium tetra-isopropoxide as *Ti* precursor. SiO_2 nanopowder was subsequently added respecting the proportion of 25% SiO_2:Ti. All samples were heat treated at 450°C in air. TiO_2-SiO_2/graphene oxide composites (10:1 weigth ratio) were prepared by ultrasonic dispersion of TiO_2-SiO_2 powders and graphene oxide into 20% ethanol solution, and then dispersions were dried and annealed at 300°C in argon atmosphere. The obtained TiO_2-SiO_2 powders were denoted TS-M1 and TS-M2, while TiO_2-SiO_2/graphene oxide based composites were denoted: TS/GO-M1 and TS/GO-M2. The UV protective properties of the composite coated cotton fabrics were investigated by measuring the UV transmittance through composite-coated cotton samples, using mean percentage transmission in the UVA region (315–400 nm) and UVB region (280–315 nm). On the basis of the recorded data, Ultraviolet Protection Factor (UPF) was calculated as follows: $\boldsymbol{UPF} = \frac{\sum_{\lambda=280}^{400} E\lambda \, x \, S\lambda \, x \, \Delta\lambda}{\sum_{\lambda=280}^{400} E\lambda \, x \, S\lambda \, x \, T\lambda \, x \, \Delta\lambda}$, where: Eλ is the relative erythemal spectral effectiveness, Sλ is the solar spectral irradiance, Tλ is the average spectral transmission of the sample and Δλ is the measured wavelength interval (nm). According to the Australian/New Zealand Standard (AS/NZS 4399:1996), the UPF value describes textiles providing good (UPF = 15-24), very good (UPF = 25-39) or excellent (UPF > 40) UV protection. The cotton fabrics coated with TiO_2-SiO_2 and TiO_2-SiO_2/graphene oxide powders that were prepared by chemical method showed moderate ultraviolet protection factor (UPF) values, whereas 50+ UPF values were measured for the similar physical powder-coated cotton samples. No significant differences in UPF values by increasing plasma pre-treatment time of cotton fabrics were reveal. In conclusion, it is possible to obtain fabrics with UV protective abilities using relatively low-cost materials and procedures could be obtained.

Table 1. UPF values and UV protection rating of obtained powder-coated cotton fabrics

Sample	UVA	UVB	UPF value	UPF range	UPF protection rating
cotton	17.23	7.59	9.4	< 10	non-ratable
cotton/TS-M1_30 sec	5.88	0.92	64.75	50+	excellent
cotton /TS-M1_3 min	6.34	1,08	56.82	50+	excellent
cotton /TS-M1/GO_30 sec	3.29	0.37	134.00	50+	excellent
cotton /TS-M1/GO_3 min	4.70	0.82	76.07	50+	excellent
cotton /TS-M2_30 sec	9.34	3.70	20.05	20	good
cotton /TS-M2_3 min	8.67	3.16	22.56	20	good
cotton /TS-M2/GO_30 sec	8.50	3.59	21.61	20	good
cotton/TS-M2/GO_3 min	7.87	3.36	23.03	20	good

Acknowledgments

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Analysis of nano-composites with TiO2 Ag for applications in cotton textile industry

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Nanoparticles of TiO2 show enhanced domestic and industrial use due to self-cleaning, antimicrobial, photocatalytic and anti-pollution characteristics. The improvement of the properties for leather and other textile material by using modified nano-composites has large applications and possibilities.
Due to its excellent photocatalytic properties, TiO_2-based coatings are widely used in textile stain removal processes under light irradiation.
Cotton samples were initi aplasma treated (using Ar si Ar/O3, for 30 sec / 3 min) and then imersed in a solution with TiO2 Ag 3% in distilated water and dried in Argon atmosphere.
The purpose of this study was to investigate by WAXD - Wide Angle X-Ray Diffraction, TEM, SEM, the thin changes in crystalline structure of precursors after chemical and / or thermal treatment, step-by-step.

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Thermal process for obtaining titanium nitride nano-powder via vinyl polymer composites

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Due to its unique properties, titanium nitride is a ceramic of considerable interest for both, materials science and industrial applications. The research intends to develop a unique TiN ceramic powder with high performance and quality parameters by an innovative manufacturing process.
This work is aimed to obtain titanium nitride ceramic via hybrid polymer composite. Our technology proposes a new approach for designing materials generating a unique class of ceramics with distinguishing features related to mechanical properties and higher thermal stability than similar materials. Also, this *new route to synthesize nanocrystalline ceramic powder, offers the possibility of an economically attractive production method for Ti(C,N).*
This study presents the pyrolisis of polymers inside inorganic porous structures (till 600 °C, in nitrogen atmosphere to obtain carbon nanocomposites) and complex characterization of raw materials and polymer nanocomposites by WAXD – Wide Angle X-Ray Diffraction, DSC - Differential scanning calorimetry, TGA - Thermal Gravimetric Analysis and SPM – Scanning Probe Microscopy.

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Graft Conjugated Polymers: Toward Smarter and Versatile Materials for Biomedical Applications

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Bioinspiration involves the study, understanding and the attempt to apply what the Nature is revealing us after its billions of years of refinement during the process of evolution of life on Earth. In this context, the conjugated polymers' (CPs) electro-chemistry could be seen as being biomimetic (Otero et al, 2012), while the use of CPs to interface with biology can be advantageous for numerous reasons including potential low cost of the materials, mechanical flexibility, mixed electronic/ionic conductivity, improved interfaces and tunability of the materials due to their organic nature.
The present communication will reveal how a particular polymers' architecture and appropriate building blocks combination based on CPs and biocompatible/biodegradable oligomers counterparts can results in alternative biomaterials with tunable properties for specific envisioned bioapplications, such as tissue engineering (Fabregat et al , 2013, Bendrea. et al, 2013, Maione et al, 2015), cell imaging (Cianga et al, 2014, Bendrea et al 2013) or biosensing (Molina et al, 2017, 2018)

Acknowledgments (10pt, bold, align left)
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Chitosan/poly(2,2-dimethyl trimethylene carbonate) composites

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Chitosan is a naturally occurring biodegradable polymer with sought after functionalities and properties. The biocompatibility, biodegradability and low immunogenicity make chitosan a very valuable material for many applications in the biomedical field.[1] To extend the range of applications of chitosan, various derivatives, including different polymer conjugates and composites, have been prepared.
Aliphatic polycarbonates are increasingly used in biomedical areas as during degradation they do not form the undesired acidic products.[2] Within the family of aliphatic polycarbonates, the homopolymers of 2,2-dimethyl trimethylene carbonate (DTC) can be considered as material precursors with promising mechanical and thermal properties.[3]
The purpose of the present work is the preparation of new composites made of biocompatible poly(2,2-dimethyl trimethylene carbonate) (PDTC) and chitosan (Figure 1) by applying different synthetic strategies:

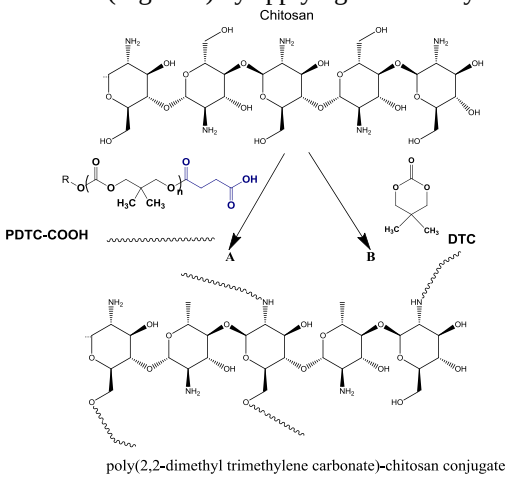

Figure 1. Schematic representation of the synthesis of PDTC-chitosan graft copolymers

(A) grafting - through reaction between suitable functional groups, and (B) the ring opening polymerization of monomeric DTC. In parallel, a third approach will be investigated: (C) the composites formation using star-shaped poly(2,2-dimethyl trimethylene carbonate)s having carboxylate end-groups [PDTC-$(COOH)_4$] and chitosan, using the grinding technique under solvent-free conditions.

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NEW SERIES OF CHITOSAN BASED COMPOSITES FOR BIOMEDICAL APPLICATION AS BONE SUBSTITUTES

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Chitosan (CTS) based biocomposites and hybrid biomaterials are nowadays some of the most appealling materials in terms of applications for hard and medium soft tissues, due to a successful combination of desired properties as result of a wise selection of components. Based on specific requirements for each type of tissue, various formulations and manufacturing protocols were designed and the resulted materials have been tested with good to excellent results. Among them, the chitosan-hydroxyapatite (CTS-HAp) biocomposites are highly appreciated as graft materials in orthopedics [1,2]. They are flexible, but their mechanical characteristics are inferior to natural bone, so that these composites are employed as scaffolds for orthopedic applications as bone and cartilage graft substituents because they have enhanced osteoconductivity and improved mechanical strength as compared to CTS, as well as a promising ability to mimic the host tissues and favor the stabilization and proliferation of the specific living cells [3,4].
New series of CTS-Hap were prepared by a simple experimental protocol, using low to moderate loads of Hap, and the properties of the new materials were evaluated (FTIR, XRD, SEM, mechanical testing) in order to assess their level of performance in correlation with their envisaged application.

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Detection of the biological constituents in solution using metamaterial slabs with special properties

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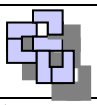
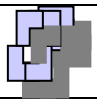
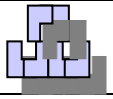
Using of the metamaterials for detecting has applications in biomedicine for medical diagnosis. The procedure is fast, very sensitive and represents a nondestructive material testing method.
The used metamaterial presents negative refractive index and has a nonlinear behavior under the testing conditions. The structure was developed like a 3D metamaterial with periodic geometrical constituents having dimensions of tens of micrometers, exposed to the electromagnetic field in Ghz range (7 – 28 GHz). The material interacts with the wave and modifies its properties in function of the design. Structure was conceived on a FR4 substrate, consisting of nested ring resonators with different configurations (see Table 1).
The electromagnetic wave propagates distinctly through the structure impregnated with a solution containing a biological material samples with different constituents. By estimating the modification of the metamaterial sample parameters, like refractive index and effective permittivity, the detection of the concentration level of a biological product (biomolecules) in the biological liquid (biological sample) can be performed. Particle diameter of the inclusions inside the liquid sample, which cause modifications of the field propagation can be of nanometers order. The detected substances were considered like: *a* – protein in blood (albumin / globulin, indicating hyperproteinemia), *b* – lipid in blood (fatty acids and cholesterol, indicating hyperlipidemia), *c* – carbohydrate in blood (indicating diabetes disease).
A theoretical model of the metamaterial structures has been considered. Analysis was performed by simulation methods at structure level, with *S* parameters determination for the propagation cases through the metamaterial with biological sample inside. As a result, the electromagnetic properties were determined.

Table 1. Strategy for detection of three biological constituents (*a* - protein, *b* - lipid, *c* - carbohydrate) inside the biological sample inserted in the metamaterial structures. Conclusions obtained by analyzing the propagation modes.

Metamaterial configuration / slab thickness	Model for the unit cell (600 x 400 x 80 nm)	concentration level [%]			refractive index variation, Δn			effective permittivity variation, $\Delta\varepsilon_r$		
		a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
I. first variant	 (60 x 40 x 16 µm)	modifying the refracted wave intensity 2-3 …20% expected			modifying plasmons propagation up to 4% expected			modifying the electric induction of the sample up to 6% expected		
II. second variant	(52 x 42 x 12 µm) 									
III. third variant	 (74 x 42 x 10 µm)									

The obtained 3D graph will be available for the biological constituent concentration level versus metamaterial constituents dimensions, for different material models. The analyzing method is solving a task like: choosing the optimal design for the detection structure and synthesis of the unit cell in function of the parameter which has to be detected in our nondestructive control.

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Observations On The Spinning Disc Micromixing Characteristics

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The spinning disc technology is one of the most versatile process intensification techniques used in different application fields, from food industry to environmental technologies.
The intense micromixing is one of the strong features the spinning disc is used for. The current study includes data related to the residence time and the dispersion coefficient values, determined from the residence time distributions obtained experimentally using the pulse-response technique, at different working parameters, namely the feeding liquid flow rates and the disc rotational speeds. These were used to calculate the characteristic SD micromixing time and compare it to the time for turbulent dispersion. The ratio between the two parameters, indicating whether the micromixing is predominant in comparison to the turbulent dispersion, proves the disc enhanced micromixing capabilities.
Also, the maximum shear stress attained at different locations on the spinning disc and its increase with the liquid flowrate and the disc rotational speed was discussed. At the same time, one has to consider the dependence of residence time values on the working parameters. The shear stress is increasing faster than the residence time is decreasing with the rotational speed, but slower with the respect to the liquid flow rate. Furthermore, the residence time to the micromixing time ratio is calculated for the investigated liquid flowrates and disc rotational speeds and the largest values are obtained at the highest rotational speeds, meaning that despite the shorter residence time, the decrease in the micromixing time is faster, especially at smaller flowrates. Thus, despite the increased micromixing corresponding to large rotational speeds, the shorter time spent by the liquid on the disc can be a restricting factor, since the processed liquid cannot take advantage of the enhanced turbulence.
Concluding, the benefit of intense micromixing lies within an intermediate range of the studied parameters, when the micromixing intensity is superior and the residence time is large enough to allow the liquid film stay on the disc, so that the SD technology can be efficiently used.

Non-Intrusive Visualization Techniques For Flow, Temperature And Concentration Fields

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The study covers some of the non-intrusive visualization techniques used to characterize the flow, the temperature and the concentration fields, in different systems. It focuses particularly on depiction of convection fields studied in vertical two-phase flow and steady or unsteady thermal convective flow, in temperature induced Marangoni convection (thermocapillary convection), investigated previously [1, 2].
The Photochromic Dye Activation technique utilizes the photochromic properties of a colorless indicator dissolved in a fluid, activated by a laser beam pulse, with a change in color, resulting in traces following the flow and it can be used to measure instantaneous velocity profiles near the gas-liquid interface/walls. The method was employed to highlight the liquid film penetration along a Taylor bubble, in slug flow and to visualize the flow field in the bubble wake. The Particle Image Velocimetry, another non-intrusive optical laser technique, provides instantaneous velocity vectors in a cross-section of a flow. In case of the above-mentioned two-phase flow, the velocity fields around the bubble and in its wake were mapped. These techniques were also used to characterize the convection field in temperature-induced Marangoni flow, in both vertical and horizontal plans, steady and non-steady regimes.
The temperature field in thermocapillary flow was measured using an infrared camera that provided information about the temperature field in a steady flow and also, was capable to detect instabilities occurrence, which were subsequently linked to the instabilities register in the convection field. The Mach-Zehnder interferometry consists of splitting a laser beam into two beams, one of reference and the other to be passed through the investigated system. By recombining them, one can obtain a fringe pattern characterizing changes in the system temperature or concentration field. This technique was used to depict the integrated vertical temperature field occurring in the thermocapillary flow, when steady-state or unstable regimes were attained.
Comments on the strengths and the limitations of each technique are discussed.

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Iron oxide nanoparticles conjugated with cerium oxide nanoparticles as free radical scavengers with magnetic properties

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Cerium oxide nanoparticles present the mimetic activity of superoxide dismutase. They are able to inactivate excessive reactive oxygen species (ROS) which play a role in atherosclerosis or cancer. The purpose of this study was to prepare and characterize, for the first time, a nano-size cargo-complex having a magnetic core with PEI shell, able to load and to deliver precise amounts of radical scavengers of cerium oxide nanoparticulate type, being spatially guided in the human body (by means of magnetic field) and supplying species capable of inactivation of active radical species.
The nanoconjugated were characterized by multiple techniques and the antioxidant activity was evaluated in vitro and in vivo. Nanoconjugates have an average diameter of 8 nm, possess superparamagnetic properties and adequate saturation magnetization. Conjugation of nanoceria with magnetic nanoparticles improves the in vitro free-radical scavenging properties of the first. Also, nanoconjugates have the ability to reduce oxidative stress,as proved by in vivo studies, which revealed an increased antioxidant activity in all organs and fluids collected from mice. These results indicate the possibility of using the nanoconjugates for theranostic applications.

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Natural compounds architecture for drug delivery system

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Biomacromolecules such as cellulose, collagen and lignin attracted a lot of attention due to their antioxidant and antimicrobial properties while polyurethane is a biocompatible synthetic polymer often used for its elasticity and has a great potential to be utilised for biomedical applications (Spiridon et al., 2020; Tran et al., 2013; Larrañeta et al., 2018). This work present the synthesis and characterization of new materials obtained by dissolution of cellulose, collagen and polyurethane in 1-ethyl-3-methyl-imidazolium chloride ([EMIm+Cl-] for potential drug delivery. Lignin (L), lignin-metal complex (LMC) and ketoconazole (K) as fillers were added into above mentioned polymeric matrix. 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).

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

Sample	TCI (A_{1376}/A_{2902})	HBI (A_{3336}/A_{1336})	LOI (A_{1437}/A_{899})
Cellulose	1.844	5.140	2.174
CCP-K	1.625	4.114	2.849
CCPOL-K	1.143	6.148	4.557
CCPLMC-K	1.855	4.637	3.333
CCP	1.901	3.620	1.842
CCPOL	1.870	3.969	1.979
CCPLMC	1.436	3.985	1.836

*CCP-K = Cellulose-collagen-polyurethane-ketoconazole; CCPOL-K = Cellulose-collagen-polyurethane-organosolv lignin-ketoconazole; CCPLMC-K = Cellulose-collagen-polyurethane-lignin metal complex-ketoconazole; CCP = Cellulose-collagen-polyurethane; CCPOL = Cellulose-collagen-polyurethane-organosolv lignin; CCPLMC = Cellulose-collagen-polyurethane-lignin metal complex.

The drug release profile shows that lignin addition into the polymeric matrix induces retard properties and influences the amount of ketoconazole released into medium (Figure 1), which makes it prone for the manufacturing of patches with dermato-cosmetic applications.

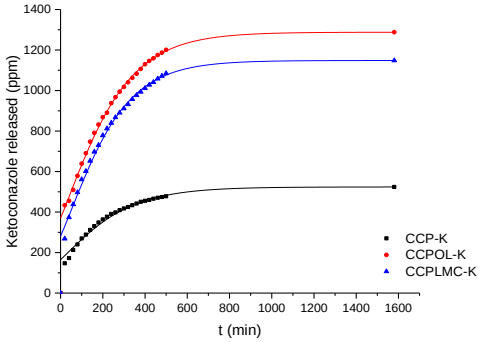

Figure 1. The amount of drug released in medium over time at pH=7.2 for 30h.

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The Properties of Potassium Carbonate/Bicarbonate Concentrated Solutions Promoted with Ethylenediamine or CO_2 Capture

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The carbon dioxide (CO_2) emissions have continually increased in the last years, especially due to the fossil fuels combustion and industrial processes. The CO_2 concentration increased from 400 ppm in 2016 to 415.7 ppm in May 2019. For this reason it is mandatory to find new methods to reduce concentration of this pollutant responsible for global warming. Several methods for CO_2 reduction have been applied, including physical and chemical methods. Among these, absorption is considered one of the promising method. From absorbents the most effective are considered to be aqueous amines or hot potassium carbonate solution. Potassium carbonate has advantages: low cost, low toxicity, efficient and economical regeneration process, and other economic concerns like corrosion problem. For absorption, an aqueous solution of 20 - 40% K_2CO_3 is used as close as possible to the saturation without the phenomenon of crystallization. One of the biggest weaknesses of the potassium carbonate solutions in the absorption of CO_2 is the slow rate of reaction. In this work, the transport properties of aqueous blend solution of potassium carbonate/bicarbonate activated with ethylenediamine are studied, in order to find the optimum amine's concentration for absorption process. The density (fig 1) and viscosity (fig 2) are measured over the wide range of temperature (293-348 K) and 1-7 % EDA concentrations. The results are useful in determination of diffusion and mass transfer coefficients in the analysed solutions, for modelling and simulation of the absorption process.

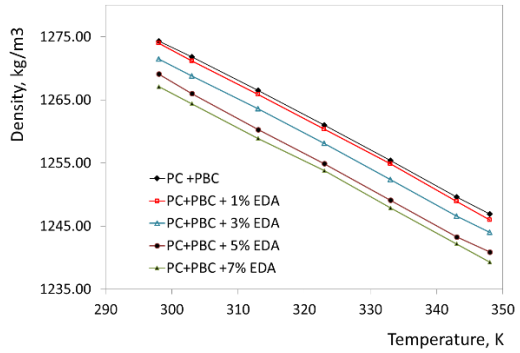

Fig. 1. Plot of density of K_2CO_3 + $KHCO_3$ + EDA solution function temperature

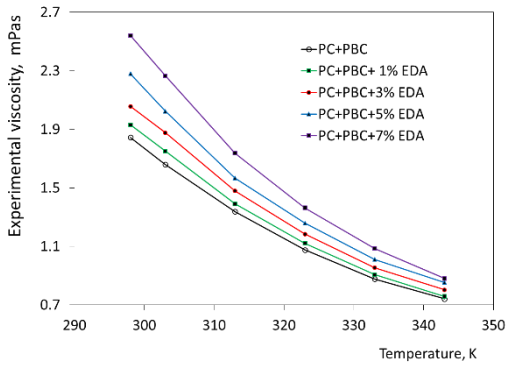

Fig. 2. Plot of viscosity of potassium carbonate/bicarbonate promoted solution function of temperature

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BOOK OF ABSTRACTS

Section 2 Biotechnology and Bio-industries

Health promoters from potato and pumpkin instant purée

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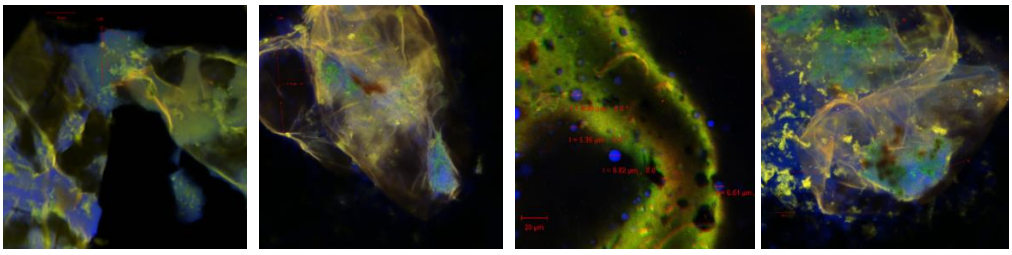
Vegetables and fruits are good sources of dietary fibers, vitamins, minerals and bioactive compounds indispensable for well-balanced diets in relation to human health. The aim of this research was to examine the effects of conventional drying method on the quality parameters of a non-dairy solid product based on potato (*Solanum tuberosum* L.), pumpkin (*Cucurbita moschata* L.) and *Lactobacillus delbrueckii* subsp. *bulgaricus* Lb12 strain. All the purée samples were evaluated by the microbiological, microstructural, flow, thixotropy, oscillatory rheological measurement, Texture Profile Analysis and phytochemical properties point of view. All the purées presented a high content of total carotenoids, β – carotene and total antioxidant activity, as it can be seen in Table 1. The textural parameters (firmness, cohesiveness, adhesiveness) of the reconstituted samples did not present significant differences compared to fresh samples.

Table 1. Phyto-chemical characteristics of fresh and reconstituted vegetable purée

Purée sample	Total carotenoids, mg/g	β-carotene, mg/g	Antioxidant activity, µg Trolox/mL
Fresh vegetable purée			
Potato purée	4.10 ± 0.48	3.63 ± 0.37	0.070 ± 0.003
Potato and pumpkin purée	23.74 ± 1.25	20.47 ± 0.65	0.135 ± 0.018
Reconstituted vegetable purée			
Potato purée	21.82 ± 1.37	22.48 ± 0.62	0.133 ± 0.016
Potato and pumpkin purée	278.63 ± 0.74	247.20 ± 0.85	0.671 ± 0.025

The initial Lb12 population for both fresh and dried samples was approximately 8.9 log CFU/g and it varied between 7.47 and 7.09 log CFU/g during the storage period. Confocal analysis of vegetable purée for fresh and dried samples (Figure 1), even after reconstitution, shows the presence of bioactive compounds in the category of carotenoids in the form of clusters with green fluorescence (505 – 530 nm) and probiotic bacteria in yellow (550 nm). The presence of these elements in the complex matrix of the product generates functionality and enhances the nutritional value.



a) b) c) d)

Figure 1. Confocal laser scanning microscopy images of fresh and reconstituted vegetable purée with potatoes and pumpkin
a) fresh potato purée, b) fresh potato and pumpkin purée, c) reconstituted potato purée, d) reconstituted potato and pumpkin purée

Keywords: bioactive compounds, vegetal materials, antioxidant activity

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Bioactive compounds from gonads using different extraction methods

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From the worldwide fish production, estimated at 171 million tons in 2016, at least 30–35w% is considered to end as waste (*FAO, 2018*), usually called by-products. The gonads, roes and fish skin are the main fish by-products, but still they could be source of valuable active compounds such as fatty acids, proteins, peptides, vitamins, etc., which could be used in various applications. Lipids from these wastes are mainly used as sources of polyunsaturated fatty acids (PUFAs) and vitamins.
Extraction of bioactive compounds can be done using classical or non-conventional methods. The latter, known as green extraction methods, are based on alternative solvents and/or more efficient ways of introducing energy into the system (microwaves, ultrasounds, high gravitational fields) and used to obtain high quality products with lesser energy consumption (*Selvamuthukumaran and Shi, 2017*).

In this context, different extraction methods of bioactive compounds from fish gonads have been studied (maceration, reflux extraction, classic extraction and ultrasound assisted extraction). To improve oil extraction yield and optimize extraction procedures, the influence of various parameters (solvent concentration, ratio of solvent to solid, time, temperature) was studied. Fatty acid ethyl esters were synthesized in order to be enriched in PUFA and vitamins by molecular distillation.
The analysis of bioactive compounds was performed using GC-MS/MS TRIPLE QUAD (Agilent 7890 A) and LC-MS/TOF, MODEL 6224.

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Separation of 2-ketogluconic acid by synergic reactive extraction

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2-Keto-D-gluconic acid is a compound produced over 40,000 tons/year due to its wide use in food industry: as food antioxidant, as additive to maintain food color, flavors and aroma, and its ability to block the formation of ammonium nitrite (carcinogenic) during food processing. Its biotechnological production has been improved significantly, but separation needs constant attention, mainly due to involvement of multiple downstream steps that generates high costs. Taking into account that limited research has been carried out on the reactive extraction of 2-ketogluconic acid, this study was focused on analyzing the pH dependent extraction performance and the molar ratios of acid and extractant (Amberlite LA-2) dissolved in three solvents with 1-octanol as phase modifier.

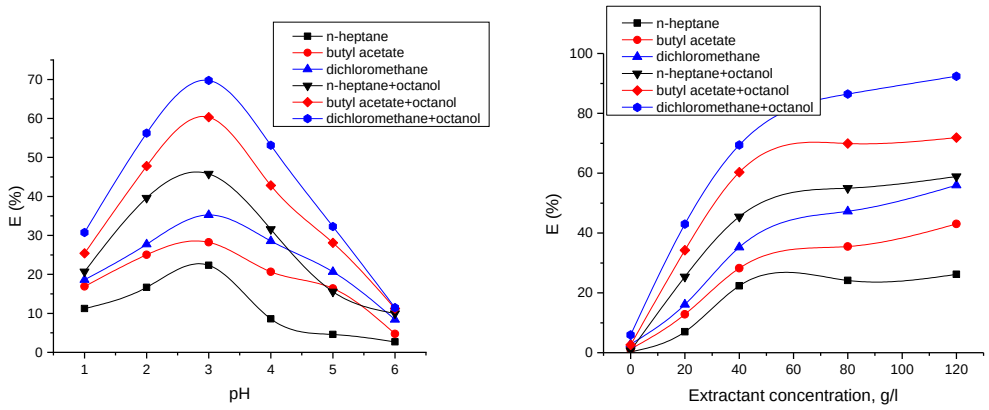

Fig. 1. pH and extractant concentration influence on reactive extraction with and without 1-octanol addition

The mechanism of the interfacial reaction pointed out that, indifferent of the pH value and solvent polarity, only one molecule of 2-ketogluconic acid and one of extractant react at the interface.

Table 1. Values of n and extraction constants for extraction systems with 1-octanol and Amberlite LA2

Solvent	n	Ke, (L/mol)
n-heptane/octanol	0.788	11.94
Butyl acetate/octanol	0.86	65.95
Dichloromethane/ octanol	1.17	311.6

The 2-ketogluconic acid production through biosynthesis is an extremely important process because of its multiple applications in food, cosmetic and pharmaceutical industries; reactive extraction could represent an advantageous alternative to current used downstream processes. Experimentally the highest extraction yield and distribution coefficient are achieved for pH of 3 and 120 g/L extractant, for all the studied solvents. The addition of 1-octanol as polar modifier strongly increased the extraction efficiency for all solvents, with bigger values for the inactive organic solvent with the lowest dielectric constant (n-heptane).

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Microencapsulation of extract of European plants, rich in phenolic compounds, with health benefits and food interest

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Several European native plants were used in the traditional medicine during centuries (Chaumun, Goëlo, Ribeiro, Rocha, & Estevinho, 2020; Marisa Ribeiro, Estevinho, & Rocha, 2019; Ribeiro, Estevinho, & Rocha, 2019). In plants, phenolic compounds are essential for diverse biological activities, participating in structural signalization roles and in defense strategies under stress conditions. On the other hand, when consumed by humans, these ingredients exhibit several therapeutic properties (e.g. antioxidant, anticancer, antiallergenic, anti-inflammatory and antiviral), allowing to reduce the oxidative stress and to prevent some health conditions like cancer, arteriosclerosis and ageing processes. So, phenolic compounds extracted from plants can provide extra health benefits, however, in general, these natural compounds are very sensitive and with low bioavailability in human body (Cardoso, Gonçalves, Estevinho, & Rocha, 2019; Chaumun et al., 2020; Goëlo, Chaumun, Gonçalves, Estevinho, & Rocha, 2020; Lucas, Ralaivao, Estevinho, & Rocha, 2020).

Microencapsulation is a promising alternative to improve their stability and bioavailability, to protect and to improve sensitive compounds with a controlled release, enabling their incorporation in active food products, nutraceuticals and in therapeutic formulations.

Different European native plants (Sambucus nigra L., Laurus nobilis L. and Salvia officinalis L.) were selected considering their health potential associated to their composition. Phenolic extracts were prepared and different microparticles were obtained by a spray drying process using different biopolymers (modified chitosan, gum arabic, sodium alginate). The microparticles were fully characterized (e.g. size, morphology and stability) and evaluated in terms of controlled release. Proper mathematical models were applied to the release profiles obtained in simulated conditions.

Microparticles with rough or smooth surface and with fast or slow release were obtained depending on the encapsulating agent used. The encapsulation efficiency was around 90-100%. Korsmeyer-Peppas and Weibull models are the models that best adjust to the experimental release profiles.

This study proves that is possible to produce microparticles with good quality and stability containing natural compounds, namely phenolic compounds. These microparticles can be easily incorporated in commercial instantaneous powder food products like gelatin or even cookies that can be fortified with bioactive compounds.

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Anti-inflammatory potential of new complexes of diclofenac hydrazones using *in vitro* methods

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Abstract. Nonsteroidal anti-inflammatory drugs, in which acetic acid derivatives (diclofenac, aceclofenac, indometacin, ketorolac) occupy an important place, are among the most commonly used drugs in the treatment of pain and inflammation of various rheumatic conditions but also in other types of pain - renal colic, biliary colic, headache, dysmenorrhea, etc. Since diclofenac therapy is associated with adverse effects at the gastrointestinal and renal level, the researchers have focused on derivatizing it at the free carboxyl group to improve the toxicological profile (Constantin et al., 2015). Recent studies have also highlighted that reactive oxygen species (ROS) are involved in triggering various diseases, with an important role in inflammation (Gan et al., 2010). The aim of the study is to evaluate the anti-inflammatory activity of 12 new complexes (**5 a-d copper complexes, 6a-d zinc complexes, 7a-d nickel complexes**) with hydrazone structure using two *in vitro* methods: inhibition of serum albumin denaturation and erythrocyte membrane stability test. **Material and method.** For the evaluation of the anti-inflammatory effect, 10 mg/mL stock solutions were obtained by dissolving the compounds studied in DMSO, from which different dilutions were subsequently made. For the serum albumin denaturation inhibition assay the samples were treated with 3 mL of 1% bovine albumin (aqueous solution), then incubated for 20 min at 37^0C, then 5 min at 72^0C, cooled for 10 min and then add 1 mL of saline phosphate buffer (pH = 7.2). The turbidity of the samples was read at 416 nm against distilled water. For the erythrocyte membrane stability assay, the samples were treated with 1 mL phosphate buffer (pH = 7.4), 2 mL hyposaline solution (0.36% NaCl solution) and 0.5 mL HRBC solution (10% v/v). Samples were incubated at 37^0C for 30 min, then centrifuged at 3000 rpm for 20 min. The absorbance of the supernatant was read at the wavelength of 560 nm compared to the sample blank (Zuo et al., 2011). **Results and discussions.** The results obtained showed that both the bovine serum albumin inhibitory capacity and the erythrocyte membrane stability for the compounds studied were increased with the concentration, the best results were obtained for the concentration of 125 µg/mL and 111.11 µg/mL for the **nickel complex 7c**. It was observed that the generation of autoantigens in rheumatic and inflammatory disorders can cause tissue protein distortion, thus leading to the accentuation of these diseases. At the same time it is accepted that the erythrocyte membrane is similar to the lysosomal membrane whose stability is crucial for limiting the inflammatory process. By destroying the lysosomal membrane, the release of cellular constituents activates neutrophils, bactericidal enzymes and proteases, causing inflammation of the tissue. **Conclusions**. The structural modulation of diclofenac at free carboxyl group has led to new hydrazone complexes that have proven anti-inflammatory potential evaluated by *in vitro* methods which opens new perspectives in the treatment of inflammatory diseases.

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PEGylated phenothiazines as water soluble building blocks for biomaterials

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Abstract: Phenothiazine is a well-known fused ring heterocyclic compound wich possess electron rich sulfur and nitrogen heteroatoms. Because of the low solubility of the phenothiazine based compounds in ordinary solvents (S. Ahmadian et al., 2011), three new PEGylated phenothiazine derivatives which keep the potential of valuable building blocks for preparing eco-materials addressed to a large realm of fields, from bio-medicine to opto-electronics, were obtained. They were synthetized by connecting the hydrophilic poly(ethylene glycol) to the hydrophobic phenothiazine via an ether, ester, or amide linking group. The successful synthesis of the targeted polymers and their purity were demonstrated by NMR and FTIR spectroscopy methods. Their capacity to self-assembly in water was studied by DLS and UV-vis techniques and the particularities of the formed aggregates were investigated by fluorescence spectroscopy, SEM, AFM, POM and UV light microscopy. The biocompatibility was assessed on normal human dermal fibroblasts and five human cancer cell lines. The synthetized compounds showed the formation of luminescent aggregates and proved excellent biocompatibility on normal cells (S. Cibotaru, et al., 2020). A concentration dependent cytotoxicity against four cancer cell lines was noticed for the PEGylated phenothiazine containing an ester unit and against two cancer cell for direct PEGylated phenothiazine.

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Cannabidiol-rich hemp oil induces apoptosis in cancer cell lines

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Introduction: Cannabidiol (CBD) is one of the major cannabinoids found in *Cannabis sativa* L., known as industrial hemp. CBD oil exhibits a versatile spectrum of pharmacological effects, including anti-cancer activity. This study aims to evaluate the *in vitro* anti-cancer effect of CBD-rich hemp oil.
Methods: Hemp oil was extracted from whole plant in ethanol and decarboxylated at 90ºC for 2 hours (soft conditions) in order to obtain maximum CBD yield. Cytotoxicity of CBD-rich hemp oil on malignant melanoma (MeWo), adenocarcinoma (HeLa), hepatocellular carcinoma (HepG2) and osteosarcoma (HOS) cells versus normal dermal fibroblasts (NHDF) was determined by MTS assay. Apoptosis induced by hemp oil in cancer cells was demonstrated using acridine orange/ethidium bromide (AO/EB) staining and real-time quantitative PCR.
Results: Decarboxylation of hemp oil at 90ºC for 2 hours yielded 98.76% CBD. We found that CBD-rich hemp oil promotes proliferation of normal fibroblasts at concentrations up to 15 µg/mL followed by cytotoxic effects at higher concentrations. Furthermore, we demonstrated that CBD-rich hemp oil was cytotoxic in a dose dependent manner for MeWo, HeLa, HepG2 and HOS cells at lower CBD concentrations than for NHDF cells. Also, HeLa, HepG2 and HOS cells were more sensitive to CBD compared to MeWo cells. The half maximal inhibitory concentration (IC50) was determined to be 26.65 µg/mL for NHDF, 21.59 µg/mL for MeWo, 16.89 µg/mL for HeLa, 16.85 µg/mL for HepG2 and 8.42 µg/mL for HOS cells. CBD-rich hemp oil induced dose-dependent morphological changes in treated cancer cells (cell shrinkage and detachment, cytoplasmic condensation, vesicle formation, spheroid disaggregation of HepG2 cells). Moreover, AO/EB staining showed that CBD-rich hemp oil induces apoptosis hallmarks (chromatin condensation, nuclear fragmentation, apoptotic bodies' formation, cytoplasmic shrinkage, cell detachment, spheroid disaggregation of HepG2 cells) in treated cancer cells at lower doses than in normal fibroblasts. Fibroblasts exhibited the first signs of apoptosis at 20 µg CBD/mL, while in cancer cells the apoptotic features appeared at 5-10 µg CBD/mL and increased in a dose-dependent manner. IC50 concentrations of CBD-rich hemp oil induced up-regulation of BCL2-associated X (BAX) and down-regulation of BCL2 gene expression, resulting in a BAX/BCL2 ratio > 1 which is characteristic for apoptotic stimuli-sensitive cells.
Conclusion: CBD-rich hemp oil showed dose-dependent cytotoxic effects and induced apoptosis at low doses in cancer cells, but not in dermal fibroblasts, suggesting that CBD oil could be used as complementary anti-cancer treatment.

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Extraction of phenolic compounds from callus biomass *Pulsatilla alba*

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The flora of the Ukrainian Carpathians is rich in a large number of medicinal plants. Among them, *Pulsatilla alba* is an interesting plant. It is a species of flowering plant in the family *Ranunculaceae*, which is listed in the Red Book of Ukraine. The plant is rich in a large number of biologically active substances, such as: anemone acid, saponins, resins, essential oils, alkaloids, tannins, vitamins, macro- and micro-elements. *Pulsatilla alba* has been used in folk medicine for a long time, but its natural reserves are constantly decreasing.

The use of the cell and tissue culture method for obtaining in vitro callus culture of the medicinal plant *Pulsatilla alba* made it possible in a relatively short time to obtain valuable medicinal raw materials with a wide range of applications in biotechnology, medicine, pharmacy and veterinary medicine.

The object of the study is the callus mass *Pulsatilla alba* obtained by us, dried to constant weight and grinded up to sizes of (*dc*) 0.5 mm, 1.0 mm, 1.5 mm (Table 1).

The extraction was performed in a Soxhlet apparatus. The ratio between the dried callus biomass *Pulsatilla alba* and the extractant - 70% ethyl alcohol was 1:10. The extraction process lasted 6 hours until complete extraction of biologically active substances. To obtain data on changes in concentration over time (30, 60, 120, 240, 360), the extraction process was stopped and the filtrate sample was taken. The pure solvent was added in the amount of sample taken and reheated to the boiling point of the selected solvent. The selected samples were filtered and analyzed for the content of phenolic compounds.

The total content of phenolic compounds was determined by Folin-Chocalteu spectrophotometric method. 1 ml of the obtained extract was mixed with 4 ml of 70% ethyl alcohol, 0.5 ml of Folin-Chocalteu reagent and 1.5 ml of 20% Na_2CO_3 solution. The mixture was kept for 2 hours in a dark place, after which the optical density of the samples was measured at a wavelength of 760 nm on a Hitachi U-2810 spectrophotometer. The control sample was ethanol. The total content of phenolic compounds is expressed in mg of gallic acid per 1 ml of extract (Table 1).

Table 1

Extraction of phenolic compounds from callus *Pulsatilla alba*, mg / ml

Time, *t*, h	Total amount of phenolic compounds (mg of gallic acid in ml)		
	d_c=*0.5 мм*	d_c=*1.0 мм*	d_c=*1.5 мм*
0,5	0,0540	0,0480	0,0320
1	0,8541	0,8011	0,7999
2	1,6073	1,0711	1,0015
4	2,1405	2,0940	2,0700
6	*2,9334*	*2,9012*	*2,8044*

The maximum content of phenolic compounds was obtained from the extracts using the callus mass grounded to a particle size *ds* = 0.5 mm within 6 h extraction and was 2.9334 mg / ml. The biotechnological approach will allow to use the callus mass of *Pulsatilla alba* as a promising alternative source of biologically active substances for applications in the pharmaceutical industry.

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Novel heavy metal tolerant bacterial strains with PGPR potential, isolated from heavy metal polluted soils

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The soil is a natural source of heavy metals (HM), but the anthropogenic activities increase the HM concentrations of soils, thus becoming harmful to plants and animals and due for its accumulation in food web for human as well (Tirry et al., 2018). Industrial activities, such as tanning, refining, mining, manufacturing processes, also the use of agrochemicals (fungicides, land chemical fertilizers), metallic nanoparticles, urban sewage sludge, industrial waste disposal, waste incineration and vehicle exhausts are the main sources of HM contamination of water resources and agricultural soils. The common toxic metals are the aluminium (Al), manganese (Mn), chromium (Cr), copper (Cu), cadmium (Cd), zinc (Zn), lead (Pb) and mercury (Hg), also some metalloids (antimony and arsenic) are considered toxic (Ashraf et al., 2017; Mishra et al., 2017).
The remediation of HM contaminated soils is very expensive and environmentally destructive method. The physical methods are not efficient, therefore biological processes are involved in remediation of soils. Phytoremediation and the use of rhizosphere microbes are an important alternative solution with high efficiency and better performance. The plant growth promoting microbes (PGPM) can protect the plant from HM stress, but can help in the accumulation of HM from soil in the host plant. The rhizospheric microbes have metabolic capabilities to adapt and live even in presence of high concentration of HM (Mishra et al., 2017). The plant growth promoting (PGP) traits of heavy metal resistant/tolerant bacteria are the following: phosphate solubilization/mobilization, indole-3-acetic acid (IAA), exopolisacharide (EPS), siderophore, ammonia, hydrogen cyanide production and nitrogen fixation (Tirry et al., 2018).
A high number of bacterial strains has been reported, but there is a growing need to find novel, heavy metal tolerant bacterial strains, which can improve the plant growth and yield in case of HM contaminated soils. The aim of this study was to isolate HM tolerant bacterial strains, then to examine their plant growth promoting traits, like phosphate (organic and inorganic) mobilization, EPS, IAA and siderophore production.
Twelve bacterial strains were isolated from Bălan (Harghita County, Romania) from HM contaminated soil (near the mining area). The PGP traits were examined in presence of several HM concentrations: 1 mM Zn, 0.5 mM Cd, 0.5 mM Zn+0.1 mM Cd. 58.3 % of isolated bacterial strains mobilized the inorganic phosphate, and only half (50 %) was able to mobilize the organic phosphate in presence of used HM concentrations. In this last case the HM improved this trait, because the bacterial strains cannot mobilize the organic phosphate in control conditions. The siderophore production of bacterial strains was detected at 75 % of isolated bacterial strains. 91.66 % of strains can produce EPS in control conditions, and also 91.66 % of bacterial strains were able to produce IAA in case of HM concentrations. 50 % of examined bacterial strains maintain their PGP traits in presence of HMs, thus our goal in future is to use this bacterial strains in a plant experiment and to examine their effect on plant growth, development and metal uptake.
Our results show that most of the isolated heavy metal-tolerant bacterial strains retain their plant growth-promoting properties even in the presence of used HM concentrations, making them a potential application in sustainable agriculture.

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Valorization of food industry byproducts towards polyhydroxyalkanoates production by mixed microbial cultures

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Availability of raw materials is not unlimited and thanks to this perception, over the last years, the world of industry has gradually changed its approach to production on a global scale. Nowadays, sensitivity to environmental issues has spread to multiple sectors, thus becoming a driving force of the development of modern society. Based on these considerations, the main objective of this study was the valorization of different types of byproducts deriving from food industry towards the production of value-added compounds, an approach which is consistent with the idea of circular economy and, more in general, of environmentally sustainable production. Indeed, the use of food wastes deriving from food industries can find a more virtuous use compared to disposal in controlled landfills or incineration plants. In this way, it is possible to valorize not only the waste itself but the entire production chain, making the waste a secondary raw material. In principle, such an approach can be broadly applied to a variety of industrial sectors and production processes. As an example, byproducts from wine, cereals and vegetables industries, can be transformed into short and medium chain volatile fatty acids (VFA) through, for instance, an acidogenic fermentation process (Lee et al., 2014). Upon production, these acids can be exploited for various applications, including the production of chemicals, drugs, food, textiles, fuels, and biopolymers such as polyhydroxyalkanoates (PHA). These latter are polyesters that can be defined as three times bio, since they are bio-based, biologically produced and completely biodegradable by bacteria and fungi in the environment, under both aerobic and anaerobic conditions (Valentino et al., 2017). Presently, a wider diffusion of PHA is however largely limited by the high production costs, mainly due to the use of axenic cultures and feedstock of defined composition. In this context, the use of mixed microbial cultures (MMC) and waste substrates as feedstock could represent a groundbreaking alternative for PHA production, which could significantly reduce the production costs. The MMC-based PHA production process involves several stages, including an initial acidogenic fermentation stage to convert the waste substrate into a mixture of VFA, an aerobic stage for the mixed culture selection in favor of PHA-accumulating microorganisms and a polymer accumulation stage whereby the intracellular PHA content is maximized, prior to the downstream polymer extraction and purification stages.
Here, the possibility of converting different food industry byproducts into PHA has been assayed by setting up an MMC-based lab-scale process. As for the acidogenic fermentation step, preliminary batch experiments have been performed by using 9 types of food-industry byproducts, at room temperature and acidic pH (i.e. 5.5), in order to inhibit the methanogenic activity. Overall, a high yield of conversion (up to about 70%) of waste substrates into fermentation products (mostly VFA), which can be easily converted into PHA, has been found. Hence, a synthetic mixture of VFA, formulated based on the results of the acidogenic fermentation experiments, has been used to feed a sequencing batch reactor (SBR) for the selection of PHA-storing microorganisms. In particular, the SBR was inoculated with an activated sludge and operated with a cycle length of 12 hours with an uncoupled feeding of the carbon and nitrogen source in order to trigger the establishment of the feast and famine conditions required for a good microbial selection (**Reis et al., 2011**). Finally, with the microbial culture selected in the SBR, PHA accumulation tests have been carried out in a batch reactor in order to maximize the intracellular polymer content. Taken as a whole, the obtained results indicate the great potential of the selected byproducts to be used as feedstock for a sustainable MMC-based PHA production process.

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Autoinduction fermentation: a new viable pathway for biosynthesis

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The biosynthesis of recombinant proteins with non-native structure and expressed in a non-soluble state is a major challenge. More than 30% of the recombinant protein produced by the most commonly used prokaryotic expression system (Escherichia coli) is produced in insoluble form, further steps are required to solubilize it.
Autoinduction fermentation is an approach to protein biosynthesis that may provide a solution to this problem. Autoinduction broth contains three sources of carbon: glucose (which the cell utilizes most rapidly to inhibit induction), lactose, and glycerol. When glucose is depleted, the cells begin to use the inducing lactose. In the absence of glucose, glycerol is able to maintain growth and expression of the recombinant protein to the same extent. After inoculation, the autoinduction system does not require continuous monitoring; resulting in higher protein yields than conventional lactose analog inducers.
In our experiments we monitored the parameters of the autoinduction broth and the amount of recombinant protein produced in soluble form, thus examine the effectiveness of the autoinduction media.

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Genetic markers associations in endangered cattle breeds to resistance on environmental conditions

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According to the *Food and Agriculture Organization of the United Nations (FAO*), about one third of the recorded livestock species are listed as having a significant chance of extinction and about 1,000 have vanished in the last 100 years. All over the world, many local cattle breeds became endangered due to their substitution by high- yielding breeds. In Romania, for example, two local cattle breeds, Grey Steppe and Pinzgauer, are listed as endangered (Scherf, 2000). Although, they have low milk and meat yields, they are very resistant to diseases and temperature changes. Reducing the size of their populations and their genetic purity, many desirable allelic complexes for environment resistance will be lost. Thus, there is an urgent concern about the survival of their *„wild"* genes pool, the depletion in individuals' number contributing to a decline in the biological diversity of animal genetic capital and even to the reduction of the national cultural heritage. In this respect, in developed countries, native breeds were included in various genetic preservation programmes, assessing their genetic structure using molecular markers in order to facilitate the creation of strategies for their management and protection (Davidescu et al., 2019; Grădinaru et al., 2018). The genetic analysis is the first step in these programmes, molecular methods being used to investigate the individual DNA. Now, a broad variety of genetic markers are used, and microsatellites are especially sensitive for the assessment of genetic diversity and, in addition, to approximate phylogenetic connections between various breeds. Furthermore, whatever their type, genetic markers may be used to reduce the risk of inbreeding and to maintain genetic variability in these kind of populations (Demir and Balcioglu, 2019). Microsatellites are especially used in this regard due to the fact that they reveal a higher amount of alleles per locus comparing to other classical investigations (Ladyka et al., 2019, Grădinaru et al.2018, Ilie et al 2015). The purpose of this study is to investigate the genetic status of threatened with extinction cattle breeds in Romania through molecular data analysis, the desire to protect their genetic purity being generally recognized for environmental, economic and cultural purposes.

Keywords: endangered cattle breeds; genetic resistance; genetic conservation; environmental conditions

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Influence of extraction conditions on properties of *Salvia officinalis* L. polyphenolic extracts, free and encapsulated into mesoporous titania matrices

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Salvia officinalis L. (common sage) that belongs to the *Lamiaceae* family is a valuable source of phytochemicals with antioxidant and antimicrobial properties, which are promising ingredients for the development of cosmetics, nutraceuticals, supplements, or ingredients for the food industry.[1,2] The aim of this research was to assess the influence of the extraction conditions on chemical profile, radical scavenger capacity and antimicrobial potential of common sage polyphenolic extracts. To improve the phytochemical stability, selected polyphenolic extracts were embedded into mesopores of titania nanoparticles.

Ethanolic and hydroalcoholic (ethanol-water 1/1 v/v) polyphenolic extracts from *Salvia officinalis* were prepared at different plant/solvent weight ratios, at reflux or 50 °C, either by conventional method or microwaves-assisted extraction. The ethanolic and hydroalcoholic phenolic extracts were characterized by spectrophotometric determination of total polyphenols (Folin-Ciocalteu method), total flavonoids using aluminum chloride, chlorophyll a and b pigment contents, as well as radical scavenger capacity (DPPH and ABTS assays).

It was observed that a lower temperature, 50°C, and water-ethanol mixture as solvent favored the extraction of phenolic compounds. Concerning the radical scavenger properties, the hydroalcoholic extracts exhibited better capacity. The reverse phase HPLC-PDA analysis was applied for the identification and quantification polyphenolic compounds in prepared extracts. In all samples, rosmarinic acid was the most abundant substance, besides protocatechuic; chlorogenic, *p*-coumaric, and caffeic acids that were found in lower amounts. The bactericidal activity of coomon sage polyphenolic extract was tested against reference bacteria, *Staphylococcus aureus* and *Pseudomonas aeruginosa*, all prepared extracts being active against both tested bacterial strains, the highest values of inhibition zone diameter being observed for the polyphenolic ethanolic extract.

Mesoporous titania powders with anatase structure were loaded with selected common sage extracts through incipient wetness impregnation method, followed by solvent evaporation in vacuum. The total amount of polyphenols from the extract-loaded materials was determined by thermogravimetric analysis. Mesoporous titania nanoparticles were prepared by sol-gel method assisted by solvothermal treatment in the presence of structure directing agents and were characterized through X-ray diffraction, FTIR spectroscopy, nitrogen adsorption/desorption isotherms, as well as SEM and TEM. The extract-loaded materials exhibited an enhanced radical scavenger activity than the free extract assessed by DPPH assay after 3-6 months storage at 4 °C, which means a better stability of phytochemicals when were embedded into a mesoporous matrix.

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High antioxidant capacity of cannabidiol oil extracted from hemp

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Introduction: The antioxidant capacity of vegetal bioactive compounds is related to anticancer activity and can be quantified by the compounds' capacity to neutralize reactive species (RS), including reactive oxygen species (ROS) and reactive nitrogen species (RNS). Often, in tumours and cancer cells the concentration of RNS is higher than in normal tissues, acting as oxidative molecules to influence cancer progression (M.Wu et al., 2019).
The aims of this study were: (a) to test in vitro antioxidant capacity, by different methods, of the cannabidiol (CBD) which is found in extracted oil from industrial hemp (D. Fiorini et al., 2019) and (b) to increase the CBD concentration of extracted oil by decarboxylation reaction of cannabidiolic acid, found as an inactive form on antioxidant activity (F. Vuolo et al., 2019).
Methods: The extracted hemp oil was decarboxylated at 90ºC in order to obtain oil with maximum active CBD yield. The antioxidant activity of CBD oil was measured *in vitro* using various antioxidant assays, including ferrous ions (Fe^{2+}) chelating activity, lipid peroxidation inhibitory assay, ferric ions (Fe^{3+}) reducing power, superoxide anion radicals ($\bullet O_2^-$) and hydroxyl radical (•OH) scavenging activity.
Results: The antioxidant activity of CBD oil was performed by using CBD concentration of 15 µg/mL, which induced the maximum proliferation of normal fibroblasts. The ferrous ions (Fe^{2+}) chelating activity was 27.26 %, showing that CBD oil can be a protector in peroxidation reactions which facilitate the production of ROS in living systems. The lipid peroxidation inhibitory assay is a complementary method for ferrous ions chelating activity, while the ferric thiocyanate method quantifies the amount of peroxide produced during the initial stages of lipid oxidation. The neutralization of peroxide radicals is the first stage in treatments of diverse human pathologies such as cancer, atherosclerosis, or aging. The high index obtained (59.77 %) suggests a high capacity of CBD oil in neutralizing pathological effects. Ferric ions (Fe^{3+}) reducing antioxidant power assay demonstrated that the results (55%) showed a high neutralization capacity of free radicals by forming stable products. The scavenging activity of superoxide anion ($\bullet O_2^-$) and hydroxyl (• OH) radicals (the most important free radicals in living cells) by using CBD oil, was verified. The values obtained for CBD oil (69.1 %) related to superoxide anion radicals' and 221.5% to hydroxyl radicals' scavenging show a very high capability of CBD oil to inactivate super reactive radicals that can extremely damage all living systems.
Conclusion: Hemp oil of 15 µg/mL CBD showed a high capacity against inactivation of both super reactive radicals produced in healthy organisms and in patients diagnosed with cancer (D. Fiorini et al., 2019). Our results suggest that CBD oil could be used as complementary anti-cancer treatment and in other pathologies as well.

Acknowledgments
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Obtaining and characterization of natural anthocyanin extracts with fluorescent properties

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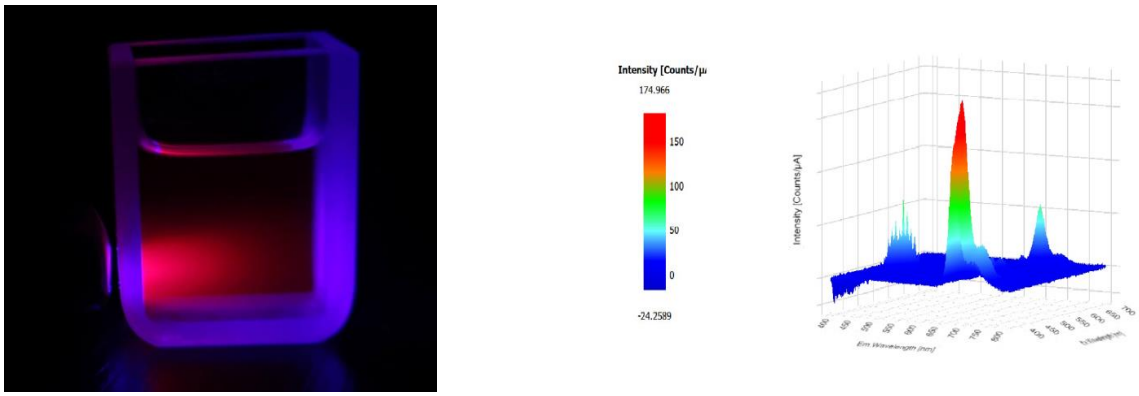
Selected extracts with amplified fluorescent properties were obtained from different parts of various plants. UV-VIS spectrophotometric methods were used for characterization in order to quantify the total anthocyanin content and to determine the total polyphenol content. Fluorescence measurements were performed to highlight the special properties of purified and concentrated selective extracts.
The hydro-alcoholic extracts were obtained from petals of *Petunia Night Sky*, *Pelargonium zonale red*, *Delphinium grandiflorum* and fruit cuticles of *Parthenocissus tricuspidata* and *Vittis vinifera*. The extracts were separated and purified by known methods involving physical-chemical processes and methods such as solid-liquid extraction, purification by C18 column liquid chromatography , redissolution in compatible solvents, advanced purifications by HPLC chromatography. The characterization of the separate fractions from the selective extracts was performed at controlled pH values. To highlight the fluorescence of the extracts, qualitative (laser excitation at different wavelengths: 450 nm, 550 nm) and quantitative (Horiba Duetta fluorescence spectrophotometer) investigations were performed. The results obtained revealed that from *Parthenocissus tricuspidata* was obtained the most fluorescent extract.

Keywords: anthocyanin extracts, *Petunia night sky*, *Pelargonium zonale red*, *Delphinium grandiflorum*, *Parthenocissus tricuspidata*, *Vittis vinifera*, HPLC, fluorescence, total anthocyanin content, total polyphenol content.



(a) (b)

Figura 1. (a) Fluorescence answer of the *Parthenocissus tricuspidata* liquid extract in isopropanol by laser excitation with a wavelength λ= 450 nm and (b) The emission and excitation fluorescence spectrum of the isopropanol extract *Parthenocissus tricuspidata* made using the Horiba Duetta fluorescence spectrophotometer.

Superior adsorption capacity of organochlorine pesticides mixtures on biochar derived from soybean straw

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Pesticides are conventional pollutants used in modern agricultural system. Among different treatment methods, adsorption is the most widely used due to its low cost and simple operation. However, the current studies focuses on single pesticide instead of multiple molecules under coexistence conditions. In this study, an eco-friendly straw based adsorbent was produced through a simple modification process (KOH/NaOH activation and mineralization) for remove organochlorine pesticides mixtures from aqueous solution. The physico-chemical properties of the produced biochar were characterized by XRF, FTIR and SEM. Furthermore, batch sorption experiments were conducted to determine the sorption capacity of the biochar under initial concentration of mixed system, contact time and pH. The adsorption equilibrium data onto biochar were analyzed by Langmuir and Freundlich isotherm, while pseudo first order and pseudo-second order models were adopted for the analysis of kinetic data. The results showed that the present biochar has abundant and highly reactive surfaces. For the isotherm, the Langmuir equation fitted the data better than the Freundlich equation. Thermodynamic parameters obtained showed that the adsorption was spontaneous, chemisorption and endothermic under tested conditions. These results indicate that biochar derived soybean straw is a potential adsorbent for the removal of pesticides mixtures from aqueous solutions.

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Improved *E. coli* biomass and enzyme production using oxygen vectors

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β-galactosidase (EC 3.2.1.23) is an important enzyme in medical industry, proposed as a solution for the synthesis of β-galactosides from nucleosides and acyclic nucleoside analogues from lactose and can be obtained by *Escherichia coli* aerobic fermentation. Oxygen vectors can be used for successfully enhancement of oxygen transfer, biomass concentration and hence process performance in a number of different aerobic culture systems. The addition of n-dodecane (between 1-3%), to the *E. coli* fermentation broth in a mechanically agitated and aerated bioreactor, revealed improved DO (dissolved oxygen) levels during fermentation that lead to an increase in biomass productivity and faster glucose consumption.

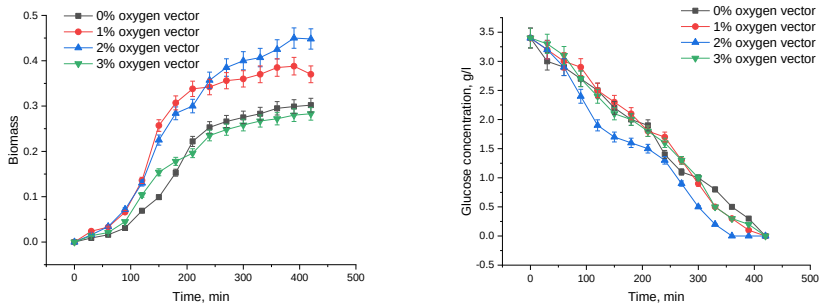

Figure 1. Influence of n-dodecane concentration on biomass accumulation and glucose consumption

The maximum values for enzyme activity (increased with 43% compared with the control) and kLa (the volumetric mass transfer coefficient) was obtained for the addition of 2 % v/v n-dodecane in the bioreactor, due to the fact that oxygen limitation during the exponential growth phase of the bacterium can repress β-galactosidase production during the exponential and stationary phases.

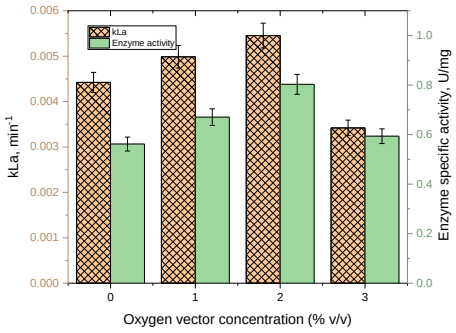

Figure 5. Influence of oxygen vectors concentration on k_La and enzyme specific activity

The oxygen vector addition increased the available dissolved oxygen and activated a redox-sensitive regulation and an elevated intracellular oxidative metabolism that lead to the enhancement in *E. coli* biomass accumulation and a more accurate protein folding of β-galactosidase that would increase its activity.

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Synthesis and characterization of novel cryogels based on dextran and polyphenolic extract from spruce bark

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Polysaccharide-based cryogels are attractive biomaterials for biomedical, biotechnological and environmental applications, as drug delivery systems, scaffolds, packaging materials, and adsorbents of various pollutants from wastewaters (Dragan and Dinu, 2020; Raschip et al, 2020; Tong et al, 2020) because they possess a number of advantages such as interconnected macroporous structure, a tissue-like elasticity, or superfast responsiveness. Among polysaccharides, dextran (Dx) is an important water-soluble natural polymer composed of linear α-l,6-linked D-glucopyranose residues that has been used widely in various applications starting from medicine to wastewater treatment (Bhavani and Nisha, 2010; Dinu et al, 2011; Ghimici and Nichifor, 2018). On the other hand, polyphenolic compounds are secondary metabolites of plants, characterized by great biological properties due to the presence of aromatic rings and numerous hydroxyl groups they possess. Given their well-known beneficial properties, polyphenols (either in the form of extractables from biomass, or food) can be used as reducing agents, antioxidants, or can be introduced into bioproducts to increase biological characteristics such as antibacterial, anticancer, cardioprotective, anti-inflammatory, antifungal, antiviral or antitoxic properties (Volf et al., 2014; Tungmunnithum et al., 2018).

To extend the application range of cryogel materials to food industry, we introduce here novel Dx-based films embedding a natural antioxidant compound, i.e. polyphenolic (PF) extract from spruce bark. This new alternative for packaging technology is based on incorporation of antioxidant agents into the packaging film as a way of improving the stability of oxidation sensitive food products. The cross-linking degree and the ratio between components were systematically investigated in order to obtain the optimum reaction conditions for preparation of novel bioactive cryogels. The entrapment of the PF within Dx network was proved by Fourier-transform infrared spectroscopy and energy dispersive X-ray spectroscopy. The internal morphology of Dx/PF cryogels was studied by scanning electron microscopy (SEM). The water sorption properties, the porosity, and the gel fraction yield of the Dx/PF cryogels were investigated in comparison to the individual Dx network.

The SEM micrographs revealed a heterogeneous morphology consisting of polyhedral pores with an average pore size varying from 5 to 50 μm depending on the cross-linking degree and ratio between components. The Dx-based cryogels showed a swelling behavior characteristic for macroporous morphologies with interconnected pores, the swelling equilibrium being attained in few minutes (Figure 1). The values of swelling ratio (SR) were influenced by the cross-linking degree, the increase of the cross-linker ratio decreasing the SR values. At lower cross-link density, the network has a high hydrodynamic free volume to accommodate more of the solvent molecules, thereby increasing matrix swelling. A higher cross-linking hinders mobility and relaxation of the polymer chains, which in turn impedes the mobility of water, hence lowering the SR and equilibrium water content. The same effect was generated by PF entrapment, as expected.

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Vegetal extract from spontaneous Romanian flora with bioinsecticidal effect used in the pests control during the seeds storage

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Although the intensive use of pesticides (persistent and non-biodegradable), often irrational, has led to increased productivity in the agricultural sector, they have led in parallel to the initiation and intensification of deep soil degradation, groundwater pollution, surface pollution and air, respectively to the deterioration of the flora and fauna in the respective or adjacent ones. areas. Also, the contamination of the crops on these soils was identified, which negatively influenced the quality of the food. Recent studies show that an increasing number of plant extracts have been tested on a wide range of pests, demonstrating a high efficacy, multiple mechanism of action, low toxicity to vertebrates. However, the number of commercial biopesticides based on plant extracts remains lower at the macro level, but they are becoming a treatment ~~of~~ choice for micro-farms.
The paper aim is to present the results of the experimental researches about the investigation of the effectiveness as bioinsecticidal effect of alcoholic plant extracts from spontaneous flora of Moldavia and Bucovina (Romania) (i.e. Wormwood - *Artemisia absinthium*; and Common marjoram - *Origanum vulgare*) in the pests control during the storage seeds (insect bean-*Acanthoscelides obsoletus*). Obtaining of the plant extracts was achieved by three extractive techniques, the efficiency of the processes (expressed by the degree of extraction) being studied according to a series of physical parameters, such as solid / liquid ratio, extraction time, temperature.
The experimental results showed that the most efficient method of obtaining plant extracts with a high content of bioactive substances is the combined method ultrasound accelerated extraction (UAE) + Maceration (M), followed by heat reflux extraction (HAE), ultrasound accelerated extraction, and the maceration method.
Also, the factors that were taken into account in the study of extractive techniques had a significant and different influence on the composition of these and on their effectiveness in relation with the bioinsecticidal effect on deposit pests studied. Thus, we can rank the magnitude of the influence of these parameters, presenting a descending order: temperature, S / L ratio (1/10, 1/15 and 1/20), and the time that played a less significant role (15 and 10 min). The most effective plant for controlling pests of the species *Acanthoscelides obsoletus*, was *Origanum vulgare* and *Artemisia absinthium* judging by the number of individuals deaths. The most effective method of administering the treatment was spraying on an adsorbent surface, followed by direct spraying on seeds (beans).

Synergic reactive extraction of fumaric acid obtained by fermentation with *R. oryzae*

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Fumaric acid is a naturally occurring organic acid, an intermediate in the citric acid cycle and it is widely found in nature, being isolated for the first time from the plant *Fumaria officinalis*. This four-carbon dicarboxylic acid, the trans-isomer of butenedioic acid, has many potential industrial applications, from the manufacture of chemical products (synthetic resins, biodegradable polymers) to food and pharmaceutical products (additive, therapeutic drugs).

It is produced on a large scale by the petrochemical route but the current tendency is towards implementing "green production" and environmental friendly technologies like biotechnological production of fumaric acid using low-cost raw materials. In this context, numerous studies focus on improving the fermentation process not only by using renewable raw material and genetically modified microorganisms, but also by developing and applying different downstream techniques for easy recovery of fumaric acid from the fermented broth.

This work investigates the possibility of reactive extraction of fumaric acid with Amberlite LA-2 dissolved in different solvents, with and without addition of 1-octanol as a phase modifier. Because the solvent polarity controls the extraction efficiency, the extraction mechanisms and influencing factors have been analyzed in direct correlation with the polarity of the considered solvents (dichloromethane and n-heptane).

The extraction process was analyzed by means of the extraction degree, amplification factor, distribution coefficient and extraction constant.

In the extraction systems without 1-octanol, the reduction of the polarity of the organic phase promotes the formation of amine adducts and the modification of the interfacial equilibrium expression. To highlight the positive influence of 1-octanol on the reactive extraction efficiency the amplification factor was calculated as the ratio between the fumaric acid extraction degrees for the solvent with and without 1-octanol, respectively.

Independent of the solvent used, the addition of 1-octanol in the organic phase does not change the shapes of the dependences between the reactive extraction efficiency and pH of the aqueous phase. To highlight the positive influence of 1-octanol on the reactive extraction efficiency the amplification factor was calculated as the ratio between the fumaric acid extraction degrees for the solvent with and without 1-octanol, respectively. The results showed that the amplification factor is greater than the unit for the entire considered pH-interval and increases with the increase of aqueous phase pH.

For all studied systems, the addition of 1-octanol into the solvent phase led to the improvement of extraction efficiency, the most important effect being recorded for the solvent with the lowest polarity (n-heptane) the extraction degree being η = 86 % compared to 58 % without 1-octanol.

Analysis of the polyphenols in alcoholic basil extracts

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Abstract

Currently, there is a high interest in the potential benefits of plant extracts with high content of polyphenols. In this study, three basil alcoholic extracts were analyzed using Folin-Ciocalteu method, in order to determine the total polyphenols content. Measurements were compared with the calibration curve of Gallic acid (25, 50, 100, 250, 500 ppm) and the results were expressed as Gallic acid equivalents. Values obtained ranged within very large limits of 630-2160 mg/L GAE. The lowest concentration of polyphenols was found in basil alcoholic extract obtained with the ultrasonic method and the highest concentration in the basil alcoholic extract obtained through the maceration method.

Key words: basil, polyphenols, Folin-Ciocalteu, alcoholic extract

Separation of itaconic acid by reactive extraction

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Itaconic acid is a versatile organic compound with many interesting industrial applications (monomer for plastics, resins and synthetic fibres, paints, films, detergents, cleaners, thickeners or bioactive components with anti-inflammatory and analgesic properties).

It can be obtained by fermentation processes which provide a green, renewable and environmentally favourable route to this industrially important metabolite. In the recent years there has been an increasing interest in process optimization by integration of fermentation and separation (downstream) units, known as *in-situ product recovery processes*. Therefore, the most important challenge is applying efficient methods for separation and recovery of itaconic acid from the fermentation broth. The conventional method of precipitation followed by acidification for recovery of acids has many disadvantages regarding the environmental protection. An efficient alternative is represented by reactive extraction separation method for itaconic acid.

The present study focuses on the development of an efficient reactive extraction system for the separation and recovery of itaconic acid from the fermentation broth. Reactive extraction was performed by using tri-n-octylamine as extractant dissolved in organic solvent.

The fermentation processes were carried out in 2 L laboratory stirred bioreactor (Fermac, Electrolab), provided with computer-controlled and recorded parameters. The fermentation was carried out in batch system. In the experiments *Aspergillus terreus ATCC 32588* has been used. The cultivation parameters are as follows: 30 °C, air volumetric flow rate 1 L/min, impeller rotation speed 400 rpm, pH value 3.4, inoculum volume 10 %, fermentation time 190 hours.

The experiments for reactive extraction processes have been carried out using an extraction column with vibratory mixing, which offers high interfacial area and the possibility to reach rapidly the equilibrium state. The aqueous solutions were prepared by dissolving itaconic acid in ultra-high pure water, and the pH-value was varied between 2 – 3.4. The initial concentration of itaconic acid in aqueous solution was 50 $g \cdot L^{-1}$. The reactive extraction was made with tri-n-octylamine and its concentration in the organic phase varied between 5 and 240 $g \cdot L^{-1}$. Dichloromethane and n-heptane were used as solvents. A phase modifier, 1-octanol has been dissolved into the above mentioned solvents, its volumetric fraction being 0.10.

The variations of the recorded parameters (substrat concentration and dissolved oxygen) indicated that the maximum concentration of itaconic acid was attained after 140 hours of fermentation at glucose concentration of 60 $g \cdot L^{-1}$.

The efficiency of the reactive extraction of itaconic acid with tri-n-octylamine was analyzed by means of extraction degree for extraction system without and with addition of 1-octanol as phase polarity modifier. The increase of extractant concentration in the solvent phase exhibits a favorable effect on the acid extraction, due to the increase of the interfacial amount of one of the reactants. For the solvent with the highest polarity, namely dichloromethane, the extraction degree continuously increases with the increase of tri-n-octylamine concentration only for extractant concentration below 50 g/L.

For reactive extraction of itaconic acid the highest extraction efficiency (93 %) was obtained for the extraction system with dichloromethane and 240 g/l extractant concentration. The addition of 1-octanol generates the reduction of the number of tri-n-octylamine molecules included in the interfacial compound structure, leading to the increase of interfacial reaction rate. The efficiency of the reactive extraction system is influenced by solute acidity, extractant concentration, and solvent polarity.

Growth optimization of algae for biodiesel production

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Sustainable sources of energy developed through economically viable processes are nowadays considered an alternative to fossil-based fuels, due to environmental effects of greenhouse gas emissions and the high cost of diesel price. Biodiesel represents in EU 82% of biofuels production with a total cost that implies 60–75% the price of the feedstocks. Microalgae offers great potential as a sustainable feedstock for biodiesel production, due to its many advantages: **high lipids content (15 and 75% d.w.)**, **fast growth rate**, a lower land area requirement compared to the use of crops, the production process can use existing technologies and the available distribution system can be maintained. The microalgal biomass production worldwide is about 9200 tonnes (dry weight), and extensive research has been performed on photobioreactor design, in order to improve control strategies for long-term stability and reliability of operations.
The studies objectives include the optimization of algae growth conditions for biodiesel production using two types of photobioreactos: stirred tank and flat-plate, in order to obtain high biomass productivities. The photo-bioreactors (PBR) investigated for microalgae with high oil productivities cultivation are presented below.

Figure 1. The photo-bioreactors (PBR) investigated for microalgae with high oil productivities cultivation

The main parameters that need to be investigated for achieving high growth are: **medium composition** (e.g. Modified Zarrouks medium, BG 11 medium, artificial sea water, SOT medium), **salinity, pH, temperature, CO_2 availability.**

Table 1. Correlation of environmental changes and lipid's content modification for different microalgae

Microalgae	**Environmental changes**	**Lipids modifications**
Schizochytrium limacinum	Salinity at 9–36 g/L at temperature range of 16–30 °C	Saturated FA C15:0 and C17:0 was greatly increased
Nannochloropsis sp.	Increase from 20 °C to 25 °C Nitrogen limitation	Lipid production increased by 14.92% Total lipid increased by 15.31%
Botryococcus braunii	Increase in temperature	Saturated FAs increased

The lipids production and the different fatty acids concentrations in microalgae are strongly influenced by the composition of culture media. Nutrient limitation (nitrogen or phosphorous) can be used to increase the accumulation of bioactive compounds, but with a negative effect on cell growth. In order to maximize the lipid content, different conditions of the culture medium such as: carbon dioxide supply, pH and temperature can be used.

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Separation of 7-aminocephalosporanic acid by reactive extraction

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7-aminocephalosporanic acid is the core chemical structure for the synthesis of cephalosporin antibiotics and intermediates. Chemical compounds containing this core are relatively stable to acid hydrolysis and tolerance to β-lactamases. Modifications of side-chains of 7-ACA affect the antibacterial activity and can lead to the alteration of pharmacokinetic properties and receptor binding affinity, thus creating new class of cephalosporin antibiotics with important clinical uses.

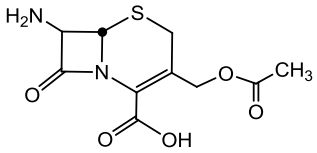

Figure 1. Chemical structure of 7-aminocephalosporanic acid

Chemical deacylation of cephalosporin C, a fermentation product, is the primary method used to produce 7-ACA industrially. In the past decade, enzymatic methods for deacylation have attracted more attention in the manufacturing of cephalosporin antibiotics and several enzyme-based methods have been developed. Following the enzymatic conversion process of cephalosporin C to 7-aminocephalosporanic acid, the product must be isolated from the reaction mixture.

Since 7-ACA is an amphoteric molecule, it exists in ionic forms of different charges depending on the pH of the media, physical solvent extraction is difficult. Therefore, a viable method for the separation of 7-ACA is extraction accompanied by chemical reaction with an extractant, namely reactive extraction. This paper presents the separation of 7-ACA from aqueous solutions obtained by enzymatic conversion by reactive extraction, using di-(2-ethylhexyl) phosphoric acid (D2EHPA) as extractant, dissolved in n-heptane. Relative to the initial aqueous solution, the total acid separation yield reached 97% by using 20g/l D2EHPA.

Brilliant Red HE-3B dye biosorption by immobilized *Bacillus* sp. residual biomass: Fixed–Bed-Column Studies

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Residual biomass from agriculture or various industries (e.g., food, biosynthesis, textiles) represents an important source of valuable compounds, used as raw materials for the production of a wide range of new products, thus responding to the principles of sustainable development, waste recovery and green and circular economy.
The aim of this work is to make use of *Bacillus* sp. residual biomass (resulting from a process of removing fatty acids from wastewater) immobilized in alginate that, although it results in large quantities from biotechnological processes, is not reported to be valorized in dye biosorption processes, except in a few applications.
The biosorption potential of *Bacillus* sp. residual biomass in a reactive Brilliant Red HE-3B textile dye removal from aqueous media was studied. The waste biomass, resulting from a process of removing fatty acids from wastewater, was immobilized in sodium alginate and used for biosorption of the dye from aqueous solution in a fixed-bed column.
The effects of various experimental parameters, such as bed depth, flow rate were investigated, and the modeling of experimental data was based on Thomas and Yoon-Nelson models.
The obtained results reconfirm that the studied residual biomass can be considered as a good biosorbent also in dynamic operating system, and it can be used in the treatment of wastewater containing small quantities of organic dyes.

This work was supported by a Grant of The Romanian Ministry of Research and Innovation, CCDI-UEFISCDI, project number PN-III-P2-2.1-PED-2019-1063, within PNCDI III.

Investigation of the potential use of Ratanhia CO_2 extract-based herbal oral products in treatment of oral mucositis

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Oral mucositis appears as erythematous and ulcerative lesions of the oral mucosa, that can be observed at patients with cancer who are being treated with chemotherapy and / or radiation therapy in regions involving the oral cavity. Oral mucositis lesions are often painful and affect oral nutrition and hygiene, and increase the risk of local and systemic infections. Recently, various natural agents in plants have been noticed in mucositis, which may improve the symptoms through different interventions. The purpose of this investigation is to focus on the potential use of Ratanhia CO_2 extract-based herbal oral products to prevent, alleviate and treat the oral mucositis. The biological action of ratanhia CO_2 extract is due to its high content of tannins such as rhataniatannic acid, which are responsible for the astringent, disinfectant, tonic and firming effects on the mucous membranes of the mouth. The studies regarding the effects of Ratanhia CO_2 extract-based herbal oral products such as herbal mouthwash and toothgel have indicated a decrease of mucositis symptoms. An effective formulation of a toothpaste based on Ratanhia CO_2 extract associated with nano-hydroxyapatite, calcium carbonate, Aloe Vera gel and a mixture of *Matricaria chamomilla, Citrus bergamia, Pelargonium graveolens* essential oils in various proportions may have reduce the lesions appeared on oral mucosa by forming a mild antiseptic protective layer on the surface of the lesion below which regeneration of new tissue takes place.

This study suggests that the use of Ratanhia CO_2 extract-based herbal oral products such as toothpaste may have a positive influence on the oral side effects of cancer chemotherapy, and that further investigations might be desirable.

Spectroscopic investigation and chemical fingerprint of *Datura ionnoxia* dry biomass

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Plant species represent a rich source of bioactive compounds. Nowadays, scientists from various fields are interested for advanced vibrational spectroscopic methods in fingerprinting secondary metabolites from plants which can either positively or negatively affect human health (Svecova et al., 2020). So far, more than 300000 have been identified in several major classes represented by the population of different plant secondary metabolites in nature: 55 % terpenes, 27 % alkaloids and 18 % phenolics (Ramawat and Merillon, 2013). For identification, isolation and characterization of these bioactive compounds from vegetal biomass extract, extremely valuable are non-chromatographic techniques. Several studies were obtained regarding spectroscopic methods, especially Fourier-transform infrared spectroscopy (FTIR) to obtain and facilitate the identification of bioactive compounds from plants (Sasidharan et al., 2011; Naumann et al., 2014; Al-Rubaye et al., 2018).

Datura innoxia is part of the nine plant species which belong to the *Solanaceae* family. Nowadays, is becoming important for medicine for its rich tropane alkaloids content, especially hyoscine (scopolamine) (Palazon et al., 2008).

In this study it is presented the application of spectroscopic methods, such as fluorescence study and Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) analysis for identification and detection of secondary metabolite specially, hyoscine tropane alkaloid, and organic functional groups from *Datura innoxia*. Dry biomass of different *Datura innoxia* structural units (leaves, flowers, seeds, stem and root) were subjected to extraction in solid–liquid system according to Soxhlet method, using two appropriate solvents (1-butanol and ethanol).

The results of ATR-FTIR analysis confirmed the presence of alkaloids e.g. hyoscine, amine, alcohols, phenolic compounds, alkanes, carboxylic acids, aldehydes, ketones, sterols, terpenes, nitrogen compounds, alcohols, carbohydrates e.g. cellulose, hemicelluloses from *Datura innoxia* dry biomass extracts. Moreover, the results showed the presence of hyoscine in all vegetative organs which is in according with other studies from literature. For brig more evidence in Figure 1 is represented the IR fingerprint spectrum of seeds extracted in ethanol. Regarding fluorescence study, the excitation and emission spectra were measured. Maximum excitation and emission wavelengths for hyoscine were found to be 350 and 560 nm, respectively, and, also in this case hyoscine was determinate in all parts of the *Datura innoxia* plant (Figure 2).

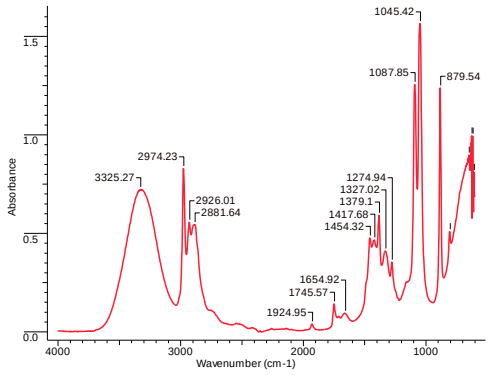

Figure 1. IR spectrum for seeds in ethanol

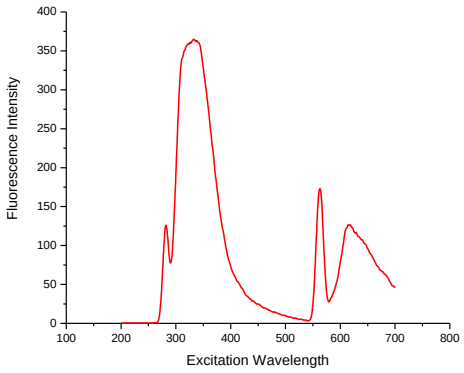

Figure 2. Fluorescence spectrum for seeds in ethanol

The experimental results confirm the fact that this plant posse's important classes of secondary metabolites useful in medicine domain. So further scientific investigation for intensification of extraction by nonconventional methods is needed.

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BOOK OF ABSTRACTS

Section 3 Environment and Sustainability

Biopolymers –Based Composites with Great Potential for Environmental Applications

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Biopolymers have received a growing scientific attention in the last decades. As a renewable, low-cost natural resource, chitosan (CS) is one of the most prominent representatives of polysaccharide biopolymers, combining in a unique manner a set of particular physiochemical and biological properties, including antimicrobial activity, non-toxicity, biocompatibility and biodegradability. CS is well-known for their sorption properties, being able to remove metal ions from dilute solutions either by electrostatic interactions or chelation (Zhang et al., 2016). Their sorption performance is controlled by the environment particularities and biopolymer properties. In this respect, we investigate here the performance of novel Co^{2+}-imprinted composite cryo-beads based on naturally available components, as CS and natural zeolites for the selectively remove cobalt ions from aqueous mixtures. CS was selected as the main component of the composite network, since their amine groups can successfully act as coordination sites for metal ions (Dinu et al., 2018; Huang et al., 2018). Natural zeolites have been involved in preparation of these composite materials to improve CS poor mechanical properties and low chemical stability in harsh aqueous conditions. To gain an increment in accessibility and availability of reactive groups towards water and metal ions, our porous ion-imprinted polymers (IIPs) were prepared by cryogelation (Humelnicu et al., 2020; Dinu et al., 2013). To extend the selectivity range of the IIP composites for Co^{2+} ions, the CS-based composites as cryo-beads were prepared by combining ion-imprinting with radial freezing in liquid nitrogen. Two types of zeolites were involved in preparation of IIPs cryo-composites, different both in terms of their provenience and clinoptilolite content. Accordingly, the composites ability to selectively remove the template (Co^{2+}) ions from multi-component aqueous mixtures, where Cd^{2+}, $Cu^{2+,}$ Fe^{2+}, and Ni^{2+} ions were the competing species, was systematically evaluated.

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The role of risk analysis in development of integrated management systems. Evidences from energy industry

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The energy industry in general and the oil and gas industry in particular are areas of activity that are constantly subject to political, financial, social and environmental constraints. In these circumstances, controlling the threats to the company and possibly turning them into opportunities can give the organization a significant competitive advantage in the market. Taking in account these considerations, managers have the opportunity to opt for the implementation of an integrated management system - a management tool that has proven its effectiveness in many practical applications. The aim of the article is the analysis of the importance of an integrated management system`s development in oil and gas enterprises. This topic is very complex because the development of an integrated management system depends essentially on the ability of management to identify risk factors and to implement an effective mechanism for their treatment and monitoring.

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A Multicriteria Model for the Assessment of Countries' Environmental Performance, GUIJARRO, F., International journal of environmental research and public health, 16(16), 2868 (2019)

Adsorption of Benzalkonium Chloride on Unmodified Adsorbents

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Adsorption is an efficient and often used method to lower the concentration of undesired species from aqueous environments. A variety of adsorbent materials are described [1], of different types and origins, both modified and unmodified prior to adsorption. This study focused on cheap, un-modified materials that are readily accessible in large amounts, with the goal of their testing in economically feasible processes. Thus, a mixture of oak and beech, household sawdust was employed. Its only pretreatment consisted in drying for 24 hours at 105 ^{o}C.

Benzalkonium chloride (BKC) is a biocide surfactant. Because its frequent use in disinfectant products, it may bring about long-term damage on aquatic life-forms [2]. Hence, BKC is a suitable species for adsorption tests employing unmodified sawdust.

Within this context, this work describes a set of preliminary experiments to verify whether sawdust is suitable for the adsorption of BKC from its aqueous solutions, as well as to assess the adsorption capacity of sawdust in various experimental conditions. Measurements were carried out in triplicate, at various temperatures, and BKC-adsorbent ratios. BKC concentrations were determined spectrophotometrically, at 262 nm, from the bulk of the aqueous mixtures. The absorbance *vs* time profiles showed that the initial content of BKC dropped with up to 80% during the first few to 24 hours, whilst equilibrium required – depending on employed experimental conditions - up to two weeks.

It was observed that the aqueous sawdust mixture turned yellowish in time, with an ever increasing absorbance at 262 nm. Meanwhile, values of BKC-sawdust mixtures exhibited a more complex profile, with a slight increasing followed by a decreasing tendency. An example of such kinetic behavior is illustrated in Figure 1. Calculus of overall rate coefficients and of equilibrium adsorption capacities required various complex kinetic models, as well as the use of individual absorbance profiles of all involved species. Results are presented and compared for these parameters, whereas description of the adsorption isotherm is still under study, although some attempts were made to describe it correctly, both experimentally and by means of a mathematical model.

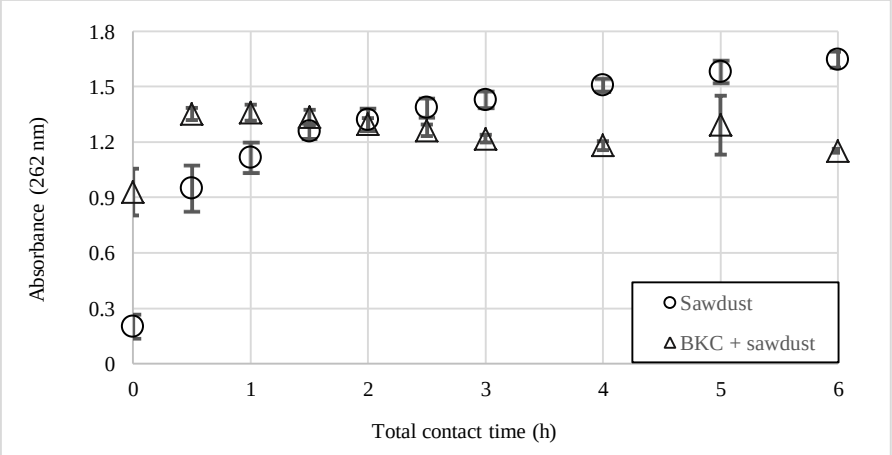

Figure 1. Absorbance *vs* total contact time profiles in aqueous mixtures, at 45 ^{o}C and BKC-Sawdust ratio of 50 mg/g.

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Synthesis of ZnO as an efficient photocatalyst for the elimination of organic dyes in aqueous suspension over solar light irradiation

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Textile industries are considered among the most polluting industrial activities in terms of volume of effluents and complexity of treatments of its effluents discharge. Wastewaters generated by textile industries are today well-known to contain large amounts of organic and inorganic hazardous pollutants (Khenniche et al., 2015). Among them, synthetic dyes represent a relatively large group of organic chemical compounds found in textile industry tailings. Many studies confirmed that these effluents represent a real source of contamination for the aquatic environment because most of these synthetic organic molecules pose toxic, mutagenic and carcinogenic effects and their large quantities of colored effluents (Rusu et al., 2014). Thus, today there is a real need to develop new effective technologies to treat textile dyes effluents before their discharge to the environment aquatic environment. During the last years, solar photocatalysis was recognized as promising green technology for the water and wastewater purification applications (Harja et al., 2020).

Therefore, in this work we examine whatever a synthesized zinc oxide (ZnO) semiconductor can enhance the photocatalytic elimination of hazardous water pollutants, as organic dyes under solar irradiation conditions. The studied catalyst was successfully obtained through a co-precipitation methodology followed by a post-calcination step at 400°C. The structural, optical and morphological properties of the ZnO samples were investigated in detail by X-ray diffraction, FTIR analysis and Scanning Electron Microscopy (SEM). Different experiments were designed at laboratory scale using an organic dye named, basic blue 41 as model molecule.

The tests were conducted under batch mode and under solar irradiation to evaluate photocatalytic activity this catalyst. The effect of several process parameters (initial solution pH, pollutant amount and catalyst load) was investigated in detail to determine the optimum process conditions. According to the obtained results the degradation of the target molecule was effective after at reaction time of 240 min at a solution pH of 6.6. In addition, it was found that experimental data fit well (R^2= 0.996) with the Langmuir-Hinshelwood kinetic model
confirming for the basic blue 41 the L-H relationship for the initial photodegradation rates.

In summary, the method used for the synthesis of ZnO seems to be a promising strategy for the preparation of photocatalytic semiconductor with activity under solar light. The ZnO nanostructures exhibit good photocatalytic activity in dyes removal. Moreover it was found that the degradation of the target compound is affected by the initial solution pH, catalyst load and pollutant concentration. To conclude, these results provide new relevant information on the degradation of basic blue 41 dye under solar irradiation conditions confirming the potential use of the prepared catalyst for future applications of the detoxification of the effluents for the textile industries.

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Phase equilibria of CO_2 + organic compounds and their potential role in CCS

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In the last years, the climate changes are more and more obvious: the air temperature has increased globally, the precipitation patterns are altered, the number and strength of natural disasters such as droughts, tornadoes, floods, wide spread melting of ice and snow, increase in average sea levels, etc. are escaladed (Parry et al., 2007). Among the factors affecting the environment, and an issue of great concern today, are the greenhouse gases (GHGs). Carbon dioxide emissions produced by the fossil fuel powered plants and energy production facilities account for over 80% of GHGs (Kenarsari et al., 2013). Therefore, many researchers focused on finding solutions for reducing the greenhouse gas effects (Peper et al., 2019). In the search for developing a tool for the selection of the best candidate(s) as physical solvent for CO_2 capture, our group focused on investigating the functional group effect on the solvent ability to dissolve CO_2 (Secuianu et al., 2016; Sima et al., 2014-2020). In this work we review and analyze the data available in the literature for CO_2 + ether, + alcohol, + alkane mixtures, with special focus on comparing isomers, when possible. In addition, we present new high pressures measured data for several binary systems at different temperatures and their modelling. In Figure 1 is illustrated the comparison of measured critical curves for carbon dioxide + 1,2-dimethoxyethane (DME) and carbon dioxide + 1,4-dioxane and the predictions by SRK/2PCMR model.

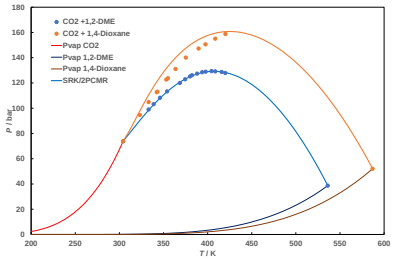

Figure 1. *P-T* fluid phase diagrams of carbon dioxide (1) + 1,2-DME (2) and carbon dioxide (1) + 1,4-dioxane (2) systems.

Acknowledgments

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Removal Cu(II) ions and Co(II) ions from aqueous solutions using *Saccharomyces cerevisiae*

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Abstract
Water is one of the natural resources most affected by pollution. As a result, the change in its qualities affects the entire ecosystem, over large areas, due to running water and infiltration. Specific contaminants that lead to water pollution include a wide range of chemicals, pathogens and physical changes. Many of the chemicals are toxic and include organic and inorganic substances. Heavy metals are natural elements that can enter food for human consumption through industrial or agricultural processing in the form of fertilizers and pesticides. These elements are not biodegradable. Some heavy metals are known to be pollutants and are toxic, and bioaccumulation in plant and animal tissues can cause unwanted effects for humans. Therefore, their amount in water and food must always be under control (Massoud et al., 2019). The development and implementation of new, cost-effective processes and the application of next-generation biosorbents for the removal or recovery of metals are essential to improve the competitiveness of industrial processing operations (Ali, 2012). Biosorption is an independent passive and metabolic process, which is characterized by the removal of heavy metals using a passive binding process with living microorganisms, including algae, bacteria, filamentous fungi and yeasts. Saccharomyces cerevisiae has received increasing attention due to its unique nature and its ability to biosorb heavy metals. It is one of the most promising biosorbents capable of removing metal ions from aqueous solutions. Heavy metals can be competently removed from water and other aqueous media by Saccharomyces cerevisiae (Fadel et al., 2014). Yeast cells are easy and inexpensive to grow, so an affordable source of biomass with high potential for biosorption of residues at low pH (Galedar et al., 2013).
The aim of this study was to remove copper and cobalt ions from aqueous solutions using yeast, Saccharomyces cerevisiae. To optimize the bisorption capacity of yeast biomass, a batch system was developed used to investigate the effects of initial pH, initial biomass dose, initial metal ions concentration and contact time. The obtained results have indicated that in optimal experimental conditions: pH = 5, the removal percent of studied metal ions is over 60 % (Fig.1.b).

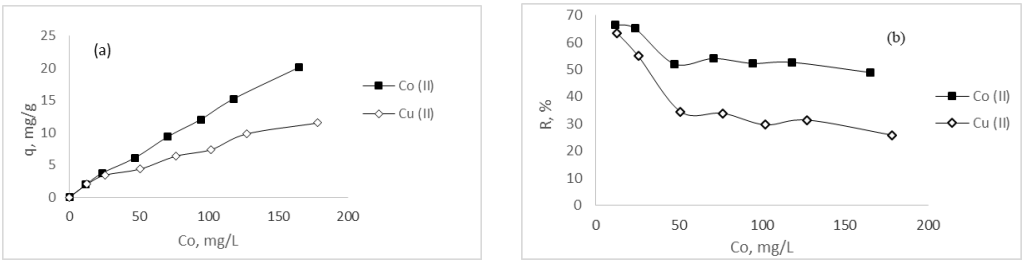

Figure 1. Influence of the initial concentration of Cu(II) and Co(II) ions on the biosorption efficiency (a) and the removal percent (b)

The modelling of the experimental results was done using Langmuir isotherm and Freundlich, and for kinetic modelling the pseudo-first order and pseudo-second order models were used. All experimental results show that Saccharomyces cerevisiae yeast has the potential to be used for the removal of heavy metals, and this could be an alternative solution for the sustainable recovery of this biomass.

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Valorisation of woody waste for non-energetic uses: natural adsorbent in industrial wastewater treatment system

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Industries produce and sometimes discharge effluents, containing residual contaminants, in public sewerage system and/or natural aquatic receptor (e.g., watercourse or accumulation basin/lake nearby), affecting in this way both environment and society.
Organic compounds present in the industrial effluent can be removed and one still possible treatment is through adsorption, using low-cost production waste such as sawdust. This adsorbent became an interesting idea for industries that search for a low-cost solution to remove organic dyes and heavy metal ions from wastewater resulting from industrial processes. In order to apply this technique, adsorbent properties have to be investigated along with economic and availability factors.
The aim of this study is to present the results of an adsorption treatment onto sawdust of some industrial effluents containing Arancio Kemazol 3R reactive dye and lead ions as reference models of organic persistent and toxic heavy metal present in wastewater, or receiving water resources. The adsorption experiments were performed using batch technique at laboratory scale setup focused on the study of some operating parameters influencing the adsorption efficiency, such as: pH, adsorbent dose, reactive dye and toxic metal ions concentration, solid-effluent contact time and temperature. An experimental planning of this adsorption treatment applied on these industrial effluents is discussed by applying a 2^3 central compositional rotatable experimental planning considering the adsorbent concentration, contact time and temperature as independent variables, while the treatment efficiency related to reactive dye and lead ions were chosen as optimization criteria.
The results of these adsorptive experiments are good and emphasize the importance of sawdust as adsorbent for retaining of polluting species from wastewaters/polluted waters.

Environmentally friendly regional reactive sources for improving drilling fluids formulation systems

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Taking into consideration the European Pact for industry sustainability and the European Pact for Youth with a deadline in 2030 which has sustainability, climate action and inclusiveness at its core, in the present study we pursue to achieve a new deal for regional partners including business agents, universities and high-schools as a challenge for approaching the instruments we have to handle for social responsibility and regional development for the next 10 years.

In this light the current study follow the directive lines for use environmentally friendly regional reactive sources for improving drilling fluids formulation systems. For this both universities with local business partners propose an improvement model for oil-based drilling fluids with environmentally friendly reactive such as biodiesel obtained from regional resources. There are many novel literature study that presents biodiesel as the external phase of drilling fluids both for the water based-drilling and oil-based drilling fluids. [1-3]

There are companies which has patents that shows the relevance for using esters containing down-hole drilling lubricating compositions and now it is time to extend the study for regional use with environmentally friendly reactive such as biodiesel. [2-3]

In this paper, there were evaluated the properties of some formulation systems for both water based drilling fluids (WBDS) and oil based drilling fluids (OBDS) ordinary used for a regional well drilling in order to model the rheological behavior of them with different methods. After we made economical calculation for 2 plants at feed 100 kg biodiesel production from 2 different types of oils as raw materials and we obtained that is more cost effectively to produce biodiesel from soybean rather than algae looking at regional resources.

The biodiesel industry already has shown its potential by quickly production increase worldwide and due to excess production capacity is a good opportunity for further investigation related to biodiesel-based drilling fluids using regional reactive sources.

Acknowledgments
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Newpark Drilling Fluids Eastern Europe SRL
University POLITEHNICA from Bucharest
University OVIDIUS from Constanta

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Study on environmental concern: evidence for several EU countries

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Environment has become one of the main issues in the discussions related to development. It is largely accepted that the environmental problems have at their roots especially behavioral and socio-economic factors that need urgent responses according to them. In this context, our study aims to measure the environmental concern across some EU member states, to investigate the profiles of the individuals with a positive environmental attitude and to provide a better understanding of its determinants. Using the available data from the World Values Survey (2010-2014), there were firstly analyzed the perceptions (care for environment, perspective on environmental pollution, alternative between protecting environment vs. economic growth), then active participation (membership in an environmental organization, financing ecological organization, participation in demonstration for environment) and, lastly, integrating both in one general composite index. Our results showed that Poland, Romania and Spain register the lowest levels of general environmental concern, while Sweden attains the highest level among the analyzed EU countries (Figure 1). Giving the fact that, although both Spain and Sweden are advanced economies, the difference between their national general environmental concerns requires a more in depth investigation. Applying component factor analysis, we observed that the common socio-economic and behavioral characteristics of an individual highly concerned with the environmental problems in both countries are: (1) having tertiary education; (2) being employed; (3) having mostly not routine and non-manual tasks; (4) being completely independent; (5) attaining post-materialist values; (6) feeling completely satisfied with personal financial situation. In the case of Spain, the belonging to the middle class is added to this profile, meaning that the social class also makes a difference in the personal position regarding environment. In addition, using the binomial logistic regression, we found that this position is mainly influenced by (1) age, nature of tasks, post-materialist values and satisfaction in life in Sweden, while, (2) in Spain, the most important determinants are educational level and post-materialist values. Utilizing a particular measuring approach that divides the environmental concern in terms of perceptions and active participation, this study attempted to better understand it in the EU countries, especially in Sweden and Spain, as countries from the same development stage, but very different in terms of environmental concern. In this way, our findings shaped the national profiles of individuals according to their attitude towards environment, emphasized its determinants and outlined the main differences between the two nations in this respect, as possible starting points for better targeted EU and national environmental policies.

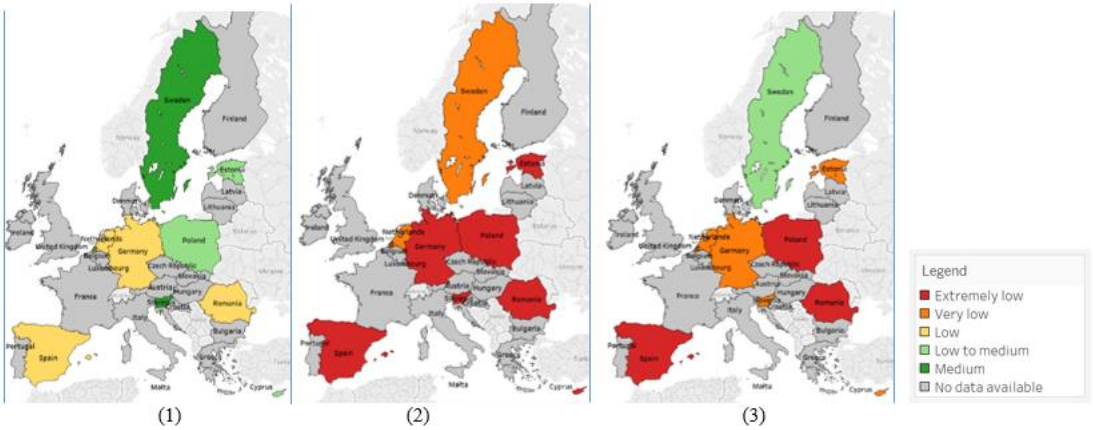

Figure 1. Perceptions regarding environment (1), Action oriented to environment (2) and General environmental concern (3) indices
Source: Authors' representation based on WVS, wave 6, 2010-2014

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Analysis of the optimal bridge piers number for reducing backwater levels

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Like much of the Vienne Valley, the area of Bouchard Island has a significant wealth in terms of environments and species. In the study area, 86 protected species are recorded, half of which are birds. The major areas of issue are located on the crossing of Vienne, along rivers and ponds and in the North sector of Bouchard Island. The presence of the *Margaritifera auricularia*, or Spengler's freshwater mussel is a major issue of the site because of its status as an invertebrate being one of the most threatened on the planet and its presence on the course of Vienne.
In order to quantify the damping of the backwater generated by the future crossing of the Vienne, we integrated into the hydraulic modelling software (InfoWorks ICM) the 2D model of the river and using 2 solutions (3 and 4 piers) to simulate the current flow conditions generated by the future bridge for each of the two floods studied as a function the width of the piles.
The hydraulic study of the Vienna crossing will be based on a two-dimensional (2D) modelling of flows because unlike conventional one-dimensional modelling, two-dimensional modeling allows to know precisely the speed in any point of the project area, to size the crossing structure and the piers and to assess more detailed the local impact of the project, in particular on the distribution of speeds in major beds.

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Efficient remediation of environmental hazardous using a carbon rich material from biomass waste conversion

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Conversion and reuse of industrial waste ascends as a promising alternative to design bio-based materials for efficient remediation of environment. In particular, the forest industry generates wastes that represent important feedstock for biorefining. Through the secondary biorefinery step the solid phase (biochar) could be considered as a matrix for generate cost-efficient adsorbent.
In fact, the biochar represents a carbonized biomass, a carbon-rich material whose characteristics depends on the feedstock and more important on the biomass conversion process and parameters. It could be a cost-efficient alternative to activated carbon, with good efficiency for various inorganic or organic contaminants.
This study focuses on the remediation performance assessment of biochar achieved in a slow pyrolysis of spruce bark residue resulted from a primary biorefinery. The chemical characterization of the pyrolysis solid phase revealed a carbon-rich material with pore volume and low surface area providing fewer sorption sites for contaminants. However, due to its various surface functionalities, the biochar could manifest strong absorption capacities for both nonpolar and polar organic contaminants or heavy metals ions.
Lead contaminated waters in single component system as well as in complex matrix with competing heavy metals ions and oxyanions were subjected to a batch-mode remediation process using biochar as selective adsorbent.
The effect of pH (range 2-8) was evaluated using initial Pb concentrations of 50 mgL^{-1} and adsorbent dosage of 5 gL^{-1}(fig.1).As seen in fig. 1, for pH higher than 4, the retention capacity of the biochar practically does not change and shows very good values, of 95% retention.

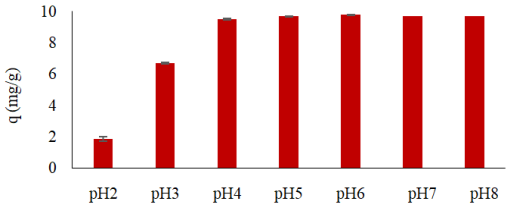

Fig 1. Effect of pH on the removal of total Pb by spruce bark biochar (initial adsorbate concentration 50 mgL^{-1}, 5 gL^{-1} of biochar, temperature of 23±1°C), 4h contact time.

Biosorption kinetics (pH 5.5, 50 mgL^{-1} Pb initial concentrations and sorbent dosage of 5 gL^{-1}) and equilibrium isotherms (pH 5.5 at different initial Pb concentration and 5 gL^{-1} biochar) were determined. Lead concentrations in liquid phase were analyzed by flame furnace atomic absorption spectroscopy. All mathematical interpretations were made by CurveExpert software. Adsorption kinetic of Pb on spruce bark biochar was fast (equilibrium reached in approx. 15 min.) and two models were applied to described it: pseudo-first order kinetic model and pseudo-second order, the second with a better fit. Adsorption equilibrium isotherms were successfully modelled by Langmuir and Freundlich.
The biochar resulted from slow pyrolysis of spruce bark have a great ability to remove Pb, even in complex system with competing ions, such as Cu, Cd, Fe or As. These results represent a new opportunity to design carbon-rich materials from biomass in order to generate cost-efficient adsorbent to remove hazardous pollutants from environment.

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Studies regarding the tolerance of *Amaranthus retroflexus L.* growing on nickel polluted soil

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Amaranthus retroflexus L. (pigweed) is one of the most widespread plant in the world with a high adaptability under variable environmental conditions. This plant can growth until 3 m height providing a tall aerial biomass which gives it efficient capacities for biosorption and bioaccumulation of toxic pollutants (Qi et al., 2017). Literature studies reported the pigweed as a suitable plant for phytoremediation of soils polluted with heavy metals (e.g. nickel, cadmium, chromium) (Khoramnejadian and Saed, 2015). In our study, the tolerance of *Amaranthus retroflexus* L. in the presence of nickel ions in soil at different concentrations (59 mg/kg, 131 mg/kg, 177 mg/kg, 233 mg/kg, 292mg/kg, 462 mg/kg) and different contact time (30 days, 37 days, 47 days, 54 days, 60 days) was tested. The experiments were carried out in polypropylene pots containing 35 g of soil. The plants were grown during 11th of July until 9th of September 2019, under laboratory conditions. Figure 1a describes the morphological aspect of pigweed after 60 days of vegetation in soil in contact with nickel ions. The growth of plants was not significantly affected by Ni(II) presence in soil, since no significant changes in plant morphology was observed (e.g. for blank probe the length of stems+leaf of pigweeds was 240 mm compared with the plant that has grown at a concentration of 462 mg/kg nickel in soil where the length of stems+leaf was 235 mm). Also, an important indicator for the physiological state of the plants is represented by photosynthetic pigments. Chlorophyll a, chlorophyll b and carotenoids were extracted from fresh leaves with 96% ethanol, and measured by a spectrophotometric method. Figure 1b illustrates the chlorophyll content (chlorophyll a, chlorophyll b) and carotenoids, showing that for all photosynthetic pigments, nickel ions have beneficial influence in the range of concentrations between 0-59 mg/kg. The chlorophyll a and b was stimulated with 15%, respectively 43%, while carotenoids with 4%. For concentrations between 131-462 mg/kg, the nickel ions determine a slight decrease in chlorophyll and carotenoids content (e.g. for a concentration of 233 mgNi(II)/kg soil, a decrease with 6% of chlorophyll content was found). Therefore, *Amaranthus retroflexus* L. may develop a good nickel tolerance in the range of Ni(II) concentrations of 0-462 mgNi(II)/kg soil, with no significant effects on morphological and physiological state. Further studies will investigate the morphological changes, as well as the behavior of other plants in terms of tolerance on nickel.

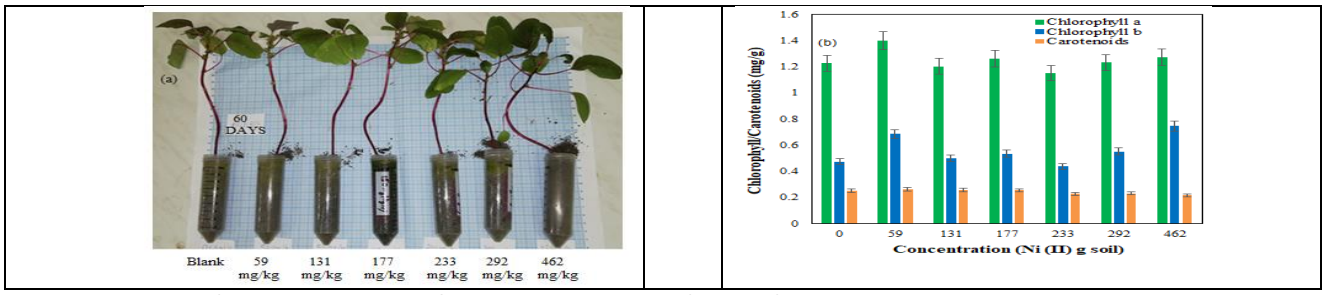

Figure 1. Growth of the *Amaranthus retroflexus* L. in the presence of Ni(II) after 60 days (a) and (b) chlorophyll/carotenoids content

Acknowledgments This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS - UEFISCDI, project number PN-III-P4-ID-PCE2016-0683, Contract no. 65/2017, and 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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Synthesis and characterization of lanthanum doped titanium dioxide for the enhanced photocatalytic elimination of an emergent water contaminant

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Nowadays, water pollution is one of the most concerning problem among environmental scientists. Due to the fact that conventionally methods used for wastewater treatment are not able to completely remove organic contaminants present in water, there is an increasing need to implement modern techniques able to efficiently degrade such kind of molecules (Favier et al., 2019). In this respect, heterogeneous photocatalysis using a semiconductor photocatalyst seems to be a promising alternative for the degradation and mineralization of organic water pollutants (Harja et al, 2020).

The aim of the present study was to evaluate the photocatalytic performance of lanthanum doped titanium dioxide (La@TiO_2) for the degradation of the main metabolite of the lipid regulator clofibrate, as target molecule.
The considered catalyst was synthesized via sol-gel method using titanium (IV) isopropoxide as precursor. Finally, obtained gel was homogenized with a lanthanum solution and then subjected to a hydrothermal treatment. The product was further filtered and washed with distilled water. Several technics such as scanning electron microscopy (SEM), X-ray powder diffraction (XRD), UV-Vis spectrophotometry and Fourier-transform infrared spectroscopy (FT-IR) were used for the characterization of the obtained nanomaterial.

The photocatalytic activity evaluation tests were carried out in a cylindrical reactor (with a working volume of 1L), with internal irradiation and magnetic stirring and at room temperature. Preliminary experiments were carried out in ultrapure water at an initial pollutant concentration of 5 mg/L and a catalyst loading of 100 mg/L. Prior to the photocatalytic experiment, the solution containing the photocatalyst was stirred in the dark in order to ensure the adsorption-desorption equilibrium.

Adsorption and photolysis tests were conducted to investigate their efficiency in the elimination of the target molecule. According to the results during adsorption and photolysis, the pollutant removal was less than 10%, after 8h of contact. Also it was observed that only in the presence of La@TiO_2 and UV-A light, the pollutant elimination was significantly improved.
Furthermore, it was shown that the elimination of the model pharmaceutical molecule is enhanced by modifying the process parameters. Thus, for a catalyst concentration of 500 mg/L, a pollutant concentration of 5 mg/L and a maximal irradiation flux (6.3 mW/cm^2), a complete elimination of pollutant was achieved after 3h of reaction time. Moreover, in the optimal conditions, a mineralization yield of about 63% was obtained, confirming the photocatalytic potential of the considered catalyst.

In summary, the results presented in this work clearly demonstrate that La@TiO_2 is suitable to be used in a photocatalytic process. Based on the collected experimental data, the process parameters are of utmost importance to enhance the elimination and the mineralization efficiency of the target molecule under UV-A irradiation conditions. Moreover, the as-synthesized La@TiO_2 catalyst is expected to have a potential use for future water purification applications.

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Bioremediation of aqueous solutions polluted with Cd^{2+} ions by *Bacillus megaterium* in a stirred tank bioreactor

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In stirred tank aerobic bioreactors the mixing among phases necessary for aerobic microorganisms growth is done mainly by mechanical agitation, but also by aeration of the culture medium. The stirrer has to ensure an adequate degree of homogeneity inside the bioreactor, but without damaging the microbial cells (Gavrilescu, 2013; Garcia-Ochoa et al., 2011; Jossen et al., 2017). In this paper we studied the removal of wastewater pollutants, such as heavy metals, by biosorption and bioaccumulation using specific microorganisms, in a laboratory stirred tank bioreactor. A series of experiments were carried out in a Sartorius bioreactor (BIOSTAT B plus control panel with UniVessel 2L) to investigate the influence of mixing rate, air flow rate and initial cadmium concentration on pollutant removal efficiency from aqueous solutions by *Bacillus megaterium* living biomass. The experiments aimed to establish the best operating conditions so as to result in high efficiencies of cadmium removal, by achieving a biomass that is not affected by Cd toxicity and shear stress.
The bioreactor with the working volume of 1.5 L was equipped with pH, oxygen and temperature probes. A few drops of sterile olive oil were used as the antifoaming agent to avoid the formation of a thick layer of foam on top of the reactor, and 0.2 μm PTFE filters to keep the sterility inside the bioreactor. The experiments were performed at room temperature of 25 ± 2^0C and according to a Full Factorial Design matrix generated by Minitab17 software. The initial concentration of cadmium varied between 10 and 50 mg/L, the air flow rate between 0.2 and 0.8 L/min and the mixing rate between 50 and 150 rpm. The evolution of biomass in bioreactor, pH variations, as well as oxygen consumption by microorganisms were monitored during Cd^{2+} removal by *B. megaterium.*
The results show that, the process efficiency decreases from 52.60% to 40.73% with increasing the mixing rate from 50 to 150 rpm as can be seen in Figure 1a (initial concentration 50 mgCd/L and air flow rate 0.2 L/min). Also, at initial concentration around 50 mgCd/L and 150 rpm, the best results were obtained at 0.5 L/min, both in terms of process efficiency and biomass growth (Figure 1b). So, for the removal of Cd^{2+} by *B. megaterium* living biomass in mechanically stirring bioreactor, 0.5 L/min and 50 rpm are the adequate values for air flow rate and stirring speed.

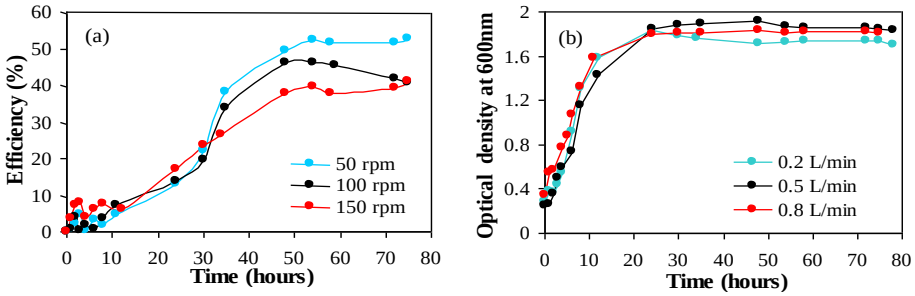

Figure 1. Influence of (a) agitation speed on Cd^{2+}removal efficiency and (b) air flow rate on biomass growth

Acknowledgments
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Researches regarding the monitoring of underground water quality in vulnerable communities to nitrate pollution from agricultural sources in Botoşani County, Romania

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The object of the national water monitoring programs is the evaluation and control of their quality. Monitoring data can be used to establish initial conditions, final pollutant concentrations, but most of the time they cannot be used to identify the stages and processes that occur during pollution.
The purpose of groundwater monitoring is a long-term research of the distribution area for pollutants, and of their concentrations in the underground. For the groundwater monitoring, we follow both chemical and quantitative stage. The investigation environments are represented by water, sediments, and biota, with qualitative elements, parameters, and minimum monitoring frequencies, in accordance with requirements of the Water Framework Directive, depending on the type of program.
Areas vulnerable to nitrates from agricultural sources represent 8.64% of our country's surface, and 13.93% of the total agricultural area of Romania. In order to determine the vulnerable areas, they were delimited following the analysis of each subsystem (soil, climate, water bodies, sources of nitrates from agricultural activities), from the perspective of the production and/or transmission of nitrates from the agricultural sources to water bodies.
The vulnerable areas were differentiated according to the type of nitrate sources: current sources (present agricultural activities, which produce a surplus of nitrates due to the high density of animals from individual households and/or zoo-technical complexes), and historical sources (zoo-technical complexes that have worked in the past and are decommissioned now). In Botoşani County, a number of four communes were diagnosed as vulnerable areas: Corni, Prăjeşti, Ştefăneşti and Truşeşti. Depending on the characteristic of each municipality, the action programs have been established to lead to the prevention of pollution with nitrates from the agricultural sources.
In order to prevent the pollution of groundwater with nitrates, a monitoring program for the physical – chemical indicators of the water collected from hydro-geological wells located in Botoşani County was prepared. This paper presents the results of the groundwater quality monitoring in the period 2012 – 2019, in a number of 37 wells, located both in vulnerable areas, and in zones diagnosed as not being vulnerable. The selected parameters for the monitoring are the indicators of the nutrient regime: concentrations of nitrate, nitrite, phosphate, and ammonium ions, From the analysis of the nitrate ions concentration of the water samples from 20 wells, we found very large exceeding of the maximum allowed limit (50 mg/l). From the nitrite loading point of view, the groundwater in monitored wells falls within the maximum permissible limits (0.5 mg/l), with two drilling exceptions, where exceeding of the maximum concentration allowed for the nitrite parameter are recorded, achieving values of 1.54 mg/l (at Sadoveni F1), respectively 1.37 mg/l (at Ştefăneşti F3).
The analysis of the results from the ammonium ions charges point of view, from the studied wells, brings into attention large exceeding, with respect to the actual standards, in most sampling points. By processing filed data, there is observed a decrease in the nitrate ions concentration from two wells, during 2017 year. In January, there were noted values much higher than in the rest of the year, fact explained by the improper application of the manure on the agricultural land with frozen soil or covered with snow, and abundant rainfall. Analyzing the physical-chemical indicators of groundwater of the observation wells from other areas than those declared vulnerable, it was found that in 2017 – 2019 period there was a deterioration of its quality in terms of the ammonium indicator, and in some localities both regarding nitrite and nitrate parameters (Sadoveni, for example). Following the research carried out, we have proposed a detailed action program for each area analyzed separately.

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Fixed-Bed Column Adsorption of Acid orange 7 onto Soil

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Synthetic dyes are used in various industries such as textile, printing, paper, food, leather, cosmetic industries and a representative percent of produced dyes are discharged in the environment (Akhouairi et al., 2019), generating hazards in water, soil, sediments and to human health (Islam and Mostafa, 2018). The main aim of this study was to assess the transport and mobility of Acid Orange 7 (AO7) dye onto soil layers. In order to achieve this objective, the experiments were performed in dynamic mode. The analysis of breakthrough curves was done using Thomas, Adams–Bohart, Wolborska, Yoon–Nelson and bed-depth service time (BDST) models.

Sorption experiments of AO7 dye at different heights of the soil column did not described a typical S-shaped breakthrough curves, the curves are depicted in Fig. 1. The saturation point of the soil column was reached when the effluent concentration became equal to 95% of the pollutant concentration in the influent (Barron-Zambrano et al., 2010). Also, it was found that an increase in soil column height has as effect the increasing both the breakthrough time (t_b) and the saturation time (t_s). The experimental results showed that the saturation time is obtained at 5 minutes for a soil column height of 5 cm, and increased to 30 min for a soil layer height of 20 cm, indicating a low pollutant uptake capacity and a high mobility potential of AO7 molecules in investigating soil. It was found that the pollutant concentration is a relevant factor that influence the process (Fig. 2). The results show that the change of the concentration gradient influences the saturation rate of the soil bed and the saturation time. The increasing of flow rate leads to the displacement of the breakthrough curves to the left and the obtaining of larger slopes, simultaneously with the decreasing of the sorption rate and the reduction of the mass transfer. The higher length of the adsorption zone is attributed to the large molecular structure of the AO7 and as well as their higher resistance to internal diffusion.

The results of this study show that the profile of breakthrough curves is not described by typical S-shaped curve, and varies with soil depth, the flow rate and initial pollutants concentration. The modeling of the breakthrough curves using the Thomas, Adams-Bohart, Wolborska, Yoon-Nelson and BDST models highlighted that the BDST model offers the best correlation of the experimental data, followed by the Wolborska and Adams-Bohart model.

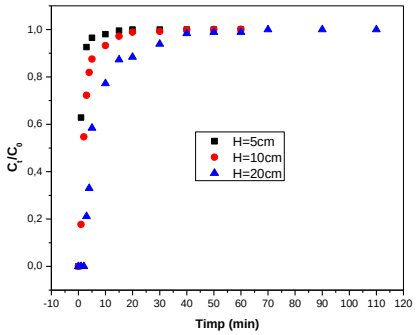

Figure 1. Breakthrough curves of AO7 sorption on soil for different soil bed height (C_0=50 mg L^{-1}; Q= 7 mL min^{-1}; soil particles diameter 0.8-2 mm)

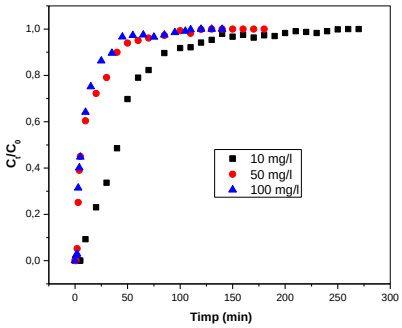

Figure 2. Breakthrough curves of AO7 sorption on soil column for different influent concentration (C_0=10-100 mg L^{-1}; Q= 7 mL min^{-1}; soil particles diameter 0.8-2 mm)

Acknowledgments

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Kinetic and isotherm studies of metal ion biosorption on alkaline treated peat

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The rapid increase in the pollution of metal ions in the aquatic environment as a result of anthropogenic activities has become an important issue, due to their accumulation tendency and toxic effect on human health (Akpor and Muchie, 2011). Among metal ions, copper(II), cobalt(II) and zinc(II) ions are most common contaminants of industrial wastewater, mainly due to their numerous uses in industrial processes. Although many methods are currently available to remove metal ions from aqueous media (such as chemical precipitation, ion exchange, membrane processes, etc.), (De Gisi et al., 2016), they have important disadvantages that have limited practical applicability. Biosorption has been identified as more attractive due to economic feasibility, simple operation, efficient and cost effectiveness (Fu and Wang, 2011). Therefore, finding adsorbent materials, cheap and easy to prepare, is still a current issue in literature. The cheapest and easiest to obtain are natural materials, which are available in large quantities and require only a few steps of preparation. One such example is peat. Unfortunately, studies in the literature have shown that peat has a moderate biosorption capacity for most metal ions (Crini et al., 2019), which is why the use of this material in large-scale metal ion removal is limited. In order to increase the biosorption capacity of peat for metal ions, a simple alkaline treatment was used, in this study. This treatment implied the mixing of peat with alkaline solution (0.1 mol/L NaOH) when an increase of biosorption capacity with 25–27% for studied metal ions (Cu(II), Co(II), Zn(II)) was obtained, while the required contact time decreases significantly (Fig. 1). The main advantage of this procedure is that the increasing of the biosorptive performances of peat is done using a common reagent, and thus the cost of the biosorbent preparation remains low.

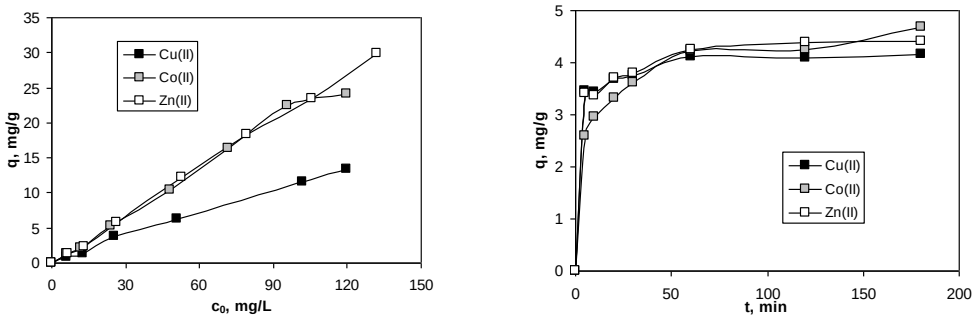

Figure 1. Biosorption efficiency of alkaline treated peat in metal ions removal processes.

In this study, the adsorptive performances of alkaline treated peat have been investigated for the removal of Cu(II), Co(II), and Zn(II) ions from aqueous solutions. The influence of metal ions concentration and equilibrium contact time was studied at room temperature, in batch-adsorption experiments. Three adsorption isotherm models (Langmuir, Freundlich, and Dubinin-Radushkevich) were used for the mathematical description of single-component adsorption on raw and alkaline treated peat. The experimental data were analyzed using the pseudo-first order model, the pseudo-second-order model, and intra-diffusion particle models, and various kinetics parameters have been calculated. The experimental results included in this study show that alkaline treated peat has better adsorptive characteristics than raw peat, and could be used as an efficient biosorbent for the removal of Cu(II), Co(II) and Zn(II) ions from aqueous media.

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Toxic effects of lead and cadmium on lettuce (*Lactuca Sativa Attraction*)

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Abstract

Although some metals, in low concentrations, are needed for plant growth, the study of the toxicity of heavy metals has found that, in concentrations that exceed certain limits, heavy metals can create specific negative effects. Important factors that determine the extent of toxic effects on the plant are, for example, the concentration of metals and plant species. Heavy metals can inhibit the photosynthetic activity of plants, can easily accumulate in the human body through ingestion, inhalation or dermal contact and can create a major risk to human health even at low levels of exposure. Given these things, the aim of the paper was to investigate the effects of the toxic action of lead and cadmium ions, alone and as a mixture on seed germination and increase in root length, lettuce shoots (*Lactuca sativa Attraction*). The tolerance of salad 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 led to a decrease in seed germination efficiency and plant growth dynamics. It has been shown that cadmium ions are more toxic than lead ions. When using the binary mixture of heavy metals (Cd and Pb), they showed that the development and growth of the salad was affected to a much greater extent compared to the individual heavy metals. A pronounced toxic effect was observed on root growth, compared to the other components of the plant (stem or leaf). Future studies will focus on the risk to human health due to the consumption of lettuce contaminated with heavy metals.

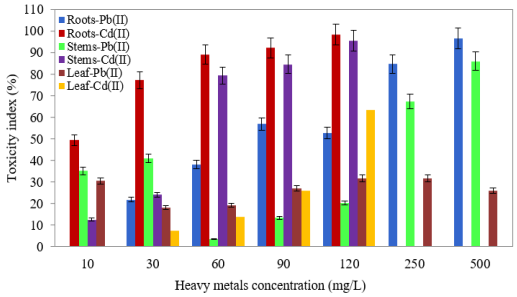

Fig.1. Toxicity index for roots, stems and leaves of Pb(II) and Cd(II) ions

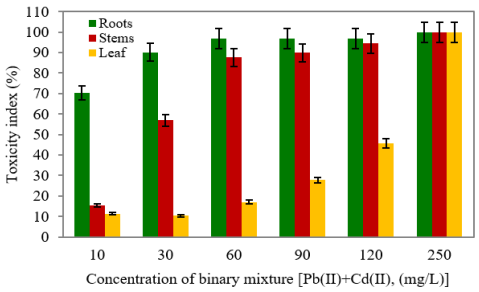

Fig. 2. Toxicity index for roots, stems and leaves of the ionic combination of Pb(II) and Cd(II)

Phytotoxicity tests are of particular importance for assessing the ecological risks of pollutants. Numerous studies have shown that the most common effects of heavy metals on plants are manifested by inhibiting root growth and inhibiting seed germination [1,2]. The objective of the paper was to evaluate the degree of affliction of lettuce (*Lactuca Sativa L. Attraction*) under the individual influence of Pb (II) and Cd (II) and the mixture of Pb(II) + Cd(II).

Acknowledgments

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Identification and evaluation of food waste management alternatives by Life Cycle Assessment methodology

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Food production and consumption have a high impact on the environment, since three quarters of food produced for human consumption is lost or wasted globally, which amounts to about 1.3 billion tonnes per year. The main sources of food waste are represented by the following sectors: residential, commercial, institutional and industrial (Katajajuuri et al., 2014) (Fig. 1).
Considering the complexity of the consequences of food waste it was found that the solutions to these problems can be obtained only based on an Integrated Waste Management which has to consider all the factors involved in food waste prevention and treatment. A number of treatment alternatives and technologies are applied to valorize these wastes as secondary sources for raw materials and energy, and also to reduce food waste volume. Among these alternatives the following can be mentioned: (i) pretreatment processes which include: mechanical biological treatment (MBT) - anaerobic digestion (AD) energy conversion process; (ii) mechanical heat treatment (MHT) – autoclaving and conversion treatments which include: incineration, gasification, anaerobic digestion (from mixed residual waste, often as part of an MBT process) (Fig. 2) (USEPA, 2016).

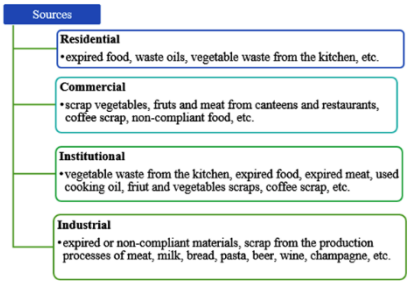

Fig. 1. *Food waste generating sources*

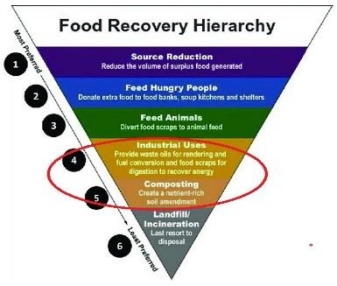

Fig. 2. *Hierarchy of food waste management*

In this context, **the goal of this study is twofold**: (i) provide an overview of sources and categories of food waste and their impact on the environment, economy and society, (ii) apply Life Cycle Assessment (LCA) methodology to compare the waste management alternatives and select the most appropriate for reducing the environmental impact of food waste. Two food waste management alternatives were considered in applying the LCA methodology: (•) obtaining bioproducts and bioenergy by anaerobic fermentation of food waste and (••) obtaining compost with a high level of nutrients.
In order to evaluate the environmental impacts for the studied processes we have applied **ReCiPe** and **Carbon Footprint** methods. The impact categories considered in our evaluation were as follows: *Climate change, Human Health (CcHh), Human toxicity (HT), Photochemical oxidant formation (POF), Climate change Ecosystems (CcE), Carbon dioxide* (CD), *Nuclear potential* (NP), *Land occupancy* (LO), etc.
All four phases of LCA were accomplished. The functional unit is the amount of food waste at national level. Input and output data were processed by GaBi software. **In conclusion**, the application of the LCA methodology was able to provide the decision support for the analysis of the two food waste management alternatives and selection of the best and sustainable method of food waste management.

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Quantitative evaluation of biochars performances obtained from algae biomass in metal ions biosorption processes

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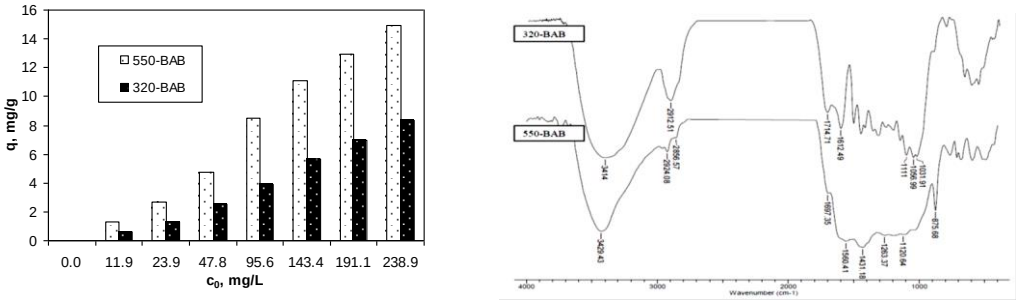
Nowadays, heavy metal pollution has become an acute problem. Due to toxic toxicity, persistence and accumulation tendency, high concentrations of heavy metals are found in the environment, becoming an important factor in the degradation of the ecosystem (Mudhoo et al., 2012). More and more cases of accidental pollution of inland or international waters, air or soil with substances or products containing heavy metals are frequently reported in the media and are also the subject of concern in the scientific world. Algae biomass is widely found and has a wide range of uses, representing a valuable biomass resource due to its properties in solving various environmental problems, such as decontamination of soil and wastewater, etc. (Gupta et al., 2015). Due to the fact that in summer these algae are undesirable, due to the uncontrolled growth and the unpleasant smell they generate, finding new uses in environmental protection has a double benefit. Based on these considerations, in this study, algae biomass (*Ulva lactuca sp.*) was transformed into biochar by a slow pyrolysis process (Bogusz and Oleszczuk, 2015; Wael et al., 2016). Pyrolysis of algae biomass was performed at two temperatures (320 and 550 °C), for 8 hours, and under oxygen-limited conditions. The obtained biochars (320-BAB and 550-BAB) were then used as biosorbents for the removal of Zn(II) ions from aqueous solution, in optimal experimental conditions (initial solution pH of 5.0; biochar dose of 4.0 g/L, contact time of 60 min.). The obtained experimental results (Fig. 1a) have indicate that the 550-BAB is more efficient in the removal of Zn(II) ions from aqueous media than 320-BAB, even if the recorded FTIR spectra shows that 550-BAB is poorer in functional groups than 320-BAB (Fig. 1b).



(a) (b)

Figure 1. Biosorption efficiency of biochars obtained from algae biomass in Zn(II) removal processes.

To explain these differences, the elemental analysis of these two types of biochars was performed, as well as their morphological characterization. Thus it was observed that even though 550-BAB has a smaller number of functional groups than 320-BAB, its specific surface area is much larger and its basic character is much more pronounced, making this biosorbent much more efficient in biosorption processes of Zn(II) ions. The quantitative evaluation of the biosorptive performances of these two biochars in the Zn (II) ion removal processes was performed using the Langmuir, Freundlich and Temkin isotherm models, and the obtained parameters were analyzed in detail.

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Removal of Chromium (iii) from tannery effluent using *Tamarindus indica* L. bark powder

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Abstract

This paper summarizes the effectiveness of *Tamarindus indica* L. bark powder as an economical bio-adsorbent to adsorb chromium from spent chrome-tanning liquor. The effect of different parameters viz. adsorbent dosage, contact time and initial chromium concentration was studied in batch mode (Loebenstein, 1962). FT-IR analysis was conducted to identify the existing functional groups in the bio-adsorbent. Physicochemical parameters of the effluent sample e.g. turbidity, conductivity and total dissolved solid (TDS) were also measured before and after treatment to examine the removal capacity of the bio-adsorbent following standard testing methods (USEPA, 1983). The results revealed that the highest chromium removal (96.71%) was found at pH 3, adsorbent dosage 20g/L, for contact time 12 hours at initial concentration 1423 mg/L respectively. The sorption kinetics was nicely explained by Langmuir isotherm that showed monolayer adsorption nature with maximum adsorption capacity (q_e) 31.1mg/g. The physicochemical parameters were significantly decreased up to permissible standard (DoE, 2008). Therefore, *Tamarindus indica* L. bark powder as an adsorbent to treat tannery effluent successfully.

Table 1. Chromium removal by *Tamarindus indica* L. bark powder at different adsorbent dose, time and concentration, and Changes in physicochemical parameters of tannery effluent after treatment

Concentration (mg/L)	Chromium removal index %										Physicochemical parameters changes after treatment, %		
	Adsorbent dosage (g)				Contact time (Hours)								
	5	10	15	20	3	6	9	12	18	24	TDS	Turbidity	Conductivity
721	27.73	55.20	77.67	96.71	32.94	56.75	68.45	76.74	81.79	84.45	92.08	87.29	91.82
1000.3	28.09	49.87	73.03	89.15	38.75	66.21	79.36	89.15	94.12	95.46	82.82	84.54	85.41
1423	23.71	44.65	66.34	76.74	42.48	72.49	86.4	96.71	98.74	97.45	71.39	83.50	70.04
1624	20.63	37.99	49.45	72.84	38.36	46.86	62.38	72.84	79.32	82.45	71.97	84.50	72.94

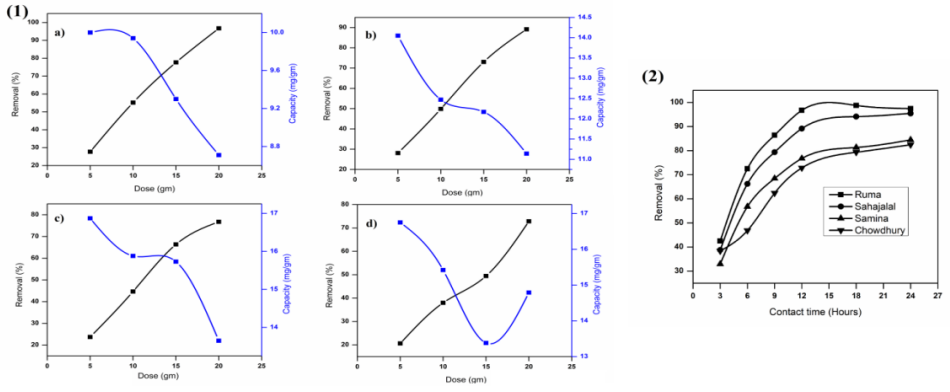

Figure 1. Effect of (1) adsorbent dosage and initial concentration ((a) Ruma, (b) Sahajalal, (c) Samina and (d) Chowdhury) and (2) contact time

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Estimation of the energy consumption at separate stages during wastewater treatment in a municipal treatment plant.

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The purpose of the present study is to analyze the energy consumption at different stages of the municipal wastewater treatment plant, (see Figure 1) and to propose measures to improve energy efficiency.

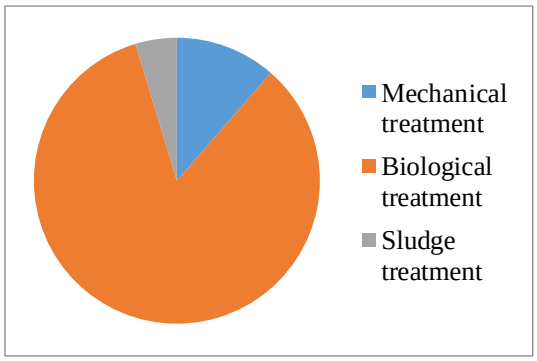

Figure 1. Energy consumption at different stages of treatment

Energy consumption depends on many constantly changing factors such as: volume, amount of pollutants in the incoming water, climatic conditions, seasonal load and others. All these factors affect the amount of energy consumed. This requires a thorough review of the individual stages of the technological treatment scheme in order to determine the specific costs of the facilities. The performed analysis provides an opportunity to evaluate the installation and to give proposals for its reconstruction. This led to reduction of energy consumption and as well as to reduction in greenhouse gas emissions. The energy balance made of the facilities appears the basis for decision making for appropriate reducing the energy consumption.

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Effects of Feeding Solution and flow rate in a sequential reductive/oxidative process for perchloroethylene (PCE) removal

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Chlorinated aliphatic hydrocarbons (CAHs) as perchloroethylene (PCE) are a common groundwater contaminant due to their improper use in the industrial operation. Specialized microorganisms, primarily Dehalococcoides mccartyi, are able to couple the reductive dechlorination (RD) of CAHs with growth in a process called organohalide respiration, on the other hand, the low chlorinated ethenes such as cis dichloroethylene (cisDCE) and vinyl chloride (VC) are more susceptible to oxidative mechanisms performed by aerobic dechlorinating microorganisms. In bioelectrochemical systems (BES) an electroactive biomass interact with an electrode by a direct or indirect mechanisms to accomplish their metabolism, BES can be used as an innovative strategy for the stimulation of both anerobic and aerobic microbial pathways [1]. In a microbial electrolysis cell (MEC), a cathode can be used as electron donor to perform the RD reaction while an anode can provide the oxygen necessary for the aerobic dechlorination reaction. The sequential process is composed by two MEC connected in series (Figure 1), equipped with an internal graphite counter electrode. In the first MEC, named "reductive reactor" the RD reaction is stimulated by the potential control of the graphite granules of the cathodic chamber while the second MEC, named "oxidative reactor" the oxidative dechlorination reaction of the RD byproducts is sustained by the oxygen evolution ensured by a rutile electrode. In the present experimental study, the effects of the feeding solution shift are presented, more in details a feeding solution simulating the composition of a groundwater from a contaminated site has been introduced in the process instead of an optimized mineral medium utilized in the preliminary operating period of the sequential process [2]. The feeding solution shift caused a temporary biomass shock that led to a transient period in which a loss of PCE removal was observed, while a consequent drop down of the RD reaction rate was also observed. Even if the PCE removal capacity resulted restored after the transient period, with an average removal efficiency of 100 ± 1 %, the RD byproducts distribution resulted in the presence of high chlorinated compounds like TCE and cis DCE with respect the previous period in which the optimized mineral medium was used as feeding solution. The presence of high chlorinated RD by-products in the reductive reactor outlet promoted the establishment of a reductive dechlorination reaction in the oxidative reactor graphite counterelectrode due to its reductive potential. Therefore, both reductive and oxidative dechlorination pathways occurred in the oxidative which was not able to completely remove the chlorinated byproducts. Finally, an increase of the average current in the reductive reactor from 19 ± 1 mA to 65 ± 3 mA has been detected according to the reduction of the sulphate ion present in the synthetic groundwater, i.e. the sulphate reduction justified the 71 ± 8 % of the average current obtained after the insertion of the sulphate-rich synthetic groundwater.

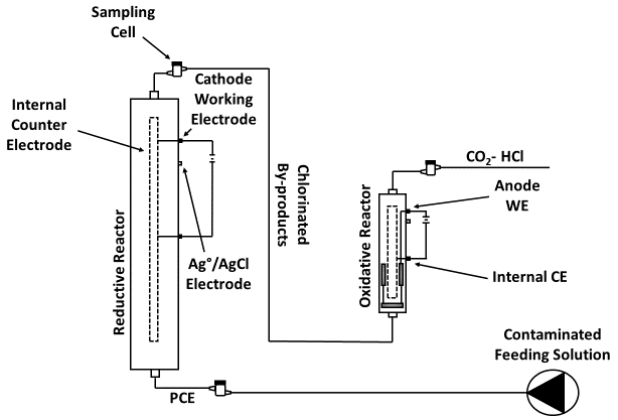

Figure 1. Scheme of the Sequential Reductive/Oxidative process for PCE removal

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An environmentally route of surface texturing polyimide films for proper light management in solar cells

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The alarming diminishment of planet resources for energy production have led to development of alternative technologies. These are working on the principles of sustainable and clean energy. In this context, photovoltaic devices have gained a huge attention in scientific community. However there are still some issues that must be solved in order to enhance the conversion efficiency (Kim et al., 2013). For instance, adequate light management can be attained by specific processing of the components in a solar cell device (Singh et al., 2013; Mustafa et al., 2019). This work is devoted to application of an environmentally route of surface texturing of a polyimide film. The proposed surface designing could be useful to control scattering and thus to harvest a greater amount of solar radiation. In this way, if the proper amount of light reaches the active region of the photovoltaic device one may attain a higher conversion efficiency. The surface morphology features and their refraction properties are in strong relation with light propagation among the layers of the device and this might lead to new insights on surface processing of polymer material for upgraded energy conversion.

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Specifics of aging of oxidized oil bitumen produced in Ukraine

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Despite to the significant advantages of asphalt concrete coating in comparison with other types of coatings, such as high mechanical strength and roughness; low rigidity of the coating; high ability to absorb vibrations, etc., there are also significant disadvantages of asphalt concrete. Among the main ones is the short term of use, which manifests itself in the breaking and destruction of the roadway after several changes of seasons. The reason for this phenomenon is the complex effect of natural and mechanical factors, which finally lead to different types of chemical and structural changes in the binder of the asphalt, which also called aging of bitumen.

The aging process of the binder begins long before the bitumen gets into the asphalt. Since the main part of the Ukrainian binders is obtained by the oxidation of tar, the conditions of the oxidation process play an important role for further transformation. In addition, there are internal irreversible reactions in bitumen, which occur under the influence of oxygen, heat, low temperatures and light.

To evaluate the intensity of bitumen aging in the coating, we investigated the change of bitumen properties before and after warming in accordance with GOST 18180, which allows simulate the thermal oxidation of bitumen - in a thin layer of binder (2 mm) at 163°C for 5 or 10 hours. As the simple we used bitumen of the BND 60/90 brand which is made on PJSC Ukrtatnafta.

Thereafter, a comparison of baseline data and indexes, determined after the aging process was performed to evaluate changes due to the aging of bitumen. Among the main ones are weight loss and softening temperature change, needle penetration depth (penetration), brittleness temperature and elongation (ductility), determined by standard methods. Structural-group analysis, infrared spectroscopy and thermogravimetric analysis of the original bitumen and aged samples were made for control changes occurring in the aging process.

According to the obtained results, as a consequence of aging in the bitumen, penetration and ductility are significantly reduced, which is explained by the loss of bitumen plasticity, which causes a decrease in the number of olive components and an increase in the content of asphaltenes. An increase in the softening temperature is also a confirmation of this phenomenon.

Significant structural changes that occur with the aging of the binder are also confirmed by the results of structural group analysis and comparison of the IR spectra. According to the results there are no qualitative changes that would occur during aging, but changes occur quantitatively, which is explained by the transition of some structural-group components to others - some of the olive components, mostly the most volatile compounds - evaporate, and some turn into resins, at the same time resins turn into asphaltenes. In numerical terms, that can be shown as follows: oils before aging are 48.05% of the mass., while after 5 and 10 hours spent in a thin film and at a temperature of 163°C, their percentage by weight is already 47.98 and 47.95% respectively; the reduction of resins is sharper, so with 31.13% of the mass before aging, the content after a 5-hour process is 27.75% of the mass and 24.30% of the mass after 10 hours. As for asphaltenes, then before aging, their content is 20.82% of the mass., while after 5 hours of the experiment is 24.27 and 27.75% of the mass after 10 hours in total.

The following groups of hydrocarbons were determined by overlaying the obtained IR spectra of the samples: normal paraffinic hydrocarbons, mononuclear aromatic hydrocarbons, polynuclear aromatic compounds. The results confirm the assumptions about the groups of components that are constituent in the bitumen structure.

Based on the obtained results, it can be argued that the main loss of properties of bitumen occurs at the technological stage of aging, when bitumen and pavement are only being prepared for use. Thereafter, when bitumen is put into operation, the effect of negative factors only continues.

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The assessment of human health effects of particulate air pollution ($PM_{2.5}$ and PM_{10}) in Romania

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The particulate matters (PM), with aerodynamic diameter smaller than 2.5 μm are less studied due to the limited availability of $PM_{2.5}$ data. Hence, informations regarding the human health effects attributable to $PM_{2.5}$ and PM_{10} in Central-Eastern Europe are scarcely available in the literature. The objective of the current study was to assess the human health risk and characterize the spatial and temporal variation of particulate matters ($PM_{2.5}$, PM_{10}) in eight Romanian regions (B-Bucharest, C-Central, NE-North East, NW-North West, S-South, SE-South East, SW-South West, W-West) between 2009-2018. The PM concentrations showed high variability over temporal and spatial distribution. The highest concentration was detected in the Bucharest region in the cold period, meanwhile the lowest was measured in the West region in the summer period. The relative risk caused by the PM_{10} for all-cause mortality varied between 1.017 (B) and 1.025 (W), with an average of 1.020. The results revealed a positive relative risk 1.26 (±0.023) and 1.42 (±0.037), for cardiopulmonary and lung cancer diseases, respectively, due to exposure to $PM_{2.5}$. According to the calculations the excess risk and attributional fraction for cardiopulmonary mortality can be prevented by 26.7% and 21.0%, if the $PM_{2.5}$ concentration levels are around 3 μg/m^3, and also can reduce by 2.04 and 2.00% if the annual mean concentrations of PM_{10} is reduced by 10 μg/m^3.

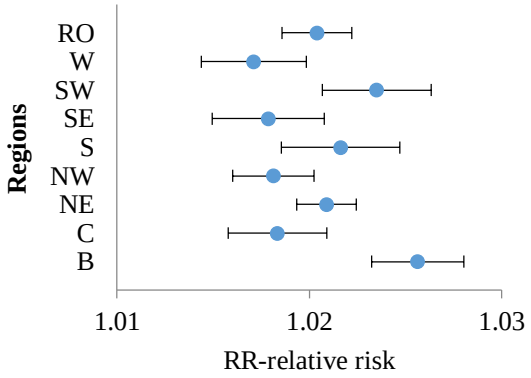

Figure 1. PM_{10} all-cause mortality risk

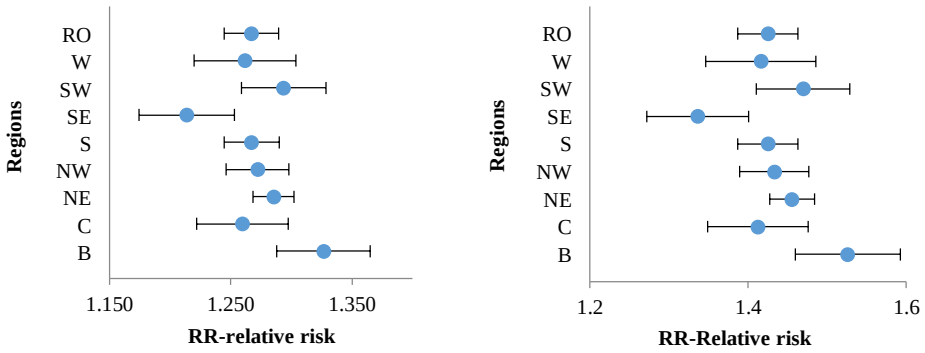

Figure 2. $PM_{2.5}$ - cardiopulmonary disease (left) - lung cancer (right)

Polyimide films for solar cell applications

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Environmental issues caused by global energy demands impose research of new materials that upgrade the performance of current devices that use natural resources to produce electricity (C.E. Brown, 2002). Among them, solar cells have received special attention since solar radiation is one of the most abundant source of energy on our planet (Lee et al., 2017). Shielding solar cells with lightweight materials that resist in harsh conditions (sun heating, wind erosion, etc), but also induce low optical losses represent a hot topic in this domain (Hulubei et al., 2019). The present work is devoted to the study of some thermostable imide polymers from the point of view of their optical, morphological and surface properties. Transmittance and light dispersion features of the polyimide films are closely examined. Also, morphology and surface tension characteristics are discussed in regard to adhesion to solar cell components. All these aspects affect the device reliability and provide perspectives on designing photovoltaics for green energy.

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Novel heavy metal tolerant bacterial strains with PGPR potential, isolated from heavy metal polluted soils

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The soil is a natural source of heavy metals (HM), but the anthropogenic activities increase the HM concentrations of soils, thus becoming harmful to plants and animals and due for its accumulation in food web for human as well (Tirry et al., 2018). Industrial activities, such as tanning, refining, mining, manufacturing processes, also the use of agrochemicals (fungicides, land chemical fertilizers), metallic nanoparticles, urban sewage sludge, industrial waste disposal, waste incineration and vehicle exhausts are the main sources of HM contamination of water resources and agricultural soils. The common toxic metals are the aluminium (Al), manganese (Mn), chromium (Cr), copper (Cu), cadmium (Cd), zinc (Zn), lead (Pb) and mercury (Hg), also some metalloids (antimony and arsenic) are considered toxic (Ashraf et al., 2017; Mishra et al., 2017).
The remediation of HM contaminated soils is very expensive and environmentally destructive method. The physical methods are not efficient, therefore biological processes are involved in remediation of soils. Phytoremediation and the use of rhizosphere microbes are an important alternative solution with high efficiency and better performance. The plant growth promoting microbes (PGPM) can protect the plant from HM stress, but can help in the accumulation of HM from soil in the host plant. The rhizospheric microbes have metabolic capabilities to adapt and live even in presence of high concentration of HM (Mishra et al., 2017). The plant growth promoting (PGP) traits of heavy metal resistant/tolerant bacteria are the following: phosphate solubilization/mobilization, indole-3-acetic acid (IAA), exopolisacharide (EPS), siderophore, ammonia, hydrogen cyanide production and nitrogen fixation (Tirry et al., 2018).
A high number of bacterial strains has been reported, but there is a growing need to find novel, heavy metal tolerant bacterial strains, which can improve the plant growth and yield in case of HM contaminated soils. The aim of this study was to isolate HM tolerant bacterial strains, then to examine their plant growth promoting traits, like phosphate (organic and inorganic) mobilization, EPS, IAA and siderophore production.
Twelve bacterial strains were isolated from Bălan (Harghita County, Romania) from HM contaminated soil (near the mining area). The PGP traits were examined in presence of several HM concentrations: 1 mM Zn, 0.5 mM Cd, 0.5 mM Zn+0.1 mM Cd. 58.3 % of isolated bacterial strains mobilized the inorganic phosphate, and only half (50 %) was able to mobilize the organic phosphate in presence of used HM concentrations. The siderophore production of bacterial strains was detected at 75 % of isolated bacterial strains. 91.66 % of strains can produce EPS in control conditions, and also 91.66 % of bacterial strains were able to produce IAA in case of HM concentrations. Based on our results, half of the isolated heavy metal-tolerant bacterial strains retain their plant growth-promoting properties even in the presence of used HM concentrations, having a good potential for application in sustainable agricultural practices.
For further selection the above mentioned bacterial strains will be used in plant experiments in order to examine their effect on plant growth, development and metal uptake.

Acknowledgements
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Comparison of adsorption efficiency of the fly ash for heavy metals removal

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The aim of this study was to compare the adsorption efficiency of a locally available fly ash as a low cost adsorbent material for removal of nine heavy metals ions from aqueous solution. Removal of heavy metals from wastewater is one of the most important environmental issues studied (Harja et al., 2013). The Cu, Ni, Cr, Pb and Cd are widely used in various industrial processes such as electroplating, paint, pulp and paper mill, printed circuit board, etc. On the other hand Cs, Ba, Eu and U are present especially in mine waters. Several methods are used for the removal of heavy metals such as adsorption, chemical precipitation, solvent extraction, membrane filtration, ion exchange, etc. The adsorption process is recommended due to some advantages: there are not used expensive chemicals, and it has a low capital and operating cost, etc.

Fly ash, one of the most abundant waste materials is a potential material for the adsorption of heavy metal contaminants. The safe disposal of fly ash is a matter of great concern as it is not environment-friendly and requires a large amount of land to dispose of it in landfills. It has alkaline property and its surface is negatively charged, the matter that can be used as a potential adsorbent. Adsorption of studied heavy metals onto fly ash is affected by several parameters: pH, fly ash dosage, initial concentration, and contact time, etc.

Fly ash used in the present study was collected from Holboca power plant, located near Iasi. The fly ash contains the following chemical constituents by weight SiO_2: 53.8%, Al_2O_3: 21.9%, Fe_2O_3: 8.2%, Na_2O: 2.9%, K_2O: 2.1%, TiO_2:1.9%, CaO: 6.2%, (classified as class F) (Bucur et al., 2014). The mineralogical characterization of fly ash (determined with XRD – X'PERT PRO MRD equipment) revealed that the fly ash contains: Quartz, Mullite, Hematite, Rutile, etc. Regarding the particle size of fly ash it was found that about 25 wt. % of the particles are finer than 0.050 mm. In order to study the morphology of fly ash, SEM analysis using JEOL JSM 840A microscope was carried out at an accelerating voltage of 10 kV. FTIR spectrometer (Thermo Scientific Nicolet 6700 Model) was used to identify the functional groups.

The batch study was undertaken for the removal of heavy metals. The stock solution of each heavy metal was prepared synthetically in the laboratory. Solutions of different concentrations were prepared by diluting the stock solution. Batch experiments were conducted for establish the optimum pH, fly ash dosage, and the influence of initial concentration. The filtrates of the remaining heavy metal ion (C_t) were analyzed by atomic absorption spectroscopy for Ni, spectrophotometrically (Cd, Ni, Cu, U), respectively using γ-ray spectroscopy (Ba, Cr, Eu, Cs) (Noli et al., 2015). The adsorption efficiency of the process was determined using Eq. 1. All the experiments were carried out triplicate and the average values are presented in Figure 1.

$$\text{Adsorption efficiency, \%} = (1 - C_t/C_o)\ 100 \qquad (1)$$

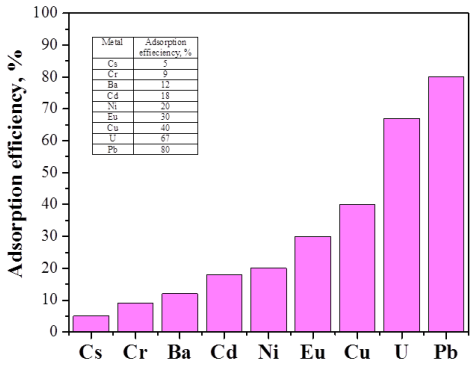

Figure 1. Comparison of adsorption efficiency of the fly ash: Cs (pH 4), Cr (pH 5), Ba (pH 5), Cd (pH 5), Ni (pH 6), Eu (pH 4), Cu (pH 5), U (pH 3), Pb (pH 9)

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E-Service Quality and Customer Loyalty and the moderating role of consumer demographics- An empirical relationship with specific reference to the Indian Organic Online Stores

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Abstract:

The Internet plays a vital role in the competitive world of retail as more customers are showing their interest to purchase products from online stores. Such type of stores has been known to provide more offers and discounts in order to attract new customers and retain their returning customers. Therefore, the main intention of this research was to examine the relationship between E-service Quality and its impact on customer loyalty. Such factors assessed included which information storage kept secure and confidential, website performance, customer loyalty, job satisfaction, and more. As such, this study made use of primary and secondary data both in carrying out the research.

From the analysis findings, a relationship between information security and confidentiality and loyalty was clearly observed, as well as a correlation between information security and confidentiality, and loyalty and website performance. Accordingly, age was found to strengthen the relationship between informational security and confidentiality, website performance, and loyalty. Similarly, the correlation between information security and confidentiality, website performance, and loyalty was improved by income, as well as the element of gender.

Optimization of experimental parameters for retention of Hg(II) ions from aqueous solution on clay adsorbent

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Abstract

Research on decontamination of water resources has led to an extraordinary boost in finding new and cheap materials that are able to remove pollutants. Pollution of water sources caused by heavy metal ions has raised global environmental problems around the world because they cannot be destroyed or degraded, have a tendency to accumulate in the environment and affect the quality of ecosystems. They also affect human health because are extremely toxic and can cause irreversible brain damage, kidney and liver dysfunctions (Safruk, 2017). The main sources of water pollution with such toxic metal ions have emerged as a result of technological progress in the development of the industry, such as the chemical industry, the oil processing industry and the metallurgical industry (Volesky, 2001). Most of methods used for the removal of Hg(II) ions like precipitation, ion exchange, flocculation flotation, etc., have proven their effectiveness at laboratory level but they have important limitations mainly because are expensive, required complex equipments, low removal efficiency and in some causes can generate large quantities of secondary sludge. On the other hand, adsorption could be considered a promising alternative for removing mercury ions from aqueous media due to its efficiency, high selectivity, low cost, ease of operations. All this conditions are fully fulfilled by using natural adsorbent materials like clay material, yeasts, peat, because there are abundant, easy to prepare and stable over time (Uddi, 2017).

Clay materials have received increased attention because they are available in large quantities and the are cheap which make adsorption a economical process, and they are easy to prepare, the main process is based on a few simple mechanical operations. On the other hand, clay materials have high adsorbent performances, which are mainly determined by: (i) numerous negatively charged functional groups that can interact with positively charged metal ions, and (ii) large specific surface area due to high porosity and size small clay particles.

In this study, a local clay material was tested as natural, low-cost adsorbent alternative for the retention of Hg(II) ions from aqueous solution. The adsorptive performances of clay materials were evaluated as a function of initial solution pH, adsorbent dose, initial Hg(II) ions concentration, contact time. The highest adsorption efficiency of clay material was found at initial pH=2, the adsorbent dosage of 4g/L, contact time 10 minutes, when the adsorption capacity of clay material for Hg(II) ions is 32.91 mg/g (Fig. 1).

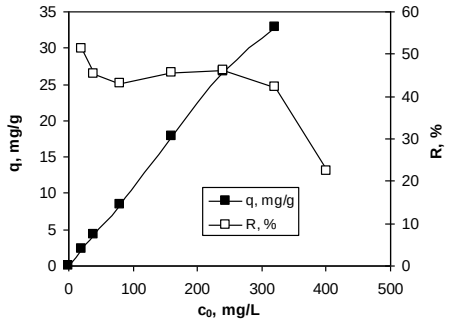

Figure 1. Adsorption efficiency of clay material in removal process of Hg(II) ions from aqueous media.

The experimental results were modelled using Langmuir and Freundlich isotherm models, and pseudo-first order, pseudo-second order kinetic models. The experimental results included in this study highlight the practical applicability and increased potential of this clay material as adsorbent in the decontamination processes of the aqueous effluents.

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Toxic effects of lead in early growth of wheat and its tolerance

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Abstract
Heavy metals are recognized as typical soil pollutants, their presence generating serious threats for the environment, but also for human health. Their capacity to accumulate in agricultural land and crops can cause substantial losses of production globally, due to their toxicity, mobility, non-biodegradability and persistence in the environment. The toxicity of metals is largely associated with their transfer in the food chain, with significant consequences on human health, dependent on the heavy metal properties. This is why it is necessary to investigate the relation between metal toxicity and plant tolerance. Also, these studies are requisite for application of phytoremediation in view of heavy metals removal from soil.
The main objective of this paper is to establish the tolerance of the *Glossa* wheat hybrid to different thresholds of Pb(II) concentrations in soil. Pb(II) is one of the most environmentally toxic heavy metals since, once accumulated in the soil, it can affect flora, fauna and generates threats for human health by inducing multiple damage to the body, even in low concentrations. Therefore, Pb(II) toxicity was tested based on phenological observations and determinations, considering growth indicators such as the degree of germination of wheat seeds, the growth of roots and stems and their rate of inhibition. For this purpose, *Glossa* hybrid seeds were subjected to synthetic contamination with $PbCl_2$ solution in concentrations ranging in the interval 50-400 mgPb(II)/L, after their sterilization with NaOCl. For experiments, a number of 10 wheat seeds were evenly distributed in Petri dishes containing a layer of Whatman filter paper and 10 mL of $PbCl_2$ solution of known concentration, to create metal stress. In parallel, a volume of 10 mL distilled water was added in a control samples. Each experiment lasted for a period of 5 days. It was observed that the germination efficiency of wheat seeds was affected by the presence of $PbCl_2$ ions, and the degree of damage to the roots and stems intensified with increasing metal concentration. According to the data from the experimental study and those in the literature (Table 1), plant growth inhibition depends on the values of metal concentrations.

Table 1. Findings of some studies on the effects of lead toxicity on wheat seed germination

The inhibitory effects of different concentrations (0; 1; 2; 4 mM) of $Pb(NO_3)_2$ on wheat seeds, Xihan variety, were studied. The results showed that high concentrations of $Pb(NO_3)_2$ significantly inhibited germination and root growth, and dimethylthiourea, catalase or diphenylene iodonium could reverse the inhibitory effects of $Pb(NO_3)_2$ on seed germination.	Yang et al., 2010
The toxicity of lead on the germination of the Achtar wheat variety was studied. For 6 days wheat seeds were subjected to different concentrations (0; 0.15; 0.3; 1.5; 3 mM) of $Pb(NO_3)_2$. The rate of seed inhibition increased with Pb(II) concentration, and the roots were most affected by the toxic effect of lead ions, as they are the first organs exposed.	Lamhamdi et al., 201165

Due to its acceptable tolerance to Pb (II) toxicity, wheat can be considered a bioaccumulator for this metal. It can be used for phytoremediation, but with the mention that, after harvesting the crop, it should not be intended for human consumption or animal feed. Biomass can be processed as a secondary source of raw materials for Pb (II) extraction by chemical and thermal methods.

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Assessment of human health risk associated with pesticides residues in fruits and vegetables

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Today, socio-economic development continues to negatively influence the quality of the environment and to raise different threats to human health. Population growth is directly associated with an increased demand for food sustaining thus, the agricultural progress in human society. To ensure a proper food production, the development of agricultural production needs first of all the protection of plants against diseases and pests. In this sense, different categories of pesticide are developed and applied, the majority of them belonging to persistent organics pollutants (POPs) class. These pesticides can be very toxic for humans and animals and may further contaminate the surface waters, groundwater, soils, and atmosphere. In this demand, food security should be treated as a serious public concern worldwide. In recent decades, interest in this direction has been growing and supported the development of different studies on the risks associated with the consumption of fruits and vegetables, which represent an important part of the human diet.

In this context, the major objective of our paper is to provide a dietary risk assessment of the population from Romania exposed to pesticides residues in fruits and vegetables based on PRIMo EFSA model. To fulfill the fundamental objective of this paper, the following specific objectives were established: *i)* characterization of acute and chronic health risks, taking into account the exposure to pesticide residues in fruits and vegetables on the Romanian and European markets considering a possible export of fruit and vegetables; *ii)* providing information that can improve the available agricultural practices and food safety protocols in Romania; *iii)* enriching the information to the citizens regarding the correct use of pesticides by taking into account the principle of respect for the environment and human health and promoting alternative methods for plant protection.

In order to achieve the proposed objectives, the assessment of the potential exposure of the population to chemical contaminants in food considering different scenarios was based on modeling the data from the National Pesticide Monitoring Report using the PRIMo-EFSA modeling software (version 3), developed by the European Food Safety Authority (EFSA). As a study area, the Moldova area was selected, especially the cities of Iași, Galați, Bacău, Botoșani and Vaslui. The study was conducted for different categories of population taking into account the consumption rate of each category of selected fruits and vegetables (apples, strawberries, cherries, green onions and salad).

The results of our study confirmed that the residue levels in plant-based foods may pose a threat to consumers' health (especially for children). According to our results, we observed some threats only in case of acute exposure related to the presence of *lambda-cyhalothrin* pesticide in apples from the Galați area, which exceeded the corresponding limit for the children category. This was also the case of lettuce, where an acute risk was obtained for the *carbendazim* pesticide in case of children category. The long-term exposure of consumers to selected fruit and vegetables can be excluded for all age groups, since no exceedance of pesticide residues were obtained.

Based on our findings, it is recommended to further continue and develop studies on dietary risk assessment and estimation of human health associated with the consumption of food contaminated with pesticides. These studies will contribute to a proper information/protection of the end user regarding the exposure to pesticides but also for warning farmers regarding of compliance with the code of good agricultural practices (GAP).

Acknowledgments
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Comparative study of Pb(II) ions adsorption on PET waste fibers and flakes

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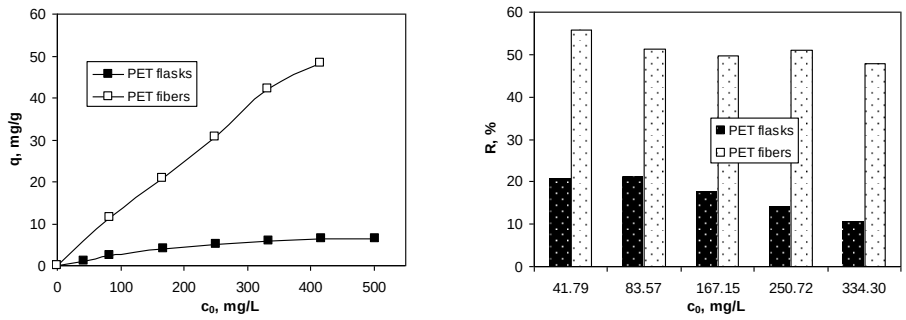
The use of polyethylene terephtalate (PET) for the manufacture of food packaging and beverage containers has led to the discharge of huge amounts of such waste into the environment, causing its pollution. In addition, as the degradation of PET waste requires a very long period of time (over 180 years) (Mendoza-Carrasco et al., 2016), environmental pollution with this waste can be considered permanent. But, the extensively utilization of PET for package manufacturing has caused important environmental problems, due to huge quantity of PET packages which must recycled (Shukla et al., 2008). In order to found some practical applications in environmental remediation, PET waste fibers and flasks have been tested as adsorbent materials for the removal of Pb(II) ions from aqueous media. Thus, PET waste (fibers and flasks) they were cut into pieces of 0.2 cm^2, and after washing (with distilled water and drying) were contacted with aqueous solutions containing Pb(II) ions of known concentrations (42 – 500 mg/L), at room temperature (22± 1°C). The adsorption capacity (q, mg/g) of these two PET-based materials, calculated after 24 hours of contact time (Fig. 1a) increases with the variation of initial Pb(II) ions concentration, on entire studied interval. Such variations are common and are mainly determined by the fact that high initial concentrations of heavy metals cause a higher probability of collisions between the functional groups of PET waste adsorbents and Pb(II) ions in the aqueous solution (Cochrane et al., 2006), which has as results the increase of adsorption efficiency.



(a) (b)

Figure 1. Adsorption efficiency of PET waste-based adsorbents in the removal of Pb(II) ions from aqueous media.

The obtained results show that the absorption capacity of PET waste fibers is clearly superior to that obtained when using PET waste flakes as adsorbent material. This is mainly due to the clearly superior morphological characteristics of the fibers compared to those of flakes (demonstrated by FTIR spectra, EDX and SEM images). However, in both cases the removal percent does not exceed 57 % (Fig. 1b), which is an important drawback of these materials. Therefore, the detailed modelling of experimental isotherm, and detailed interpretation of the structural particularities of each PET waste-based adsorbent used in this study, will provide a clear image of the possibilities of functionalization of these wastes, in order to obtain high-performance adsorbent materials.

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Insights into toxicity and risks caused by heavy metals found in medicinal plants

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Humanity has been using plants in different types of therapies for centuries. The use of plants as alternative to conventional medicine is considered by many people more safe, available and affordable. However, due to the continuous increase of environmental pollution caused by our demand in consumption, major concerns have been raised by researchers on safety and quality issues related to the use of herbal plants (Ozyigit et al., 2018). On the other side, heavy metals are of special concern since they cannot be degraded and are the subject of plant and animal bioaccumulation causing toxicity (Hlihor et al., 2017). Given this context, a possible contamination with heavy metals of plants used in phytotherapy and cosmetology for specific preparations, could cause risks to human health even in low concentrations. For example, metals found in cosmetic products can act locally on the skin or accumulate in the body after absorption and cause systemic toxic effects (Fischer et al., 2017).
In the current national and international context, the assessment of the human health risk generated due to plants which are exposed to heavy metals and used for different purposes is a challenge for researchers, assessors and risk managers, especially considering the limitations of current methodologies in terms of the relationship between terminology and problem formulation, uptake mechanisms, the toxicological profile and human exposure conditions. The aim of our paper is to investigate the complexity of human health risks generated by the exposure to herbal plants contaminated with heavy metals used in phytotherapy and cosmetology according to the state of the art, given the following objectives: i) defining key issues at national and international levels related to the risks generated by the use of herbal ingredients exposed to different amounts of heavy metals in holistic medicine and cosmetology and ii) to provide insights into the mechanisms by which plants take up metals and their detoxification/antioxidative pathways.

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Impact of beet sugar manufacturing activity within S.C. AGRANA ROMANIA S.A. – Roman, Neamţ County on the environment

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The industrial activities have a major impact on all environmental factors, by affecting the quality of air, water, soil, generation of different waste types, and through use of natural resources and energy.
In this purpose, it is necessary to monitoring these activities, to ensure compliance with existent legislation in the field of environmental protection, and with principles of sustainable development.
Regarding the impact on water and soil quality, it is due to the age of installations, the improper operation of the technological wastewater treatment / pre-treatment plants / installations as well as the inefficiency of the air de-pollution installations.
Sugar beet production has gained momentum and reached approx. 30% of today's world beet sugar production. Also called "white gold", sugar came to be taxed with astronomical sums due to growing demand for it. Since 2005, the company S.C. AGRANA Romania S.A. is one of the largest suppliers of sugar for both sweeteners and soft drink industry, for the retail sale of sugar internationally, but it it especially a supplier for retailers who sell sugar in small towns and villages across the country.
The sugar production unit obtained from sugar beet is located in Roman, Neamţ County, and represents the most important partner for thousands of sugar beet growers and for the owners of agricultural lands in Eastern Romania, from the border with Ukraine to the South of Galaţi County.
The present paper analysis the impact of beet sugar manufacturing activity on the main environmental factors, starting with technological wastewater, domestic water, purified and directed through pipes in the natural emissary, studying the concentrations of nitrites, nitrates, iron and nickel ions, in three different analysis period, calculating the retention yields at the station for the most important chemical indicators.
We studied emissions into atmosphere from technological sources, from micro-power-plants, checking the flue gas circuits, by measurements at the flue gas dispersion basket, by checking the dust entrainments.
We also identified, one by one, the local pouring areas inside, we measured the pollutants concentrations in soil, and previous and present damage of the soil.
Following the findings, we analyze the degree of pollution on each environmental factor, establishing conclusions and recommendations.

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Identification of economic and environmental criteria for evaluating the soil remediation processes performances

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Due to the intensification of industrial activities and technological evolution, environmental pollution with inorganic and organic pollutants is becoming an increasingly worrying issue. Contamination of soils with heavy metals as a result of anthropogenic activities is quite common in Europe with an undesirable impact on the quality of life and the environment. As it is known, metals can last in soils for thousands of years, being non-biodegradable and usually immobile compared to inorganic pollutants. In the literature, we often find several types of remediation processes, but in order to choose the appropriate remediation alternative for sites contaminated with heavy metals, decision makers must consider aspects economic and environmental.

Currently, there are a number of tools for (i) assessing the economic and environmental performances of alternatives for the removal of heavy metals ions from contaminated sites, or to (ii) choose hyperaccumulator plants for decontamination of soils polluted with heavy metals: Cost-Benefit Analysis (CBA), Life Cycle Assessment (LCA), Multi-criteria Decision Analysis (MCDA) etc. (Comanita et al., 2018).

The goal of this paper is to identify economic and environmental criteria to apply the three mentioned economic and environmental assessment tools in order to find the most viable soil remediation processes.

The criteria used in evaluating the performance of a remediation process express the views of decision makers which aim to establish comparisons of products/ processes/ technologies by applying decision models. A number of principles are used to determine the set of criteria, which reflects the ways of constructing a problem.

In general, for all types of processes it was identified a set of criteria in the literature for assessing the economic and environmental performance (Cipullo, 2013): (i) environmental quality; (ii) approach/ logic; (iii) transparency; (iv) ease of applicability; (v) correlating data with the importance of the problem; (vi) the policy of adapting to the importance of the problem; (vii) time and human resource requirements for analysis; (viii);) economically viable processes; (ix) software availability, where required.

In Table 1 it is presented a set of identified and applicable criteria for to evaluate the performance of soil remediation processes. These criteria will provide a solid database and will facilitate the making of the best decisions as a consequence of the results obtained from the application of environmental and economic performance assessment tools for the soil remediation alternatives to be analyzed.

In conclusion, the identification of the applicable criteria, based on the decision-making instruments, was undertaken to make the evaluation of alternatives for remediation of soils contaminated with heavy metals, more sustainable, adequate and robust, from an economic and environmental point of view.

Table 1. Criteria for evaluating the performance of soil remediation processes

Nr. crt.	*Economic criteria*	*Environmental criteria*
1.	Duration project	Climate change effect on ecosystem
2.	Direct project cost	Human toxicity
3.	Land value increase	Agricultural land occupation
4.	Space creation	Terrestrial acidification
5.	Employment	Natural land transformation
6.	Nearby property	Marine ecotoxicity
7.	Project closing costs	Fossil depletion

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Carbon biocapture in the frame of the climate change and air quality issues: a preliminary microbiota screening

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Abstract

This work is addressing coupling VOC-degraders and microalgae in order to enhance the carbon capture in the biosystems involving such microbiota for air treatment. In such process, carbon dioxide generated from the degradation of the volatile organic compounds (VOCs) can be used for microalgae growth. Therefore, preliminary batch-test have been undertaken in order to determine the opportunity of this approach. Different composts have been used as a source of VOC-degraders, while *Arthrospira platensis* and *Chlorella vulgaris* are the tested microalgae. Both co-immobilisation (e.g. alginate) and suspended cell-based options are screened in this regard.
The growth characteristics (biomass and cell productivity) and biochemical composition (proteins, carbohydrates and antioxidant enzymes) of the microorganisms grown in the presence of a single VOC and in different media is presented and discussed. The proposed approach can be considered for further enhancing the carbon capture in the traditional biosystems (e.g. biotrickling filters) treating air contaminated with VOCs, with many forecasted benefits related to climate change and air quality issues.

***Keywords*:** microalgae, VOC-degraders, *Arthrospira platensis*, *Chlorella vulgaris*, air atmospheric protection, sustainable bioprocess for air treatment

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Vegetable wastes – environmentally friendly and low-cost adsorbents

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In many developed countries, urban and rural areas, disposal wastes are a stinging and widespread problem. A new trend regarding food and vegetable waste recycling is starting to become an important topic among researchers. In order to eliminate various pollutants from the environment, a wide variety of potential adsorbents were tested, following their retention capacity and the costs involved in this process. Vegetable wastes proved to have the capacity to adsorb and desorb pollutants from wastewater, quantify the environmental impacts generated during the process life cycle and useful potential for energy production (Abdel-Shafy et al., 2018).

In literature the most popular adsorbent used for the adsorption process is the activated carbon. This adsorbent is very expensive by comparison with vegetable wastes and there is a need for its regeneration after each adsorption experiment (Saka et al., 2012). Therefore, these weighty resources (vegetable waste), which are available in large quantities and are environmentally friendly, can be exploited as adsorbents since they have an increased potential to be used as low-cost sorbents (Hlihor and Gavrilescu, 2009). An important source of vegetable waste is represented by plants used in phytoremediation already containing heavy metals, which can further be loaded by metals during adsorption. Then, the waste can be used as secondary source for (critical) raw metals, being processed by chemical treatment and/or extraction.

Vegetable adsorbents have been evaluated for their adsorption properties. In Table 1 there are presented some vegetable adsorbents used for the elimination of the Pb^{2+} ions from wastewater.

Table 1. Vegetable adsorbents properties

Adsorbent	Uptake capacity(mg/g)	Removal (%)	Optimum pH	Sorbent dose (g)	Concentration (mg/L)	Temperature (^{0}C)
Banana peels	72.79	-	5	1	200	25 ± 2
Cereal chaff	12.5	-	5.5	0.1–0.6	8 g/L	20
Onion skins	200	93	6	0.15	25–200	30
Seed hull of the palm tree	3.77	-	4	6	100	60
Sunflower seed peel	-	99	6	-	-	60
Sunflower waste	33.2	-	4.0	-	10	-

Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of metals from wastewater. In subsequent cycles with low costs, the removal occurs in a relatively short operating time and no other toxic compounds are released at the end of the process.

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Improvement the water management on the Sulina Chanel by implementation of an automated water quality monitoring system on the passenger ship

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Abstract

In the frame of international collaboration, an automated monitoring system for the surface water quality on the Sulina Chanel will be implemented on the passenger ship (ferry) which will scan alternately day by day the distance from Tulcea to Sulina and back to Tulcea, respectively, with a sampling frequency of 5 minutes. The data will be transmitted to the water management authorities (Administration of Biosphere Reserve of Danube Delta, National Research Institute for Danube Delta and Water Company "Aquaserve" Tulcea). Particularly, "Aquaserve" Tulcea is a water company stockholder, which is responsible with both drinking water preparation and wastewater treatment for inhabitants located between Tulcea and Sulina. The drinking water is prepared from water pumped from Sulina Chanel (the main part of Danube river), while the wastewater is discharged in the same chanel that further is discharged to the Black Sea.
The main objective is to point out the correlation between the algae development and the concentration of the nutrients in terms of nitrate/nitrite, COD, and phosphates and to transmit an early warning message to the water authorities and water stockholders in the case of overcoming the Maximum Allowed Concentration of each water quality indicators (Nitrite/Nitrate, COD, and Phosphate).
The expert system works on the basis of a microprocessor motherboard, which has the role of reading the data from the probes, storing them temporarily on an SD Card type memory, and transmitting the data to a Smartphone with an Android operating system, which will run dedicated software developed for this purpose.
The reading of the data from the probes will be done through the RS-485 interface and the Modbus RTU protocol, and the communication with the Smartphone or tablet will be done through Bluetooth and an interface converter, from Bluetooth to UART.
The motherboard will also have digital inputs and outputs to interact with existing systems on the ship, for example to be able to detect when the ship's diesel engine is running, or when the water pump is running.
The designed system will have the following roles: communication with the authorities responsible for water management and environmental protection; to decrypt and store data in a local database; to determine the ship coordinates (location) using the GPS network and to store data for each reading from the probes; to analyze the obtained data allowing to observe the nutrients concentration evolution in order to predict the further eutrophication potential in the polluted area; transmission of warning messages in the case of concentrations that exceed the maximum allowed limits for each water quality indicator involved in this study as it was above mentioned.

***Keywords*:** water quality indicators**:** nitrate/nitrite, COD and phosphates; nutrients monitoring; algae development, eutrophication potential, early warning system.

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Anodic vs cathodic potentiostatic control of a tubular pilot scale microbial electrolysis cell for biogas upgrading

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Biogas, the main product of the anaerobic digestion (AD) process, is a gas mixture mainly composed by carbon dioxide and methane. Several upgrading processes have been developed to refine the anaerobic digestion biogas into biomethane (CH_4 > 95%), through the CO_2 removal from the gas mixture. An innovative biogas upgrading process consists in the utilization of a microbial electrolysis cell (MEC) in which a biocathode performs the bioelectromethanogenesis reaction reducing the CO_2 into CH_4 (so increasing the methane content) while the alkalinity generation in the catholyte promotes an additional CO_2 removal mechanism consisting in the CO_2 sorption as HCO_3^-. Here, a two chamber 12-liter tubular MEC has been developed in order to upgrade biogas by using bioelectrochemical organic matter oxidation at the anode to partially sustain the energy demand of the process. In the tubular MEC, the electroactive microorganism's selection was obtained by polarizing the anode chamber at +0.2 V vs. SHE. Once the best organic load rate in terms of energy consumption was selected at 2.55 gCOD/ L d, the potentiostatic control of the tubular MEC was switched from the anode to the cathode. As reported in a previous experiment [1], the potentiostatic control shift resulted in a sharp decrease of the process' energy consumption thanks to minimization of the anodic potential. Moreover, three different runs were conducted with the cathodic potential controlled at - 1.3 V; - 1.8 V; - 2.3 V vs. SHE to investigate the performances of the CO_2 abatement. The lowest energy consumption for CO_2 removal was obtained during the -1.3 V vs SHE condition with a consumption of 0.5 kWh/Nm^3 of removed CO_2. Those results confirmed that the potentiostatic control switch from the anode to the cathode results permits to minimize the energy consumption of the MEC.

Table 1. Energetic consumptions for the single operation of the MEC

Potentiostatic control	Potential (V vs. SHE)	OLR (gCOD/Ld)	kWh/Nm^3 of removed CO_2	kWh/kg of removed COD
Anodic	+ 0.2	2.55	2.2 ± 0.1	9.3 ± 0.6
	+ 0.2	3.82	3.3 ± 0.2	4.8 ± 0.4
	+ 0.2	5.11	7.7 ± 0.4	13.3 ± 0.9
Cathodic	-1.3	2.55	0.6 ± 0.2	1.1 ± 0.1
	-1.8	2.55	1.7 ± 0.3	1.5 ± 0.1
	-2.3	2.55	6.2 ± 0.6	12.4 ± 0.8

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