# *Book of Abstracts*

# NeXT-Chem

## INNOVATIVE CROSS-SECTORAL TECHNOLOGIES


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A long-time partner of the scientific events organized by the National Institute for Research & Development in Chemistry and Petrochemistry – ICECHIM Bucharest, the **Romanian Chemical Society,** member of EuChemS, aims to bring together all those with higher education involved in research and design, education, industry, other sectors of the economy and society useful fields, in order to develop and achieve the following objectives:

- Promotion of chemistry in all respects;
- Organization of communication sessions, symposia, seminars, workshops, conferences or congresses of national and international interest.

On January 24, 1919, enthusiastic chemists from Romania met at the Analytical Chemistry Laboratory of the University of Bucharest to establish the scientific society called the ROMANIAN CHEMICAL SOCIETY (SChR).

Without a moment of dissolution during the war and the post-war period, SChR had a fruitful activity only two decades after its creation. Only after 1992 the scientific life of the Romanian Chemical Society was resuscitated: objectives were defined, organizational actions were taken, branches were established throughout the country, and international contacts were established and developed.

Since then, SChR has been organizing annually various scientific events for both young and renowned chemists, and editing publications of interest to chemistry lovers. Remarkable is the initiative to indicate in the "Chemical Bibliography in Romania" all the original works published in our country, accompanied by the exact quote of the original work. Also, original results have been published in international languages in the „Bulletin of Pure and Applied Chemistry".

Romanian Chemical Society actively promotes not only the established researchers, but also encourages the young researchers, at the beginning of their career, offering awards in the scientific meetings in which it is co-organizer and partner for the most valuable works.

For more information regarding the Romanian Chemical Society, please visit http://www.schr.ro or contact us:

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# FOREWORD

Since the first edition of the Exploratory Workshop "NeXT-Chem", INCDCP-ICEHIM has built a sustainable community of scientists from the industry and from academia, who are committed to make a substantial contribution to the progress of a more sustainable and circular chemistry.

The modernization of the chemical industry not only requires intensive collaboration and expertise exchange between the industrial and academic sectors, but also calls upon us to engage and join forces with other disciplines to undertake this transition towards a resilient and sustainable society.

During the Exploratory Workshop "NeXT-Chem", insights were provided into our research and multidisciplinary approaches towards circular chemistry were discussed.

As the previous three editions, the fourth edition of our workshop was addressed to young researchers (MSc, PhD students), and participation was free of charge.

In 2022, the exploratory workshop was held within the project "Supporting the competitiveness and excellence of INCDCP-ICECHIM research and innovation in the area of bioeconomy and related fields" (**NeXT-BExcel 15PFE/2021**), project financed through the National research, development and innovation plan for the period 2015-2020 (PNCDI III), Program 1 – Development of the national research & development system, Subprogram 1.2 – Institutional performance – Institutional development projects – Projects for funding RDI excellence (contracting authority: Ministry of Research, Innovation and Digitization).

The project NeXT-BExcel aims to increase the performance of **INCDCP-ICECHIM** in the area of bioeconomy and related fields, to support and develop research skills in this field, as well as the development of institutional capacity in the following directions:

- capitalization and dissemination of knowledge and research results;
- providing high-level scientific support in priority areas;
- initiating and developing viable collaborations with economic, public and private partners;
- increasing international involvement and visibility.

Through these, the project continues the line drawn by the project *Increasing the research and innovation potential of **INCDCP-ICECHIM** in the field of key cross-disciplinary and cross-sectoral innovative technologies* (31PFE / 2018), with the aim to achieve the desideratum of modern institute, at European standards.

For further information, please visit https://icechim.ro/en/institute/next-bexcel-en/.

# INVITED LECTURES

## Thursday, May 19th, 2022

1. **Dr. Roxana RĂDVAN,** The National Institute for Research and Development for Optoelectronics - INOE 2000, Romania
   ***Noncontact surface restoration methods***

2. **Dr. Federica VALENTINI,** Department of Chemical Sciences and Technologies, University of Rome Tor Vergata, Italy
   ***New strategies for Analytical diagnosis and Green Conservation for Art -Work surfaces***

3. **Dr. Mariana Emilia GHICA, Chemical** Engineering Department, University of Coimbra, Portugal
   ***Aerogel based systems: preparation and applications***

4. **Dr. Andrei SÂRBU,** Romanian Chemical Society
   ***Romanian Chemical Society and EuChemS***

## Friday, May 20th, 2022

5. **Dr. Mario PICCIOLI,** Magnetic Resonance Center and Department of Chemistry, University of Florence, Italy
   ***What can we learn from NMR spectroscopy of paramagnetic metalloproteins?***

6. **Dr. Milen I. GEORGIEV,** Center of Plant Systems Biology and Biotechnology Institute of Microbiology, Bulgarian Academy of Sciences
   ***NMR-based metabolomics and anti-obesity leads finding: perfect holistic match?***

# Session 1 - Multifunctional materials, nanocomposites, innovative technologies and cultural heritage preservation

# ADDITIVE MANUFACTURING OF $BaTiO_3$ STRUCTURES WITH POTENTIAL APPLICATION IN HARD TISSUE REGENERATION

**Ștefania CHIRIAC [1], Eliza-Maria PUSCASU [1*], Laura-Madalina CURSARU [1], Roxana-Mioara PITICESCU [1*], Gabriela NEGROIU [1]**

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***Keywords: hydrothermal synthesis, robocasting, in vitro assessment***

**Introduction**: Natural bone has a specific combination of mechanical and electrical properties that regulates its biochemical activity [1]. The presence of electrical activity in the bone plays a vital role in its growth and healing. From this point of view, the use of piezoelectric biomaterial could lead to a bone implant with promising results.

A promising candidate that can be used as a lead-free piezoelectric material in biomedical applications is barium titanate (BT, $BaTiO_3$). Barium titanate is an inorganic material which is part of the perovskite family. BT become an intensively studied material in the last few years due to its dielectric, piezoelectric, ferroelectric, good mechanical and thermal properties and an excellent biocompatibility that has been demonstrated in numerous studies, both in vitro and in vivo.

In order to achieve a bioinspired functional design, additive manufacturing techniques can be used. It should be possible to manufacture an electrically stimulating graft with personalized defect geometry, and directed osteoinduction and osteoconduction, by combining piezoelectric materials with 3D printing technique [2]. An interesting approach is to use robocasting as a processing means to obtain BT based scaffolds. In this work a hydrothermal synthesized barium titanate was processed via robocasting in order to obtain porous synthetic bone graft with interconnected pores and an adequate mechanical strength.

**Materials and methods**: Barium hydroxide octahydrate ($Ba(OH)_2 \cdot 8H_2O$, Sigma ALDRICH, Germany) and $TiCl_4$ (Sigma ALDRICH, Germany-p.a. 98%) were used as raw materials for obtaining barium titanate denoted as BT in one step process by hydrothermal method. BT powder-based 3D structures were obtained by robocasting, an additive manufacturing technique based on the extrusion through a nozzle of a ceramic paste into which various additives were introduced to control its viscosity.

**Results**: During this work, using the 3D EnvisionTec BioPlotter system, 3D parts with different printing characteristics (strand thickness, distance between the strands, infill type) were designed and manufactured based on $BaTiO_3$ hydrothermally synthesized powder. The 3D bodies thus obtained were characterized from a morphological point of view with the help of the scanning electron microscope. Preliminary in vitro cell tests have also been performed to assess their biological potential. According to them, the 3D structures immersed in the culture medium release soluble products with a certain toxicity. However, the test results demonstrate the adhesion of the cells to these structures as well as their biocompatibility.

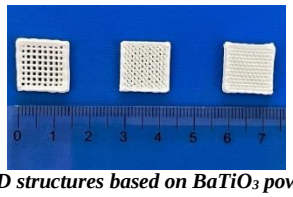


***Fig.1 3D structures based on $BaTiO_3$ powder***

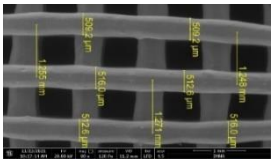

***Fig.2 SEM image of the 3D structures***

**Conclusions**: Hydrothermally synthesized barium titanate was processed by robocasting, thus obtaining porous synthetic bone grafts, with interconnected pores and adequate mechanical strength. In vitro cell tests performed on this 3D structures demonstrate their biocompatibility but also raise an issue related to the toxicity of the soluble products released by them.

***Acknowledgements**: The authors of this study want to acknowledge the help provided by the entire research and management team of IMNR institute.*

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# ALGINATE AND XANTHAN-BASED MATERIALS USED IN THE TRANSDERMAL DELIVERY OF KETOCONAZOLE

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***Keywords: xanthan, oleic acid, alginate, ketoconazole, drug delivery***

**Introduction**: Polysaccharides have widespread pharmaceutical applications as drug delivery systems [1]. The aim of this work was to develop new drug delivery systems based on alginate (Alg) and xanthan (Xa)/xanthan esterified with oleic acid (XaAO) containing ketoconazole (K) as antifungal agent.

**Materials and methods**: New materials comprising equal amounts of polysaccharides (Xa-Alg/XaAO-Alg) and 0.05 g of ketoconazole (Xa-Alg-K, XaAO-Alg-K) were obtained through freeze-thawing cycles, followed by lyophilization.

FTIR spectra of the materials were recorded using a Vertex 70FTIR spectrometer. The $^1$H-NMR spectra were recorded on a Brüker Avance DRX 400 MHz spectrometer. Mechanical performances were evaluated with Shimadzu Testing Machine EZTest. The SEM images (x200) were taken using a VEGA TESCAN microscope. UV-Vis technique was useful to assess the release of ketoconazole. The antimicrobial activity of the materials was also studied.

**Results**: FTIR and $^1$H-NMR spectra proved that the esterification reaction of xanthan took place. FTIR spectra of the obtained materials confirmed the presence of ketoconazole in the developed materials.

When ketoconazole was added into the xanthan/alginate matrix, an increment in the mechanical strength was recorded (66.68% compression). The mechanical strength of porous materials was affected by pore diameter and pore wall thickness. It should be pointed out that, as Xa-Alg-K/ XaAO-Alg-K were compressed between the plates of the testing apparatus, the solvent from the pores was completely released, which seems to hamper the fracture and the crack development within these formulations.

The release of active principle from materials is best described by the Korsmeyer-Peppas model [2]. The presence of esterified xanthan slows down the release rate of active principles through hydrophobic interactions (the interactions between the oleic acid moiety and the hydrophobic parts of the drugs). Due to its hydrophobic nature, ketoconazole was better retained by the XaAO-Alg than Xa-Alg polymer matrix. Thus, the K release rate of XaAO-Alg is much lower (0.89) than that of Xa-Alg (4.27). Antimicrobial studies have shown that the materials tested show approximately the same biocidal capacity, after 24 h, on all tested bacterial and fungus strains (*Salmonella typhymurium, Staphylococcus aureus, Escherichia coli and Candida albicans).* The system comprising unmodified xanthan and ketoconazole (Xa-Alg-K) exhibited a lower inhibition capacity for *Salmonella typhymurium* (76%), as compared to that comprising esterified xanthan (XaAO-Alg-K, about 95% percent inhibition). The association mechanism between these drugs, as well as the determination of the clonal lineages for each microorganism could clarify these results.

**Conclusions**: New drug delivery systems based on alginate, xanthan and modified xanthan have been developed and analysed. $^1$H-NMR and FTIR spectra confirmed the chemical modification of xanthan with oleic acid. FTIR spectra showed the presence of drug in the materials by the characteristic bands. When ketoconazole was added into the Xa-Alg matrix, an increment in the mechanical strength was recorded, sustaining 66.68% compression, as compared to Xa-Alg without the drug (40.59% compression). SEM images were used to determine the pore size and pore wall thickness of the materials. The release kinetics of ketoconazole through the biomaterials fitted well the Korsmeyer-Peppas model, with non-Fickian (XaAO-Alg-K) and Fickian (Xa-Alg-K) diffusion. These materials were shown the antimicrobial activity as compared with materials without drug.

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# HYDROPHOBIC Mg-Al LAYERED DOUBLE HYDROXIDES FOR USE IN THE CONSERVATION OF STONE MONUMENTS

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***Keywords: layered double hydroxide, superhydrophobic, heritage, conservation***

**Introduction**: Exposed stony masonry is especially vulnerable to deterioration. The main mechanisms that lead to the deterioration of stone monuments are associated with thermal and freeze thaw cycles as well as abrasion. In order to repair and confer a protective coating to the stone surface, different treatments based on fluorinated acrylic polymers, fluoropolyethers and siloxanes are applied. However, such treatments are not satisfying all the demands for an ideal protective coating. LDH materials have recently attracted a lot of interest in surface protection due to their tunability and mass production capacity. The general formula of a LDH can be represented as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot mH_2O$, where $M^{2+}$ is a divalent cation like $Mg^{2+}$, $Zn^{2+}$ or $Ca^{2+}$, $M^{3+}$ represents a trivalent cation like $Al^{3+}$ or $Fe^{3+}$, and $A^{n-}$ is the compensating anion that is present in the interlayer. Both the nature of $M^{2+}$ and $M^{3+}$ and the interlayer composition have a great impact of the LDH properties. Thus, modified LDH materials can be modified into hydrophobicity or super-hydrophobicity as previously showed [1]. In our work, dodecyl sulphate was introduced into the LDH structure as the compensation anions and the obtained material was tested as consolidant on test bricks.

**Materials and methods**: The LDH-DS were prepared by reconstruction of the calcined LDH in a solution containing the desired anion (DS). X-ray diffractometer with Cu-K α radiation (λ= 0.154 cm $^{-1}$), was used for the determination of the phase composition and crystallinity. Fourier-transform infrared spectrometry (FTIR), and Raman spectroscopy were used to identify functional groups of the prepared materials.

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

The colour of the treated sample was measured using a Konica Minolta-Chroma Meter CR-410 colorimeter.

**Results**: FTIR and RAMAN spectrum of the synthesized LDH-DS presents the specific peaks previously reported in the literature for pure LDH [2] with additional bands characteristic to the DS anion [3]. FTIR: The broad band located at 3500 cm $^{-1}$ arises from the stretching vibration of the hydroxyl groups of the layers, while the less pronounced band at 1632 cm$^{-1}$ is attributed to the bending vibration of water ($\nu_{H-O-H}$). Bands lower than 1000 cm $^{-1}$ could be assigned to the vibration mode of M–O, M–O-M, O-M-O, and metal hydrogen bond vibration modes, the additional bands at 2800-2950 and ~1200 cm $^{-1}$ are characteristic to the DS anion.

**Conclusions**: The consolidants, applied by brushing did not alter the colour of the test bricks, with only minor differences in chromatic parameters (ΔE* = 3) being observed after the treatment, difference that is not observable. The effect of the treatment on other properties will be further investigated.

***Acknowledgements**: This work was supported by a grant of the Romanian Ministery of Research and Innovation, PCCDI – UEFISCDI, contract no. 51 PCCDI/2018, within PNCDI III and through the Project PFE 15PFE/2021, **Supporting the competitiveness and excellence of INCDCP-ICECHIM research and innovation in the area of bioeconomy and related fields (**NeXT-BExcel).*

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# THIN FILMS BASED ON XANTHAN AND COBALT FERRITE FOR METHYL BLUE DYE ADSORPTION

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***Keywords: xanthan, cobalt ferrite, materials, dye removal, thin films***

**Introduction**: Rapid industrialization has caused increasing problems of environmental pollution. Organic dye solutions are widely used in different domains, such as textile, cosmetics, pharmaceutical or plastic industries [1]. New methods and systems have been developed to reduce pollution problems caused by organic dyes [2]. Thus, hybrid systems based on inorganic and organic compounds have been developed, combining the properties of both classes in one material. This study focused on the preparation of new systems based on xanthan and cobalt ferrite.

**Materials and methods**: Cobalt ferrite powder (CF) was prepared by co-precipitation method. Esterification of xanthan gum with acrylic acid was performed in order to increase its hydrophobic character. Further, CF powder was embedded in xanthan (XG) / xanthan acrylate (XGAC) matrix under ultrasonication, resulting new materials (XGCF and XGACCF respectively).

Fourier transform infrared (FTIR) spectrometer and a Scanning Electron Microscope (SEM) equipped with an energy dispersive spectrometer (EDX) were used for characterization of all materials. Swelling ratio were determined for all the thin films. Equilibrium, kinetic and thermodynamic studies have been performed to investigate the adsorption behavior of Methyl Blue (MB) from aqueous media at different dye solution concentration (10, 50 ang 70 mg/L).

**Results**: FTIR spectra confirm the presence of the main functional groups from the studied materials, while SEM images and EDX spectra revealed the morphological aspect and the elemental composition of the adsorbents. The swelling ratio in water of XG, XGAC, XGCF, and XGACCF was studied at different pH values (5.5, 7, 8, and 10). All the materials exhibited rapid swelling behavior, the process being pH sensitive. It seems that the protonation and deprotonation processes of carboxylate groups on the XG structure, as well as the chelation of CF particles with hydroxyl groups from the polymeric hydrogel, describe this different swelling behavior at different solution pH values.

The investigation of adsorption kinetics is helpful in predicting the adsorption rate and its mechanism. The correlation coefficients, $R^2$, of the pseudo-first-order kinetic model were found to range from 0.8467 to 0.9944 for the MB (50 and 70 mg/L) sorption. This indicates that physical adsorption is the dominant process for the MB adsorption experiments. XGACCF material shows the highest adsorption capacity for MB (65.56 mg/g). The adsorption equilibrium of MB onto CF and XGAC is best described by the Langmuir model, ($R^2$ presents values between 0.9260 and 0.9884). Also, the adsorption equilibrium of MB onto XG, XGCF, and XGACCF has been described by the Dubinin–Radushkevich model ($R^2$ values are in the range from 0.9124 to 0.9996). The effect of temperature on the adsorption capacity of the prepared materials was investigated at 295, 310 and 320 K, using a dye solution of 10 mg/L concentration. It was evidenced that the MB retention is an endothermic and spontaneous process.

**Conclusions**: Materials based on xanthan and cobalt ferrite were obtained and their adsorptive properties were studied. Batch adsorption experiments showed that the MB adsorption process followed pseudo-first-order kinetic model, the retention process being endothermic. By adding CF to the XG and XGAC matrix, the values of the percent removal rose by approximately 10%–15%. These results confirm the potential of the developed materials for application in wastewater treatment.

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# POLY(VINYLIDENE FLUORIDE)-BARIUM TITANATE NANOCOMPOSITES WITH IMPROVED INTERFACE

**Cătălina Diana UȘURELU[1], Denis Mihaela PANAITESCU[1*], Adriana Nicoleta FRONE[1], Cristian Andi NICOLAE[1], Monica RADULY[1], Laura ANDREI[2], Florin CIUPRINA[2]**

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***Keywords: microstrip antenna, barium titanate, nanocomposites, thermal properties, interface***

**Introduction**: With the intense development and infiltration of wireless technology in various fields such as medicine, environmental monitoring, internet of things, and defence, microstrip (patch) antennas received special attention. This is especially due to their relatively low fabrication cost, small size, light weight, conformity to both planar and non-planar surfaces, simple design, high-power levels, and ease of fabrication [1]. In the wireless communication systems, microstrip antennas play an essential role, representing the transducers capable of transmitting or receiving electromagnetic waves [2]. Constructively, a microstrip antenna consist of three layers: a top layer called "patch" which is made of a highly conductive material (most often a metal), a middle layer representing the dielectric substrate and a bottom layer called the "ground plane" which is a conducting surface made usually from metal. The dielectric substrate is very important in ensuring a suitable design and the best possible performance for the microstrip antennas. Particular interest as materials for the dielectric substrates of microstrip antennas has been directed towards the polymeric materials due to their electrically insulating nature, easy processing, light weight, good flexibility and stretchability, and satisfactory mechanical properties. Among polymers, poly(vinylidene fluoride) (PVDF) is preferred due to its higher permittivity, which, however, is not enough for antennas application. Therefore, barium titanate (BT) nanoparticles are usually added to improve its permittivity. The interface between PVDF and the nanoparticles plays an important role in achieving the expected performances of microstrip antennas. For this purpose, in this work, BT was surface treated with polyvinylpyrrolidone (PVP) and further mixed with PVDF for obtaining PVDF/PVP/BT nanocomposite films with potential applications as dielectric substrates for microstrip antennas.

**Materials and methods**: The PVDF/PVP/BT nanocomposite films were prepared via solution casting using dimethylformamide (DMF) as solvent followed by compression moulding. Further, differential scanning calorimetry (DSC) was used to investigate the influence of the BT treatment on the thermal transitions of PVDF. The dielectric spectra of the real part of the complex permittivity and of the loss tangent as functions of frequency were obtained by dielectric spectroscopy.

**Results**: The DSC analysis emphasized the influence of the treated BT nanoparticles on the glass transition temperature, melting temperature and the crystallinity of PVDF. In addition, the dielectric properties showed an improvement in the permittivity after the addition of surface treated BT in nanocomposites without altering their dielectric losses, which is important for microstrip antennas (Figure 1).

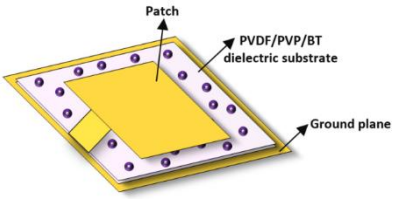


**Figure 1.** Design of a microstrip antenna where the dielectric substrate is based on PVDF/PVP/BT nanocomposites

**Conclusions**: The overall thermal and dielectric results showed the potential of considering the PVDF/PVP/BT nanocomposites as new materials for the manufacturing of dielectric substrates for microstrip antennas.

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# THE INFLUENCE OF CETRIMONIUM BROMIDE SURFACTANT ON THE SYNTHESIS AND MICROSTRUCTURE OF $PbCrO_4$

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***Keywords: lead chromate, precipitation, microemulsion, nanorods***

**Introduction**: Crystallized lead chromate is an inorganic compound well known as "chrome yellow" and which was widely used as a yellow compound in paints or in decorative systems [1]. The aim of this work is to emphasize the influence of the addition of different amounts of cetrimonium bromide (CTAB) surfactant on the microstructure of lead chromate ($PbCrO_4$).

**Materials and methods**: The materials applied in the present work for chrome yellow synthesis were lead (II) acetate, sodium chromate, and cetrimonium bromide. Lead chromate nanorods were prepared via precipitation technique, based on the reaction between $Na_2CrO_4$ and Pb $(CH_3COO)_2$. Using different amounts of CTAB in the microemulsion, we can control the size and morphology of lead chromate nanorods [2],[3].

**Results**:

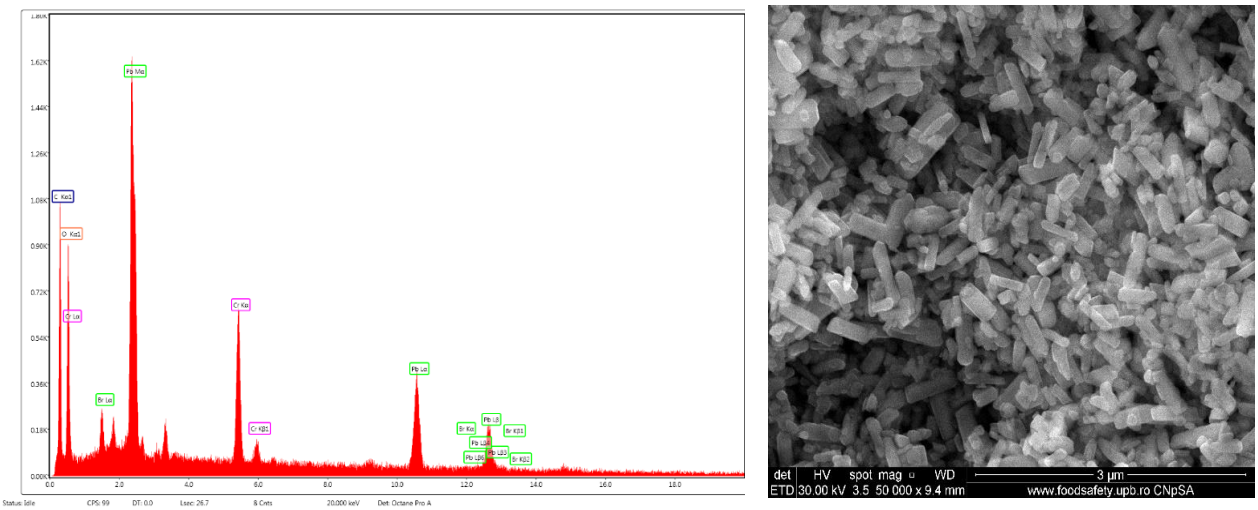


**Figure 1**. EDAX diagram (left) and SEM image for $PbCrO_4$ (right)

Based on the SEM micrographs with the addition of certain amounts of CTAB, the length of $PbCrO_4$ nanorods are reduced significantly from 934.8 nm (for the sample without cetrimonium bromide) to 403.9 nm, for the samples with the maximum amount of surfactant. The FTIR spectrum reflects specific bands (847-885 $cm^{-1}$) assigned to chromate groups present in the chemical structure of this pigments.

**Conclusions**:

Based on analytical techniques (FTIR, Raman, SEM and EDAX), could be concluded that the lead chromate nanorods were successfully obtained.

***Acknowledgements**: This work was supported by a grant of the Romanian Ministery of Research and Innovation, PCCDI – UEFISCDI, contract no. 51 PCCDI/2018, within PNCDI III and through the Project PFE 15PFE/2021, Supporting the competitiveness and excellence of INCDCP-ICECHIM research and innovation in the area of bioeconomy and related fields (NeXT-BExcel)***.

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# APATITIC MATERIALS ENHANCED WITH HEAVY METALS HAVING POTENTIAL ANTIMICROBIAL PROPERTIES FOR THE PRESERVATION OF CULTURAL HERITAGE

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***Keywords: nanomaterials, apatitic materials, cultural heritage***

**Introduction**: Nowadays, the idea of protection and preservation of cultural heritage is cultivated more than ever, so we can say that it has become synonymous with its conservation. Globally, people seem to be much more aware of this idea than in the past, the importance of cultural heritage and the fact that it must be preserved for future generations gained more attention in the last years. This new mentality is perfectly helpful due the weather conditions which are becoming more and more extreme, leading to the acceleration in the degradation of the cultural heritage (immobile cultural heritage). This problem has led to the development of various scientific fields in order to find new, innovative and versatile materials, efficient, cheap and easy to synthesize as possible solutions for the conservation of cultural heritage.

**Materials and methods**: The aim of this study is to present the synthesis of some apatitic materials substituted with heavy metals (Pb, Co, Cu, Zn) (**Figure 1**) by the method of co-precipitation at different molar ratios. The obtained materials were characterized by analytical methods (XRD, XRF, FTIR, TGA) and their antimicrobial efficiency was demonstrated.


**Figure 1**: Apatitic compounds substituted with heavy metals

**Results and conclusions**: The obtained results allowed us to conclude that the substituted materials have increased properties than simple apatitic compounds.

***Acknowledgements**: The authors gratefully acknowledge the financial support obtained through a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PTE-2019-0579, contract 61PTE/2020.The authors also acknowledge the support of the Ministry of Research, Innovation and Digitization through Program 1 - Development of the national research-development system, Subprogram 1.2-Institutional performance- Projects to finance excellence in RDI, Contract no. 15PFE/2021.*

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# MESOPOROUS SILICA-POLYPHENOL DELIVERY SYSTEMS WITH BIOMEDICAL APPLICATIONS

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***Keywords: polyphenol, mesoporous silica, controlled release***

**Introduction**: Polyphenols are secondary plant metabolites and are known to show beneficial properties in the human body, helping against various diseases such as diabetes, hypertension or even cancer [1]. However, many of these phenolic compounds exhibit a low bioavailability, due to their low aqueous solubility and stability in metabolic conditions. Resveratrol is such a polyphenol, having a poor-water solubility and showing promising results in cancer studies [2], [3]. Some of its drawbacks can be solved by encapsulation into a carrier, such as mesoporous silica, which has been shown to have good properties when it is used as vehicle for drug delivery. The beneficial features of silica are: high specific surface area and porosity, tuneable pore size and shape and possibility of functionalization, which lead to excellent adsorption properties [4].
In this study, several type of mesoporous silica carriers were used to encapsulate resveratrol and study their effects on its release profiles. The carriers were used in either a pristine form such as MCM-48, or in an organic functionalized form such as SBA-15-$NH_2$.
**Materials and methods**: Sol-gel method was used for the synthesis of the carriers followed by post-synthesis functionalization. Resveratrol was loaded through incipient wetness impregnation method. The resulted materials were characterized using several techniques such as X-ray diffraction, FT-IR spectroscopy and $N_2$ adsorption-desorption isotherms. A theoretical kinetic model was used to better describe the release profiles.
**Results**: The pore size of the silica-type carriers and their surface properties had a significant impact on resveratrol release profile.
**Conclusions**: The encapsulation of resveratrol in an amorphous state is promoted by small pore of mesoporous silica and depending on the functional groups linked on silica surface, a better interaction with the hydrophobic resveratrol molecules was achieved.

***Acknowledgements**: The financial support from UEFISCDI, project no. 525PED/2020 is greatly appreciated.*

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# COMPOSITE MATERIALS WITH IMMOBILIZED PEPSIN FOR WATER CLEANING

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***Keywords: silica microparticles, layer-by-layer deposition, enzyme immobilization, biocatalyst***

**Introduction**: Enzymes are protein structures that act as catalysts in biological processes. Unlike chemical catalysts, enzymes operate in milder conditions of temperature and pH, reason why their use in industrial processes is of growing interest [1]. The use of enzymes in large-scale processes is limited by their instability to temperature, pH and solvents and by their difficult recovery and reuse. For this reason, alternative methods have been sought to improve the characteristics of the enzymatic catalysis, with a reduction in the costs of using biocatalysts. In order to limit these disadvantages, as well as to increase the stability of enzymes in process conditions, the immobilization of enzymes was proposed. By immobilization, composite materials of different sizes and shapes are obtained, with different properties and characteristics, but with the main advantage of increasing the stability over time and under the reaction conditions of the biocatalyst [2]. This study proposes an economical and versatile method for enzyme immobilization leading to the fabrication of stable polymer/enzyme composite materials that can be further used in catalysis.

**Materials and methods**: The fabrication of composite materials was achieved through layer-by-layer deposition of branched poly(ethylene imine) (PEIB), poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMAA) on silica microparticles (SP1000 and SP2000, Daiso Co., Japan) of about 40-60 μm and different pore size (100 or 200 nm). The composites were stabilized by chemical cross-linking and then the polyacid chains were removed in strong basic media. The composite core/shell materials were characterized by polyelectrolyte and potentiometric titrations and were further used for the immobilization by sorption of pepsin, an endopeptidase involved in breaking down proteins to smaller peptides.

**Results**: The layer-by-layer deposition of PEIB and PAA or PMAA on silica microparticles led to the fabrication of stable composite materials, as demonstrated by the potentiometric titrations. The successful immobilization of the pepsin both on the PEIB/PAA and PEIB/PMAA composites and on those after PAA extraction was demonstrated, the amount of pepsin increasing after the extraction of polyacid chains, irrespective of the silica pore size and the number of organic layers (Figure 1).

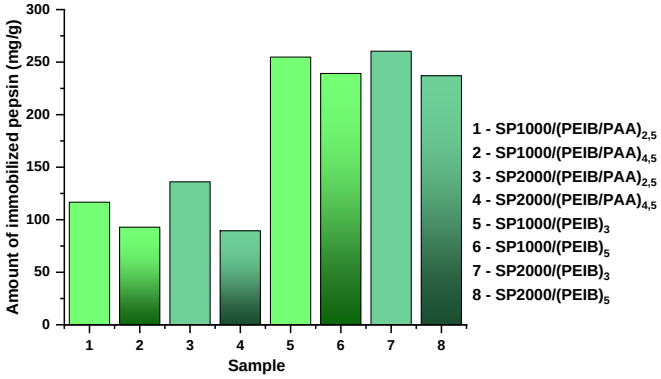


**Figure 1**. Amount of pepsin immobilized on Silica/$(PEIB/PAA)_n$

**Conclusions**: The successful immobilization of pepsin in layer-by-layer composite materials was achieved. The higher amount of enzyme immobilized after polyacid chains extraction demonstrates the affinity between pepsin and PEIB functional groups. The results recommend the enzyme/polymer composites for their potential use in catalytic and environmental applications.

***Acknowledgements**: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PED-2019-1996, within PNCDI III.*

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# RED-EMITTERS BASED ON DINUCLEAR CYCLOMETALLATED PALLADIUM (II) COMPLEXES

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***Keywords: Pd (II) complexes, luminescence, Schiff base, N-benzoylthiourea***

**Introduction**: Cyclopalladated compounds have interesting photophysical properties due to the strong ligand field imposed by the cyclometalated organic ligands and are excellent candidates for practical applications in the design of red-shift emitters and OLEDs [1],[2]. With the aim to enhance the emission efficiency, double cyclopalladated complexes were designed and investigated, that combine in one molecule the two cyclometalated units: the phenylpyridine and the Schiff base unit, with augmented rigidity. These complexes were prepared starting from the imine ligand, obtained by a condensation reaction between the 4-(2-pyridyl)benzaldehyde and the corresponding 4-aniline derivatives, followed by the treatment with palladium(II) acetate. Then, the previously resulting acetato-bridged complexes were mixed with the suitable N-benzoylthiourea compounds in order to develop the double cyclopalladated complexes [3].

**Materials and methods**: NMR ($^{13}C$, $^{1}H$) and IR spectroscopy were used to demonstrate that the desired compounds have been obtained. The luminescence measurements were performed in solid state and liquid state at room temperature. The phosphorescence quantum yields ($\Phi_{em}$) were estimated from the emission and absorption spectra by a comparative method using $[Ru(bipy)_3]Cl_2$ ($\Phi_{em}$ = 0.042, in water) as standard.

**Results**: All the compounds were obtained in good yields. The structure of Pd (II) complexes was confirmed by NMR ($^{13}C$, $^{1}H$) and IR spectroscopy. The double cyclopalladated complexes with square-planar geometry have the two Pd (II) ions in different coordination modes: one coordinated to the 2-phenylpyridine moiety and the second, in a similar cyclometalated design, coordinated to the imine core, the complete coordination of both being provided by the deprotonated BTU ligands. The solid-state and solution luminescent properties of the new complexes were studied at room temperature. The emission spectra have two maxima at $\lambda_{max}$ around 624-631 nm and 676-683 nm, respectively, as it can be observed in Figure 1. Interestingly, these complexes proved to emit in solution at room temperature, with the highest quantum yield of 0.003.

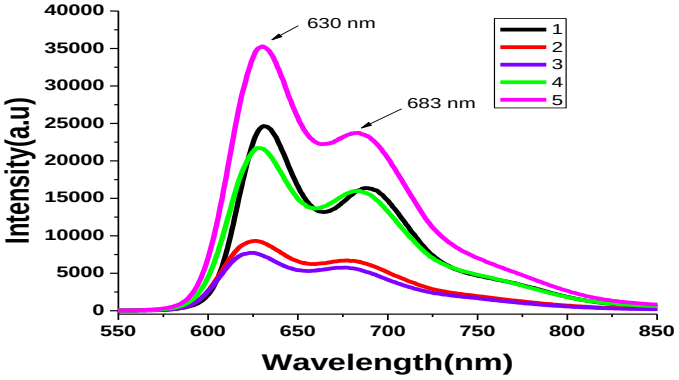


Figure 1. The solid-state emission spectra of palladium(II) complexes 1-5**.**

**Conclusions**: The cyclometallated Pd(II) complexes based on Schiff bases and N-benzoylthiourea (BTU) ligands show low emission quantum yields in dichloromethane solution and good photostability. Their emission properties were slightly affected by the different N-benzoylthiourea used as auxiliary ligands.

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# THE EFFECT OF LAYERED DOUBLE HYDROXIDES USED AS CORROSION INHIBITOR IN REINFORCED CONCRETE

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***Keywords: reinforced concrete, layer double hydroxide, corrosion***

**Introduction**: One of the major problems of the building constructions are the cracks caused by corrosion of metal from reinforced concrete structures. The metal normally is in a passive state against corrosion because the formation of a film layer on the interface with the high alkaline environment of concrete. But when anions migrate this process while induce depassivation and the next step is represented by corrosion [1]. It is well known the capacity of layered double hydroxides to capture anions like $Cl^-$, $SO_4^{2-}$ [2]. The study of this paper has the purpose to demonstrate the efficiency of adding a layered double hydroxide based on Mg and Al in reinforced concrete to delay the corrosion process for as long as possible.
**Materials and methods**: The brick samples with the dimensions of 29x9x3.5 cm was manufactured using a cement: sand: water ratio of 6:1:1 (w/w). The LDH was produced via a coprecipitation method which was describe in one of our recent studies [3] and have the molecular formula $Mg_{0.75}Al_{0.25}(OH)_2](Cl)_{0.25}$. They were incorporated in the mass of the brick in a 1% from total mass. The analysis was performed using a PROCEQ Resipod, this device being able to evaluate if the concrete allows corrosion to occur.
**Results**: The graphic representation (**Figure 1**) shows a real improved in corrosion resistance for the sample where LDH was added. The mean values were 1518.8, 302.5 and 811.7 kΩcm for the empty (without wire) sample, without LDH and with LDH respectively.

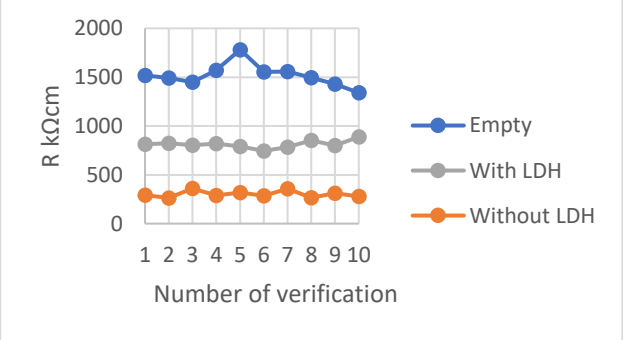


Figure 1. Graphic representation of corrosivity resistance

**Conclusions**: The class of LDHs can be used with significant results as inhibitor corrosion additives for reinforced concrete.

***Acknowledgements**: This work was supported by a grant of the Romanian Ministery of Research and Innovation, PCCDI – UEFISCDI, contract no. 51 PCCDI/2018, within PNCDI III and through the Project PFE 15PFE/2021, Supporting the competitiveness and excellence of INCDCP-ICECHIM research and innovation in the area of bioeconomy and related fields (Next-BExcel)*

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# INVESTIGATION OF AESTHETIC PARAMETERS OF MARBLE AFTER SHOCK THERMAL TREATMENT

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***Keywords: Cultural heritage, marble, thermal degradation, colour change, gloss value***

**Introduction**: Many of Romanian cultural heritage buildings are made of marble, this material however, when it is exposed to environmental factors will suffer a series of changes over time that compromises its physico-chemical properties. The aim of this paper is to study the changes in the aesthetic parameters of three types of marble (Ruschița, Albesti, Carrara) after their exposure to 20 cycles of high temperature (400 $^0$C).

**Materials and methods.** The samples were obtained by cutting large pieces of marble with a diamond blade. They were exposed to 20 high temperature cycles (according to BS EN 16306: 2013). The analysed samples are: black and white Carrara marble (CBWM), pink Rușchița marble (RPM) and white Albești marble (AWM). The thermal treatment is administered to the samples using a Nabertherm socket oven. The samples are first placed in the oven and then heated to 400 $^o$C at a speed of 5 °C / min, at atmospheric pressure. Samples were kept for 1 h at 400$^o$ C. After switching off the oven, the specimens were allowed to cool naturally. After 20 cycles, the samples surface was analysed by stereomicroscopy (with Euromex Binocular Stereomicroscope), by chromatical analysis (with a Konica Minolta CR-410 chromometer) and by glossometry (with Glossmeter HG268).

**Results:** Visual and stereoscopic analysis, revealed that exposure to high temperatures can cause the formation of microcracks and microfissures on the samples surface, changing the appearance of the specimens.

Colour analysis: Parameter values show a slight change in colour, which occurred at the end of the 20th heat treatment cycle.

Gloss analysis: Gloss reflects the ability of surfaces to reflect light. In this study, the gloss was measured at an angle of 60 degrees. During the 20 temperature cycles there were no major changes in gloss.

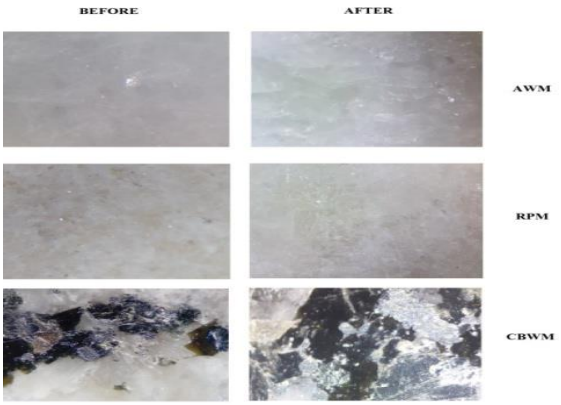


**Figure 1.** Stereomicroscopy images

**Conclusions**: Based on the results of this study, it could be concluded that the thermal cycles caused the mechanical disintegration of the outer part of the marble, starting from the discontinuities present in the rock and between the faces of the different minerals that form the stone. Also, the gloss and colour changes could indicate the damage degree of the marble.

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# DESIGN, CHARACTERIZATION AND LUMINESCENT PROPERTIES OF PALLADIUM (II) COMPLEXES WITH MIXED LIGANDS

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***Keywords: luminescence, palladium (II), Schiff base, N-benzoylthiourea***

**Introduction**: Palladium (II) cyclometallated complexes represent a limited family of emissive compounds that are chemically stable, and provide luminophores with strong and controllable ligand fields. The latter properties are essential because they may facilitate the synthesis of compounds in which low - lying metal - centred excited states required for room - temperature radiation less processes are deactivated. By judicious design, new palladium (II) complexes with high quantum yields and luminescence lifetimes can be obtained [1],[2].

**Materials and methods**: A series of cyclometalated palladium (II) complexes based on Schiff bases and N-benzoylthiourea ligands having different substituents at their periphery, with different number of carbon atoms, has been designed and prepared. The intermediates and the final compounds were characterized by $^{1}H$ and $^{13}C$ NMR spectroscopy and IR spectroscopy, while their thermal stability was studied by thermogravimetric analysis (TGA). The luminescence properties of palladium (II) complexes have been investigated both in solid and dichloromethane solution at room temperature. The phosphorescence quantum yields ($\Phi_{em}$) were estimated from the emission and absorption spectra by a comparative method using $[Ru(bipy)_3]Cl_2$ ($\Phi_{em}$ = 0.042, in water) as standard.

**Results**: The formation of the cyclometallated mononuclear complexes was confirmed by $^{1}H$-NMR spectroscopy where a pattern specific to 1,2,4,5-substitution of an aromatic ring can be seen as singlets for both signals; the absence of the absorption band in the range of 1610-1690 $cm^{-1}$, in the IR spectra of palladium(II) complexes, corresponding to the typical range for ν(C=O) stretching vibration, confirmed the coordination of the O atom together with S atom to the palladium ion. The results of the thermogravimetric analysis show that the complexes have a high thermal stability up to 260°C. These complexes show a yellow-orange solid-state emission at room temperature with two emission maxima at $\lambda_{max}$ around 590 and 640 nm, respectively, with a shoulder around 710 nm, when the samples are irradiated at 375 nm.

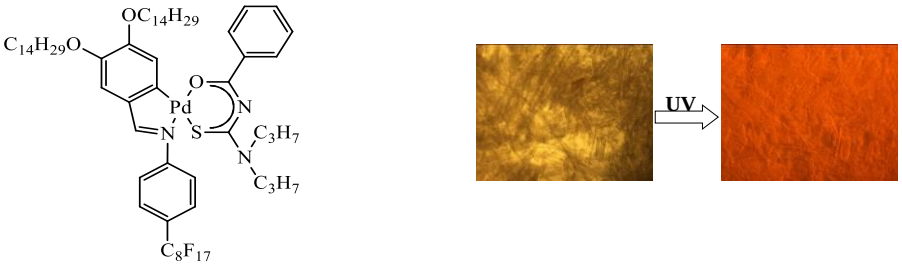


**Figure 1.** Structure of palladium (II) complex and POM pictures in normal light and under UV light.

**Conclusions**: This study represent one of the few examples that provide room-temperature luminescent palladium (II) complexes based on Schiff bases. The quantum yields of the palladium (II) complexes, recorded in non-degassed $CH_2Cl_2$ were found in the range 0.19%–0.22%.

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# COBALT-BASED METAL-ORGANIC FRAMEWORKS CONTAINING DICHROMATE AND CHROMATE ANIONS AS SPACERS

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***Keywords: coordination polymers, bidentate ligands, self-assembly, metal-organic frameworks***

**Introduction**: Due to their wide range of uses, extensive study has indeed been committed to the synthesis and analysis of MOFs. MOFs are excellent in storing, separating, and transporting gases, as well as water absorption, catalysis, luminescence, magnetism, and medication delivery [1]. Porous coordination polymers (PCPs) are known for their great applications in heterogeneous catalysis, drug delivery, magnetism, gas adsorption, separation and storage etc. due to their structural properties, namely: high regularity, tuneable pore sizes, and high surface area [2], [3].

**Materials and methods**: The chemicals used for the synthesis of the complexes were cobalt perchlorate hexahydrate ($Co(ClO_4)_2 \cdot 6H_2O$), exo-bidentate bipyridine-based ligands, such as 4,4'-bipyridyl (bipy), 1,2-bis(4-pyridyl)ethane (bpa), 1,2-bis(4-pyridyl)ethylene (bpe), **1,3-bis(4-pyridyl)propane (bpp), as well as** ammonium dichromate ($(NH_4)_2Cr_2O_7$) and potassium chromate ($K_2CrO_4$)**.** Reagents and solvents were purchased from Sigma-Aldrich, being characterized by high purity. The elemental analysis was performed using the Euro EA Elemental Analyzer (Euro Vector) and Callidus software. Molecular structures were determined by single-crystal X-ray diffraction with a Rigaku XtaLAB Synergy S diffractometer using SHELT-2018 and Diamond 3.2 software for calculations and graphical representations. A XRD Benchtop Powder Diffraction system was used to acquire the powder diffraction data, which were processed with NIST software. IR spectra were recorded on a Bruker Fourier Transformance Tensor V-37 spectrophotometer, using OPUS software. Solid-state electronic spectra were recorded using the UV-Vis-NIR Jasco V670 spectrophotometer, equipped with Spectra Manager software. Thermal analysis measurements were accomplished using a thermal analyser Netzsch STA 409 PC connected with a Bruker Tensor 27 FTIR spectrophotometer equipped with a gas cell. The experimental data were resolved using the Proteus software.

**Results**: The self-assembly of polymeric networks from cobalt(II) salt and different N-donor ligands: bipy, bpa, bpe, and bpp along with $Cr_2O_7^{2-}$ and $CrO_4^{2-}$anions, has been systematically investigated in order to obtain some basic information useful for the crystal engineering of coordination frames upon variation of the spacers. The crystal structures of the resulting assemblies have been determined and the intermolecular interactions of the compounds in the crystalline phase have been investigated. The new synthesized compounds present neutral tridimensional networks with various topologies. Crystal-structure packing model of $[Co(bipy)_2(Cr_2O_7)]_n$ is represented in **Figure 1**.

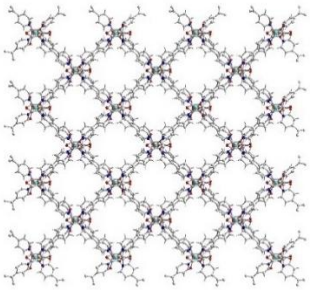

**Figure 1.** Crystal-structure packing model of $[Co(bipy)_2(Cr_2O_7)]_n$

**Conclusions**: Herein we report the synthesis and physicochemical characterization of a new series of Co(II) coordination polymers with both organic and inorganic spacers. The obtained compounds were analysed by elemental analysis, **single-crystal and powder X-ray diffractions, different spectroscopic techniques, such as FTIR and UV-Vis, as well as thermal analysis**.

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# ADSORPTION STUDIES OF IBUPROFEN AND PHENOL FROM AQUEOUS SAMPLES USING PHOSPHATIC MATERIALS

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***Keywords: phosphatic materials, ibuprofen, phenol, adsorption, water depollution***

**Introduction**: Rapid industrialization and population growth have led to the globally contamination of most water resources, thus increasing the demand for drinking water. The discharge of industrial effluents from the agricultural, pharmaceutical and textile industries, is improper, sometimes even illegal. The disposal of waste and the discharge of leachate from landfills are just a few examples of environmental pollution sources. Non-steroidal anti-inflammatory drugs and phenolic compounds are widely found in the aquatic environment, in significantly high concentrations [1],[2].

**Materials and methods**: In this study, we have prepared two partially metal-substituted hydroxyapatite adsorbents, with Ba and Mn, using $MnCl_2$ and $BaCl_2 \times 2H_2O$, at different molar ratios, based on a recipe previously presented by our group [2]. The obtained compounds were calcinated at 300°C, thus obtaining four materials, which have been considered in the following studies. In order to make sure that the adsorbents have the desired properties, we have characterized them through modern analytical methods (**Figure 1**). Adsorption studies were also performed to demonstrate the effectiveness of the materials used at different concentrations, in order to remove ibuprofen and phenol from aqueous samples.

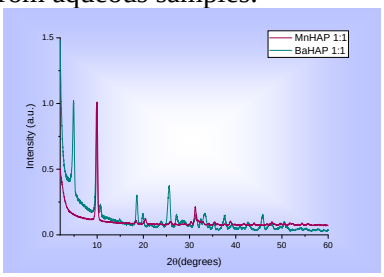


**Figure 1**. X-Ray analysis of BaHAP and MnHAP

**Results**: The obtained materials present the desired properties, and, also, they showed good results regarding Ibuprofen and phenol adsorption from the prepared aqueous solutions. The higher uptake concentration of ibuprofen was obtained in the case of calcined MnHAP, while, in the case of phenol adsorption, BaHAP showed the best results. Overall, we obtained significant results for all the obtained materials.

**Conclusions**: Considering all the obtained analytical data, the synthesized phosphatic materials represent potential candidates as adsorption materials for environmental depollution.

***Acknowledgements**: The authors gratefully acknowledge the support obtained by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI—UEFISCDI, project No PN-III-P2-2.1-PED2019-3166, contract 299PED/2020 within PNCDI III, and by a grant of Romanian Ministry of Research, Innovation and Digitization Research and Innovation MCID (Ministry of Research and Innovation MCI) through INCDCP ICECHIM Bucharest 2019-2022 Core Program PN. 19.23 - Chem-Ergent, 2018 Project No.19.23.03. The authors also acknowledge the support of the Ministry of Research, Innovation and Digitization through Program 1 - Development of the national research-development system, Subprogram 1.2-Institutional performance- Projects to finance excellence in RDI, Contract no. 15PFE/2021.*

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# PHYTOSYNTHESIS OF MONO AND BIMETALLIC NANOSTRUCTURES USING VINE SHOOTS EXTRACTS – CHARACTERIZATION AND AMTIMICROBIAL EFFECT

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***Keywords: green synthesis, viticultural waste, phytochemicals, nanostructures, antimicrobial effect***

**Introduction**: In Europe, Romania represents the 5th country in terms of wine-growing area, with over 150,000 hectares of vines used for wine production [1]. On the one hand, pruning practice plays an important role in vine's development and implicitly in obtaining high quality grapes, but it produces considerable quantities of vine shoots and canes which are classified as waste. On the other hand, in these residues large amounts of phytochemicals are found, that may have further applicability in other industries such as cosmetics, medical and even food [2]. The aim of the current study is to present two different extraction methods (classical and modern) of bioactive compounds from autochthonous vine shoots, in order to obtain both mono-metallic (AgNP) and bi-metallic (Ag-AuNP) nanoparticles with antimicrobial and antioxidant effects.
**Materials and methods**: In order to extract the phytochemicals from vine shoots, two methods of solid-liquid extraction were approached, namely a classical one, at temperature, and a modern method with microwave digestion system (MILESTONE ETHOS EASY), being applied a solid / liquid ratio of 1:10 (w/v). The Folin Ciocâlteu spectrophotometric method was chosen to determine the total phenol content and for the evaluation of the antioxidant capacity of extracts and the phytosynthesized mono-metallic and bi-metallic nanoparticles, the DPPH test was used. Furthermore, UV-VIS spectrometry was used to evaluate the formation of nanoparticles in the wavelength range of 300-700 nm. To visualize the size and shape of mono-metallic and bi-metallic nanostructures, Transmission Electron Microscopy (TEM) was performed. The antimicrobial activity of extracts, mono-metallic and bi-metallic nanoparticles was determined on gram-positive, gram-negative and fungi strains.
**Results and conclusions**: The obtained results suggest the formation of Ag-NP and Ag-Au-NP with extracts obtained through both extraction methods. Also, it can be concluded that the microwave extraction method, compared to the classical one, significantly improves the recovery of phenolic compounds from viticultural wastes, in order to obtain mono-metallic (AgNP) and bimetallic-nanostructures (Ag-Au-NP) with significant antioxidant and antimicrobial activity, which can be successfully used for further applications.

***Acknowledgements**: The authors gratefully acknowledge the financial support obtained through grants of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P3-3.5-EUK-2019-0226, contract 220/2020, and project number PN-III-P2-2.1-PED-2019-3166, contract 299PED/2020, within PNCDI III. The authors also acknowledge the support of the Ministry of Research, Innovation and Digitization through Program 1 - Development of the national research-development system, Subprogram 1.2-Institutional performance- Projects to finance excellence in RDI, Contract no. 15PFE/2021.*

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# CHIRAL COBALT(II) COMPLEXES BASED ON CARBOXYLATO AND AMINOALCOHOLS LIGANDS

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***Keywords: metal clusters, carboxylato ligands, chiral complexes***

**Introduction:** Chirality is a fundamental feature of the living world. The most used synthetic strategy for introducing the chiral information into a metal-ion based network consists of choosing of an enantiomerically pure ligand [1]. In this respect, the usage of lactic acid as chiral precursor is a simple and practical alternative. In addition, carboxylates and amino alcohols complexes have a wide range of potential applications in materials science, catalysis and molecular magnetism.

**Materials and methods:** Following this idea, we present herein new Cobalt(II) chiral compounds with different dimensionalities. The complexes were synthesized using cobalt perchlorate ($(Co(ClO_4)_2 \cdot 6H_2O)$), triethanolamine ($H_3$tea), lactic acid (lac) and triethylamine ($Et_3N$) for deprotonation.

**Results:** Changing the molar ratio between the ligands and metal ions affords discrete compounds (mononuclear or tetranuclear complexes) and monodimensional cobalt(II) coordination polymer with helical topology. Electronic and circular dichroism spectra were also performed according to their relevance for each compound.

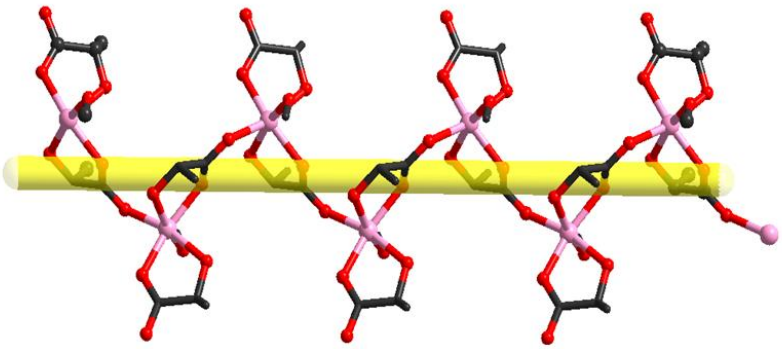

Fig.1 Structure unit in helical cobalt(II) coordination polymer

**Conclusions:** The crystal structure of the compounds confirm the presence of the Cobalt(II,III) metal ions and homochirality of the complexes. The dichroism spectra suggest the transfer of the chirality from the ligand to metal centers.

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

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# RELEASE STUDIES OF TETRACYCLINE FROM ZWITTERIONIC CROSSLINKED COPOLYMER WITH CARBOXYBETAINE UNITS

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***Keywords: porous microparticles, zwitterionic polymer, drug delivery, tetracycline***

**Introduction**: Crosslinked porous microparticles have received great attention as drug delivery systems due to their unique set of properties: the capability to form various polymer-drug combinations, low toxicity, low immunogenicity, patient compliance, and ability to release drugs in a delayed or controlled manner [1]. Polymers having betaine groups (both cationic and anionic groups in the same structural unit) show some unique features such as antifouling, antimicrobial activity, biocompatibility, and strong hydration properties [2]. This study aims to obtain zwitterionic porous microparticles with betaine units, with a spherical shape, high specific surface area, swelling and sorption capacities adapted especially for drug delivery applications.
**Materials and methods**: The zwitterionic porous microparticles were prepared by suspension polymerization technique followed by the betainization reaction. The synthesis of zwitterionic porous microparticles took place in two stages. The first step involves the synthesis of porous microparticles by suspension polymerization using glycidyl methacrylate (GMA), N-vinylimidazole (NVI) and four types of crosslinking agents, such as ethyleneglycol dimethacrylate (EGDMA), diethyleneglycol dimethacrylate (DEGDMA), triethyleneglycol dimethacrylate (TEGDMA) and divinyl benzene (DVB). The impact of different reaction parameters (monomer ratio, types of crosslinking agents, types of diluents, crosslinking degree) on the reaction yield and microparticles swelling capacity in different solvents was studied to find the optimal conditions for the synthesis. Microparticles with monomer ratio GMA:NVI:TEGDMA = 40:30:30 (mol:mol) and toluene as the porogenic agent were chosen for further transformation. The second step was the synthesis of zwitterionic porous microparticles by polymer-analogous reactions in the presence of sodium monochloroacetate as betainization agent. The microparticles were characterized by FTIR spectroscopy, thermogravimetric and elemental analyses, particle size distribution as well as surface morphology. The microparticles were loaded with tetracycline, and the concentrations of the drug in the supernatant solutions, before and after sorption, were determined using UV-Vis spectrophotometry based on a calibration curve.
**Results**: The results showed that depending on the reaction parameters, particles of micrometric size with different structures and properties can be obtained. The tetracycline loading into zwitterionic porous microparticles was also followed. The tetracycline can interact with functional groups belonging to the crosslinked network chains through ionic and physical interactions. The maximum tetracycline loading capacities onto porous and zwitterionic porous microparticles were: 87 mg/g and 135 mg/g, respectively. To elucidate the drug transport mechanism involved in the release process of tetracycline from zwitterionic porous microparticles, various models were applied: Higuchi, Korsmeyer-Peppas, and Baker-Lonsdale models. The release of the drug takes place gradually *via* the dissociation of ionic interactions followed by the diffusion of the drug through pores.
**Conclusions**: Zwitterionic porous microparticles are suitable drug carriers due to their high surface area and good drug load-release capabilities. Tetracycline can be loaded on the zwitterionic beads due to both physical and chemical interactions. Korsmeyer-Peppas diffusion coefficient is approx. 0.6 suggesting a non-Fickian transport mechanism.

***Acknowledgements**: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1541, within PNCDI III.*

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# STRUCTURAL DIVERSITY OF NEW POLYNUCLEAR COORDINATION COMPOUNDS WITH ORGANOTIN(IV) KNOTS

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***Keywords: polynuclear coordination compounds, organotin knots, synthesis and characterization, structural diversity***

**Introduction**: In addition to their medicinal and pesticidal impact, tin compounds have a fascinating solution and solid phase chemistry, which led to countless publications, reviews and books based on structural elucidation in both phases [1][2][3][4].

**Materials and methods**: Synthesis of the crystals was done through slow evaporation. X-ray diffraction on single crystal, elemental analysis, as well as spectroscopic technique, FTIR, were used to obtain the required data for characterization. The elemental analysis of the obtained compounds was performed using the Euro EA Elemental Analyzer (Euro Vector) using a Callidus software. IR spectra of all samples were recorded in the range of 4000-400 $cm^{-1}$ using a Bruker Fourier Transformance Tensor V-37 spectrophotometer, using OPUS software and KBr as reference. The single-crystal X-ray diffraction was performed using the STOE IPDS II diffractometer using the SHELX-97 and Diamond 3 software.

**Results**: In this work, a new series of coordination compounds with different organotin(IV) subunits as knots and organic bridging ligands as spacers have been synthesized and characterized. The crystal structures of the resulting assemblies have been determined and the intermolecular interactions of the compounds in the crystalline phase have been investigated. The structural characterization of the new compounds conducted to a large structural diversity, obtaining 0-D, 1-D, 2-D, and 3-D structures (an example is given in Figure 1). The influence of the nature of organotin(IV) knots and the bridging ligands on the structural properties of the new systems obtained was investigated. The ligands, metal precursors and their corresponding organotin(IV) complexes have also been screened for antimicrobial activities.

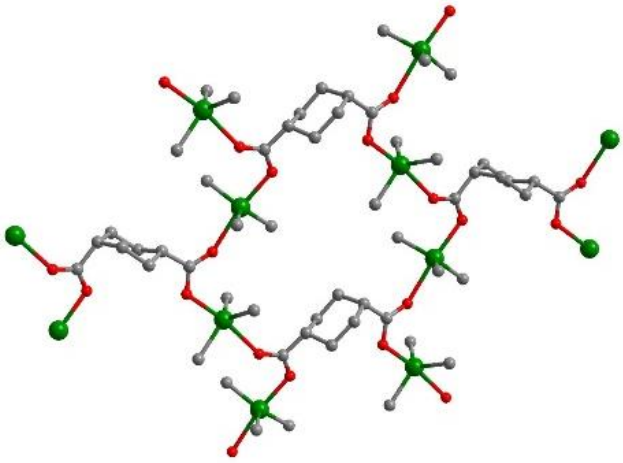

Figure 1. Crystal structure of $[Sn(Bu)_3(1,4\text{-}CHD)_{0.5}]_n$

**Conclusions**: The influence of organotin(IV) nodes on the dimensionality of the obtained polynuclear coordination compounds with different linkers was investigated. The biological activity of all obtained compounds is under investigation.

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# STUDY OF ANTIMICROBIAL ACTIVITY OF ZNO NANOPARTICLES WITH DIFFERENT SIZE AND MORPHOLOGY

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***Keywords: ZnO, nanoparticles, photocatalysis, reactive oxygen species, nanoflowers, antibacterial***

**Introduction**: Zinc oxide is a well-known semiconductor and an efficient photocatalyst that is also more environmentally friendly and biocompatible than other widely used photocatalysts such as $TiO_2$, CdSe, and SnO2[1]. However, the fact that it absorbs light with a photon energy of more than its bandgap (3.37 eV), which corresponds to light with a wavelength of less than 375 nm (UV), makes it a poorer choice as less than 3% of solar light reaching the ground is in the ultraviolet range. As a photocatalyst, zinc oxide is used for the photodegradation of organic pollutants [2], dye sensitized solar cells [3], photodynamic therapy and photocatalytic disinfection among others. The photocatalytic antibacterial and antitumoral activity of ZnO is due to the generation of highly reactive oxygen species (ROS) upon illumination such as hydroxyl radical, superoxide anion and singlet oxygen [4]. The photocatalytic properties of ZnO, and thus the antibacterial activity can be improved by altering the size, morphology and the dopant used, making it suitable for use in the visible range

**Materials and methods**: Zinc nitrate hexahydrate, sodium hydroxide, sodium citrate and ammonia solution were used as reagents. The morphological features were determined by scanning electron microscopy (SEM), the size and the size distribution were investigated by dynamic light scattering (DLS), the crystallinity and size by XRD and the photophysical properties by UV-Vis and fluorescence spectroscopy.

**Results**: In this study, we synthesized zinc oxide nanoparticles by hydrothermal method, precipitation method and also by a microwave assisted method. The resulting ZnO NP's morphology, size, photophysical properties and antibacterial activity were investigated. We also evaluated the generation of ROS upon illumination. The particles formed large aggregates confirmed by a high polydispersity index. The nanoparticles formed nanoplates and flower-like structures, as it can be observed in **Figure 1**.

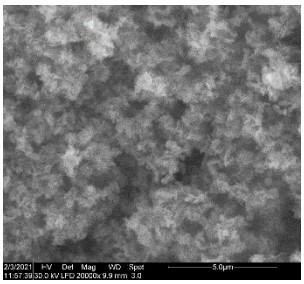

**Figure 1.** SEM image of ZnO prepared in 1M citric acid

**Conclusions**: According to the experimental results, we have concluded that the reaction conditions have an important role on the size, size distribution and the morphology of the NP's. Therefore, the photocatalytic properties of the resulting nanoparticles are strongly influenced by the characteristics previously mentioned.

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# Session 2 - Bioresources, biotechnologies and biorefinery

# LIGHT EFFECTS ON SUPERNATANT PROPERTIES OF *TRICHODERMA ATROVIRIDE*

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***Keywords: Trichoderma, plant germination, phytotoxic, cerato-platanins, supernatant***

**Introduction**: The introduction of beneficial microorganisms in crop production systems is known as a good sustainable strategy to ensure competitive yields in many crops and to improve the resource use efficiency[1]. *Trichoderma* spp. are soil-borne fungi that have developed the ability to establish a beneficial symbiosis with plants[2]. It promotes plant growth through various mechanisms, such as increasing phytohormone synthesis, nutrient absorption and translocation, increasing root development, the rate of carbohydrate metabolism and photosynthesis[3]. Proteins from *Trichoderma* such as cerato-platanins (CPPs) and cellulases act as elicitors in plants and can stimulate the induction of defence responses in plants[4]. CPPs are amphiphilic proteins that can self-assemble at hydrophobic/hydrophilic interfaces. The aim of this study was to test the influence of laser light on the characteristics of *Trichoderma atroviride* supernatant (SN), including its effect on plant germination, hydrophobic-hydrophilic/amphiphilic balance, cellulase activity and capacity to degrade filter paper.

**Materials and methods**: *T. atroviride* were incubated in basal medium (BM) supplemented with 5% w/v whey and 1% w/v yeast extract and irradiated after 5 days of growth with a blue laser source (400 nm) at 0,398 µmole/$m^2$·s intensity for 5 min. The strain was further incubated for 72h after which the SN was sterile filtered and its effect on seed germination of *Sorghum saccharatum* and *Sinapis alba* was investigated: germination rate, root and shoot length, root proton pump on agar medium + bromocresol purple, and total reactive oxygen species (ROS) by nitro blue tetrazolium (NBT) staining test and ImageJ analysis. Surface tension and contact angle on hydrophilic and hydrophobic surfaces of SN was determined with OCA 50 EC, DataPhysics, Germany. The capacity of SN to degrade filter paper was tested on Whatman no.1 filter paper by incubating at 38°C with shaking at 320 rpm for 3 days.

**Results**: *Trichoderma* SN does not have significant impact on seed germination. The SN had significant effect on roots and shoots of *S. alba*, with root inhibition and shoot stimulation, but radiation of SN did not influence this effect. *Trichoderma* SN, especially the irradiated one, stimulated the root lateral branches of *S. alba*. In the case of *S. saccharatum* the root was not significantly influenced by SN, but irradiated SN induced higher inhibition of the shoots than non-irradiated SN. The root proton pump was slightly stimulated by SN, and the root ROS production was slightly inhibited by SN, especially by the irradiated one. Both irradiated and non-irradiated SN had lower surface tension (42.91 mN/m and 49.06 mN/m, respectively) than the non-inoculated culture medium (51.6 mN/m), but laser significantly reduced the value. Irradiation of SN had significant effect on contact angle, on cellulase activity and on filter paper degradation.

**Conclusions**: The influence of laser light on surface tension and contact angle of SN suggests higher production of amphiphilic species which could be responsible, together with the influence on cellulase activity, for the effects on seed germination and filter paper observed.

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# BIOACTIVE AND CYTOCOMPATIBLE POLYPHENOLS AND PEPTIDES FROM SPENT PLEUROTUS SUBSTRATE

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***Keywords: polyphenols, peptides, biocompatibility, antioxidant activity, antibacterial activity***

**Introduction**: Spent *Pleurotus* Substrate (SPS), made of partially degraded lignocellulosic material interwoven with *Pleurotus* mycelium, is a valuable source of bioactive compounds. It is well known that oxidative stress is associated with tissue damage [1]. The aim of this study was to obtain bioactive polyphenols and peptides from SPS for tissue regeneration.

**Materials and methods**: The proteins from SPS were extracted in water by orbital shaking, after which alkaline polyphenols extraction was applied to the sediment. The polyphenols were subjected to ethyl acetate liquid-liquid extraction, N2 drying and resuspension in 50% ethanol. The molecular weights of the proteins were analysed by SDS-PAGE. The protein extract was subjected to tangential ultrafiltration and also to enzymatic hydrolysis in order to obtain different peptide fractions. Antioxidant activity was assessed by a method that include single electron transfer i.e., DPPH [2]. The samples were further characterized using Fourier transform infrared spectroscopy (FTIR). Biocompatibility tests were performed on dermal fibroblasts (CCD-1070Sk, ATCC). Cell viability and proliferation were assessed after 24 and 48h by combining LIVE/DEAD and CCK-8 assays. The cytoskeleton was observed by labelling actin filaments with Alexa Fluor 488-conjugated phalloidin and the nuclei were marked with DAPI. For the *in vitro* cellular antioxidant effect, the cells were exposed to ferrous sulphate (positive control) as an inductor of reactive oxygen species (ROS). Antioxidant activity was determined after 24h of cell culture by labelling and quantifying total ROS with 2',7'-dichloro-dihydro-fluorescein diacetate (DCFH-DA). The antibacterial activity was tested against *Pseudomonas aeruginosa* (ATCC 27853) and *Escherichia coli* (ATCC 25922) strains by the diffusimetric method.

**Results**: The SDS-PAGE profile showed a tight distribution of molecular weight (MW) of proteins, with several intense bands under 5 kDa. The combined FTIR band of -$NH_2$ at 1645 $cm^{-1}$ with -OH at 1636 $cm^{-1}$ confirmed the proteic character of the aqueous extract. The alkaline extract had specific bands at 1084 $cm^{-1}$ for Ar-OH, at 1043 $cm^{-1}$ for C-O-C, respectively at 878 $cm^{-1}$ for the aromatic ring Ar, confirming polyphenols as the major component. The extracts were biocompatible for all the tested concentrations and the cells kept their characteristic phenotype. High antioxidant activity was observed for the highest tested concentrations, especially in the case of polyphenols, which induced 50% reduction of ROS in the cells compared to the stressed cells (Figure 1). The alkaline extract showed significant antibacterial activity against selected strains for the highest tested concentrations.

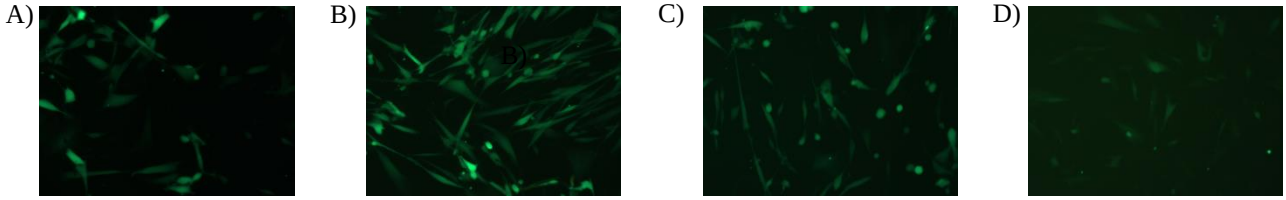


Figure 1. *In vitro* cellular antioxidant activity. A) Untreated cells (negative control), B) Ferrous sulphate (ROS inductor) treated cells (positive control), C) Peptides-treated cells and D) Polyphenols-treated cells after 24h of fibroblast exposure (in the presence of ROS inductor)

**Conclusions**: The high degree of biocompatibility as well as increased antioxidant and antibacterial activities prove that polyphenols and bioactive peptides from SPS are potential candidates for various biomedical applications.

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# COMPUTATIONAL ANALYSIS OF THE PRESENCE OF SELENOCYSTEINE IN THE CHLOROPLASTGENOME OF LAND PLANTS

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***Keywords: selenocysteine, tRNA-Sec, selenoprotein, land plants, computational***

**Introduction**: Selenium plays an important role in maintaining redox balance, immune function and defending against cancer [1]. These effects are the result of the conversion of selenium into selenocysteine (Sec), considered the 21st amino acid of the genetic code, encoded by the UGA codon and which in the ribosome is cotranslationally inserted into a special category of proteins called selenoprotein. Selenocysteine was identified in most domains of life but current data suggest a lack of the aminoacid in the genome of higher plants [2],[3].
The aim of this study was to explore the chloroplast genome of land plants in order to identify possible traces of the selenocysteine insertion machinery in their genome sequences.
**Materials and methods**: A series of chloroplast genomic sequences from various categories of land plants were acquired from NCBI Gene database in FASTA format. We used a range of computational tools: ARAGORN, tRNAscan-SE, SECISearch3 and Secmarkerto predict and observe the Sec machinery genes in the analysed genomes [4],[5]. The sequence of possible tRNA-Sec genes and identified SECIS elements were aligned and analysed through the use of MEGA 11 software.
**Results**: Two of the selenocysteine scanning software used (ARAGORN and tRNAscan-SE) showed an absence of tRNA-Sec structures in the analysed genome. Instead, using the aforementioned software, we identified tRNA-Cis genes in these sequences, analogues of selenocysteine. Using SECISearch3 we identified SECIS elements in most of the scanned sequences. SecMarker software was able to identify the presence of possible tRNA-Sec structures in several embryo phytogenomes. Our attempt to identify selenoprotein in the analysed genomic sequences did not show any positive results.
**Conclusions**: A number of bioinformatics software was used to predict tRNA-Sec and SECIS in the chloroplast genome of several higher plants. This study highlights the importance of the chosen prediction program used to detect selenocysteine in these genomes. An in-depth genomic analysis is needed to make correct assumptions about the presence of Sec in the chloroplast genome of land plants.

***Acknowledgements**: The work on this paper was supported by the Government of Romania, Ministry of Research and Innovation, Project RO-NO-2019-540," Integrated use of the next generation plant biostimulants for enhanced sustainability of field vegetable high residue farming systems – STIM4+."*

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# BIOMINERALIZATION POTENTIAL OF UREOLYTIC FUNGI FOR BIOGENIC CONCRETE REPAIR

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***Keywords: ureolytic fungi, filamentous fungi, biomineralization, bioconcrete***

**Introduction**: As concrete is widely used for construction purposes, research aims to create sustainable solutions for improving its structure and durability, thus emphasizing its susceptibility to cracks. In this regard, microbial induced calcium carbonate precipitation has been carried out. Although extensively studied, the use of bacteria is limited by significant decrease in cellular viability over time, inability to precipitate large amounts of calcium carbonate in order to repair wide cracks, and the reduction of the compressive strength of concrete [1]. Therefore, in recent years, there has been widespread interest in fungi, due to their high biomass yield and extensive mycelium networks which could consequently lead to increased amounts of precipitated $CaCO_3$[2]. The aim of this study was to test the potential of urease-positive filamentous fungi to undergo $CaCO_3$ precipitation for further applications in the biogenic healing of concrete.

**Materials and methods**: Seven fungal strains were isolated from concrete samples through the framework of project PED 392/2020 and identified by MALDI-TOF mass spectrometry, followed by quantitative and qualitative screening for ureolytic activity and assay of the carbonate precipitation ability. The ureolytic activity was determined on modified Christensen's agar medium [3]. The samples were observed on the third and sixth days after inoculation and further evaluated based on the colour intensity and rate of the enzymatic reaction [3],[4]. The fungal potential to precipitate $CaCO_3$ was tested on liquid urea-$CaCl_2$ medium [5] and observed by microscopical analysis after 14 days of incubation. Urease activity was quantified based on Nessler method and spectrophotometric analysis at wavelength of 436 nm.

**Results**: The isolated fungi were identified belonging to following genera: *Penicillium spp (A1), Chrysosporium spp (A2), Aspergillus spp (B2), Alternaria spp (C3), Arthrinium spp (F8), Torula spp (G1), Stachybotrys spp (G2)*. Performing quantitative analysis, strong urease activity, represented by a change of colour of the medium into deep pink after three days of incubation, has been identified for strains G1, A2, A1. A moderate activity, represented by a complete change of colour after six days of incubation was observed for strains C3 and respectively G2. Following qualitative analysis, high amounts of $NH_3$ associated with urease activity were identified by decreasing order for strains G2, C3, A2, G1, A1. Also, for all urease-positive fungi numerous carbonate crystals were observed by microscopical observations.

**Conclusions**: Our study successfully identified the potential of five fungi isolated from concrete as biomineralization agents for $CaCO_3$ precipitation, due to the strong and moderate urease activity and to the presence of carbonate crystals in the liquid media. Further studies will examine the effect of fungal cells on the mechanical properties of cement mortar.

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# BIOACTIVE PEPTIDES FROM FRESHWATER FISH PROTEIN HYDROLYZATE USED FOR NEW FOOD SUPPLEMENTS

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***Keywords: bioactive peptides, fish collagen, protein hydrolysate, food supplements***

**Introduction**: Marine and freshwater fish collagens can be extracted from various industrial by-products, such as bone, head, scales and skin, generated by processing factories all over the world in large amounts (50-70% from each fish). They are similar to bovine and porcine collagens, in terms of amino acid composition and biocompatibility, but have the advantage of being more available as a biological source [1]. Recent focus was on collagen-derived bioactive peptides with low molecular weight, which presented high penetration into the skin [2], rapid digestion and export into the bloodstream [3].

The aim of this work was to prepare and characterize bioactive peptides with low molecular weight from freshwater fish collagen and to investigate their effect within novel food supplements.

**Materials and methods**: Collagen was extracted from freshwater fish by-products using enzymatic hydrolysis with pepsin. Subsequently, fish collagen was subjected to enzymatic digestion by papain treatment in controlled conditions to obtain the collagen hydrolysate. The bioactive peptides with low molecular weight (<50 kDa) were separated from those with high molecular weight (50-100 kDa) by centrifugal ultrafiltration of collagen hydrolysate and each fraction was finally conditioned by atomization.

This technology was standardized at bench laboratory level and then, scaled up to pilot at the SME (Medica Farmimpex).

Collagen hydrolysate and the low molecular weight peptides were used to prepare two products in the form of oral powder (food supplement for skin, hair, nails health and food supplement to improve joint health) and one product in the form of cream (sunscreen lotion). They were characterized by the following physico-chemical determinations: protein content, hydroxyproline content, lipid content and ash content reported to the dry matter of the products. In addition, their biological activity was assessed in terms of *in vitro* biocompatibility degree in HaCaT human keratinocyte cell line by MTT assay, healing efficiency of skin wounds in a cell culture experimental model by scratch-wound healing assay and the anti-inflammatory effect on the human cell line of THP-1 leukemic monocytes.

**Results**: The results obtained from the physico-chemical characterization of the food supplements and the sunscreen lotion, containing freshwater fish bioactive peptides, have shown that the protein content had values of71.24% and 11.04%, respectively, while the hydroxyproline content varied from7.05% to0.048%. The lipid content was less than 5.6%, while the ash content was less than 2%. The biocompatibility testing results have shown that the food supplement to improve joint health product had highly cytocompatibility with human cells, in the range of concentrations of 10 - 750 µg/mL, while the sunscreen lotion was biocompatible in the range of 0.5 – 2 mg/mL at 24 and 48 h and slightly cytotoxicity at a concentration of 2.5 mg / mL. The wound healing assay results have shown that the products stimulated the cell migration, in order to restore the cell monolayer, compared to the untreated culture (control), at 24 h of cultivation.

**Conclusions**: It has been established a lab technology for collagen extraction from freshwater fish by-products and bioactive peptides preparation, which was scaled up at the SME. Novel products in the category of food supplements for skin, hair and nails health and food supplement to improve joint health, as oral powder, and sunscreen lotion, as cream, were formulated based on freshwater fish bioactive peptides. It was demonstrated that the novel products had good interaction with human skin cells and could improve the healing of skin wounds.

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# EVALUATING NATURALLY OCCURING FILLERS IN SODIUM ALGINATE FOR 3D BIOPRINTING USING A TERNARY MIXTURE STATISTICAL MODEL

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***Keywords: 3D bioprinting, diatomaceous earth, rheology, mixture design, response surface methodology***

**Introduction**: Studies involving the development of 3D-printed biocompatible materials for tissue regeneration have been developed extensively in the past decade [1]. These materials usually have a technological aspect involving the choice of bio-ink and fillers followed by a biocompatibility aspect. For this reason, sodium alginate is the bio-ink of choice in many studies, being modified by various clays [2] and other minerals which improve printability. However, in many cases the assessment of the mixtures is done by trial and error. The objective of this study is to estimate the printing performance of the studied materials by characterizing their rheological properties while assessing the possibility of synergic effects between fillers using a statistical model based on a ternary mixture design. The three fillers in the ternary mixture are diatomaceous earth, hydroxyapatite and bentonite, a novel combination of naturally occurring fillers.
**Materials and methods**: Several bio-inks were initially tested to compare the chosen ingredients to other frequently used fillers at ratios of 1:1, 2:1 and 3:1 with respect to sodium alginate added at a concentration of 2.5% (w/v) using a Discovery HR20 Rheometer from TA instruments. The materials were tested in both flow (shear rates between 1 and 200 $s^{-1}$) and oscillometric experiments (angular frequencies between 1 and 100 $s^{-1}$) at 25 °C. The dynamic viscosity as a function of shear rate was modelled by the power law giving the best-fit values of its parameters while the viscoelastic behavior was approximated by the classical Maxwell mode. These parameters were considered response variables for the overall statistical models which were assessed. ANOVA was used to compare the effects of the three ingredients of choice as pure ingredients at various concentrations to other naturally occurring fillers used frequently in 3D bioprinting studies. A simplex lattice quadratic mixture design was used to evaluate and to statistically model the rheological behavior of the ternary mixtures.
**Results**: The chosen ingredients have similar rheological behaviours to frequently used fillers when used with sodium alginate at 2.5% as it has been observed through ANOVA. The statistical model proposed for modelling the ternary mixture of fillers approximates well the experimental points and indicates a synergic effect.
**Conclusions**: The proposed fillers are low-cost materials that are expected to have good printability. A synergic effect on printability performance was observed through statistical methods showing the possibility of obtaining improved results by simply evaluating mixing effects of well-established ingredients or by considering mixing effects between novel ingredients with biocompatibility potential.

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# NOVEL PERSPECTIVES INTO CHITOSAN-BASED MATERIALS FOR ITS BROAD APPLICATIONS

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***Keywords: chitosan, nanomaterials, enzyme immobilization***

**Introduction:** Novel biomaterials based on natural and synthetic biodegradable polymers composed of long-chains molecules draw the attention of researchers. Their successful application in biotechnology, environmental and health care domains make this hybrid materials desirable. Chitosan (CS) is a linear polysaccharide isolated and purified from chitin, a major component of crustacean exoskeleton [1]. The polymorphism of CS as a hydrophilic biopolymer characterized by cationic charge allowed scientists to develop relatively gentle procedure for obtaining pharmaceuticals nanocarriers mostly involving an anionic crosslinker. CS may be shaped in microspheres, nanoparticles, thin films or can be widely used as enzyme immobilization support. Polyacrylic acid (PAA) is a water-soluble polyelectrolyte suitable for crosslinking CS chains in order to design delivery system, composites or beads which can be used in encapsulation of enzymes on support materials [2].

**Materials and methods**: CS nanoparticles were formed due to the interaction of highly charged amino groups of CS chains with phytate anions (PA) as a physical crosslinker through ionotropic gelation. PA stock solution was added drop-wise using a sterile syringe to an aqueous solution of CS at different ratios, under magnetic stirring. Coalesced aggregates were formed during stirring and afterwards separated by centrifugation. The pellets were collected, purified and further analysed [1].

Microspheres were formed by gelation of CS and PAA at different mass ratios in basic medium. The polymer mixture was let to dissolve overnight at room temperature, until a white gel was formed spontaneously. The addition of HCl solution homogenized the entire solution. After that, microspheres were prepared by passing dropwise the clear mixture through a microperfusion needle in the coagulation bath. The beads were let to solidify in the coagulation solution, further washed and analysed [2].

**Results:** In the first place, CSPA nanoparticles were successfully synthesized and their morphological features were studied. On the other hand, CSPAA microspheres were considered to be a promising support material for enzyme immobilization.

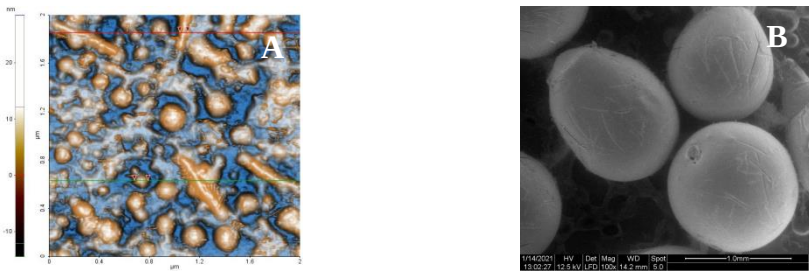


Figure 1. Chitosan based-materials. A) AFM image of CSPA nanoparticles B) SEM image of CSPAA microspheres

**Conclusions:** Hence, CSPA nanoparticles were obtained and investigated through experimentally methods and computational simulations in order to analyse the conformational dynamics. Moreover, 3 types of CSPAA microspheres with further mass ratios were obtained (CS: PAA were 10:1, 5:1 and 2:1) and characterized.

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# WASTEWATER TREATMENT WITH MICROALGAE - BACTERIA CONSORTIA GROWN AS BIOFILMS ON MOVING BED BIOFILM REACTORS

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***Keywords: wastewater treatment, microalgae-bacteria consortia, biofilm, MBBRs***

**Introduction**: Wastewaters resulting from different industries represent one of the main environmental issues [1],[2]. One solution to deal with this problem is to use microbial consortia with biodegradation potential. In this study, two optimal consortia were compared for bioremediation of synthetic wastewater from fish farming. For faster water treatment, the technology was developed based on moving bed biofilm reactors (MBBRs) [3],[4], on which the consortia should form biofilms. MBBRs provide larger exposure area for the consortia, compared to the active sludge treatment.

**Materials and methods**: Three strains of microalgae (*Desmodesmus communis* NIVA-CHL 7, *Chlorella sp.* NIVA-CHL 137, *Chlorella Sorokiniana* NIVA-CHL 176), which have high capacity to grow mixotrophic on wastewater environments, were selected. The bacterial strains were isolated from soil samples and cultivated on selective media. The best microalgae - bacteria consortia were selected from a high throughput screening (HTS) test in 96-well plates, monitoring the effect of the interaction between strains on microbial growth. The DNA of the isolated bacteria was extracted and PCR amplification of the 16S rDNA sequence was performed for specie identification. Six types of MBRR made from HDPE and different cellulose content were tested with these consortia. To determine the degree of loading (organic chemical amount) of wastewater, the chemical oxygen demand (COD) - Cr method was used.

**Results**: Putative *Azospirillum* sp. TAzRr and putative *Bacillus* sp. P1T2 formed the most promising consortia with the microalgae *Chlorella* sp. and *D. communis*. The initial COD-Cr of the studied wastewater was 92 $mgO_2$/L. High degree of efficient wastewater treatment (over 80%) was obtained using small MBBRs, with 3% to 5% cellulose composition, in combination with the consortia, reaching the detection limit of the COD-Cr method. The treatment efficiency was similar for the two algae, but the growth of *Chlorella* sp. consortia was higher than those of *D. communis*.

**Conclusions**: We have obtained efficient microalgae bacteria consortia of *Chlorella* sp. and *D. communis* with *Bacillus* sp. and *Azospirillum* sp. grown on MBBRs for wastewater treatment. The influence of MBBR characteristics such as shape, size, and percentage of cellulose on wastewater treatment was significant. The degree of loading of wastewater was reduced below the detection limit of the COD-Cr method.

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# BIOENERGY ASPECTS OF SEWAGE SLUDGE MANAGEMENT

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***Keywords: sewage sludge, anaerobic digestion, soil, heavy metals***

**Introduction**: Implementation of bioenergy innovations in waste recycling has a beneficial effect on the development of energy independence of the world's countries from each other. It also contributes to the long-term goals of increasing the share of energy produced from renewable energy sources, including reducing green-house gas emissions as part of the development of climate change adaptation technologies.

Sewage sludge compost as a fertilizer has expedient characteristics, increases the content of N, P, macro- and microelements, reduces oil acidity, and increases its moisture capacity and biological activity. Moreover, sewage sludge consists of numerous micro capillaries and has a significant sorption capacity. With increasing exposure time and compaction of waste water system sewage sludge, there is an impact on the distribution of heavy metals, which has a dual nature of further use.

Sewage sludge can become a source of the most dangerous forms of heavy metals in soils-metallo-organic compounds [1], limiting the possibility of their use in agriculture because it can carry heavy metals bound not only in the immobile formal so in the mobile fractions.

**Materials and methods**: Based on the literature research study, the applied aspects of a sewage sludge anaerobic digestion processes in the agricultural and bioenergy sectors were analysed.

**Results**: A promising direction of sewage sludge recycling namely the system of anaerobic microbiological degradation with precipitation of heavy metals by biogenic hydrogen sulphide - a product of life activity of sulphate-reducing bacteria, based on a biosulphide technology was developed [2]. In the process of biosulphide treatment, organic chelato-complexes of heavy metals are destroyed, and stable metal sulphide compounds are formed: sulphides of titanium, iron (marcasites), zinc (sphalerite), nickel, etc. Consequently, heavy metal removal is not physical but through their biochemical binding. Therefore, gassing, qualitative and quantitative composition of biogenic gas, enabling biosulphide neutralization of sewage sludge is of primary importance. For the complete precipitation of heavy metals in the form of sulphides, it is recommended to use sludge with minimal storage time (no more than six months) on sewage sludge maps together with excessive activated sludge, which will maximize the use of organic matter present in sewage sludge. Furthermore, the binding of heavy metals in sulphide fractions will reduce the hydrogen sulphide content in biogas, which means an improvement in its quality.

**Conclusions**: Systems of anaerobic microbiological degradation of sewage sludge with precipitation of heavy metals by biogenic hydrogen sulphide can be used to implement bioenergetic innovations in the energy sector and to develop a system of remediation of natural-anthropogenic landscapes part of the prevention of secondary pollution of soil toxicants. An important direction for further research and the next step is the implementation of laboratory studies of the optimal ratio of different types of sewage sludge and loading doses of the anaerobic bioreactor to achieve high biogas yields and increase its methane content.

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# STIMULATION OF *TRICHODERMA* SPORULATION BY PHYSICO-CHEMICAL FACTORS

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***Keywords: chlamydospores, conidia, light, cornmeal, strigolactones***

**Introduction**: *Trichoderma* has important applications in agriculture due to its stimulation of plant growth and defence responses [1]. *Trichoderma* spp. can be found in soil and roots as free-living fungi and produce three major types of propagules like conidia, mycelia, and chlamydospores [2]. Conidia are used as beneficial fungal commercial formulations and can act as biocontrol agents against some phytopathogenic organisms [3]. Conidiation is influenced by environmental conditions (level and type of nutrients, pH, and light) and mechanical injury [4]. Chlamydospores are thick-walled large spores that are more resistant to adverse conditions and could be more useful than conidia. The aim of this research was to study the influence of different factors such as light, strigolactones (SLs) and culture medium on *Trichoderma* spp. sporulation.

**Materials and methods**: The effects were investigated both on agar and in broth medium for several *Trichoderma* spp, both commercial and isolated by our group. For newly isolated strains, DNA extraction and PCR amplification of the internal transcribed spacer (ITS) sequence were performed for specie identification. Different growth media were used: (1) potato dextrose, (2) cornmeal medium, (3) medium with lysine (4) Medium + SLs. The light effect was investigated by using a blue (400 nm) and a red (660 nm) laser for 60 sec and 300 sec. irradiation. The microscopic analysis of sporulation was done with Leica DM 1000 LED microscope. Several techniques were tested in order to disconnect chlamydospores from parent mycelia. The stability of mycelia was determined by Thermogravimetric Analysis (TGA). We also evaluated the activity of L-amino acid oxidases (L-AAO).

**Results**: Cornmeal medium, laser light, and SLs significantly stimulated *Trichoderma* spp. sporulation. In comparison with potato broth media, the cornmeal contains a lot of amino acids, vitamins, trace elements, and some unknown growth factors and was previously shown to be beneficial for the chlamydospores production, especially in *Candida albicans* [5]. Light is known to induce sporulation, but less is known about the effects on chlamydospores. Our results indicate that laser light stimulates the production of chlamydospores. Unexpectedly, also SLs had a positive effect on sporulation. Light and cornmeal medium induced some discrete, but relevant changes in TGA suggesting higher thermal stability of mycelia and tighter bound water to it. Chlamydospores proved to be very difficult to separate from parent mycelia. In some cases, there was a correlation between the L-AAO activity and other observed effects.

**Conclusions**: We compared and identified new physico-chemical factors that stimulate *Trichoderma* sporulation, increase the number of chlamydospores and improve the stability of mycelia structures. It is not clear if these effects follow a common pathway or if the mechanisms are different, more in-depth analysis being necessary.

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# MECHANICAL STRENGTH OF BIOMATERIAL PLATES BASED ON *GANODERMA* MYCELIUM

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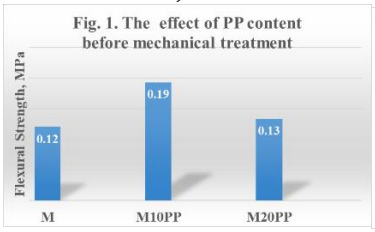
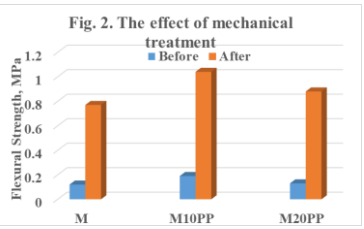
***Keywords: biopolymer composites, Ganoderma lucidum, flexural properties***

**Introduction**: The replacement of petrochemical plastics used to insulate buildings, such as polystyrene, is of major interest in research focusing on the discovery of natural renewable resources insulation materials [1]. As environmental issues arise due to increased production of oil-based products, natural compounds of biological matter are being put to the test for biotechnological use. Fungi, a renewable biomaterial, are competitive in replacing plastic foams. It allows for low-cost production, lack of oil feed-stock usage, and carbon-neutral products. Fungi are on the rise among biomaterials as they are fast growing, non-toxic, and sustainable [2],[3]. However, the main disadvantage of fungal mycelium biomaterials is their low mechanical properties. The quality of biomaterials based on fungal mycelium depends both on the composition and the technology of obtaining but also on the post-production treatment to which it is subjected. There are recent studies showing that the addition of polypropylene [3] or physical treatment (heat pressing) [4] can improve the mechanical properties required by construction applications. One of the important properties for this type of application is the resistance to outer flexural forces. In this respect, the present work aimed to study the effect of the polypropylene addition and the mechanical treatment on the flexural strength of biomaterial plates based on *Ganoderma* mycelium.

**Materials and methods**: In this study we used biomaterial plates with thicknesses of 8 and 20 ± 0.5 mm obtained according to the method described in [3] and extruded polypropylene (PP). Flexural stress at conventional deflection was determined according to ISO1209, at room temperature, with 1 mm/min, using the INSTRON 3382 mechanical testing machine. Before test, specimens with initial dimensions of 150x20x8/20 mm and respectively, after mechanical treatment, of 150x20x4 mm, were conditioned for 48 h, at 23°C and 50% humidity.




**Results**: The obtained results highlighted the dependence of the flexural resistance on both PP content and mechanical treatment after obtaining the biomaterial plates. With 10% PP, the flexural strength of biomaterial increased by approx. 58% compared to biomaterial without PP. Increasing the PP content to 20% does not further improve the flexural strength (Fig. 1). After the mechanical treatment (compression by pressing at room temperature), the flexural strength increased 5-7 times compared to the values obtained on the initial plates (Fig. 2). The flexural strength values for biomaterial plates are comparable to the flexural strength of expanded polystyrene plates with similar thickness and density (approx. 0.9-1.0 MPa for 0.12 g/cm$^3$).

**Conclusions**:

The results showed that *Ganoderma* mycelium biomaterial plates have the potential to be used for construction materials. Additional work is needed to investigate other properties required by the field of use (thermal conductivity, dimensional stability, compressive strength, water absorption).

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# BIOLOGICAL ACTIVITY OF THYME ESSENTIAL OIL ON-PLANT GERMINATION AND PHYTOPATHOGENS

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***Keywords: seed disinfection, phytotoxicity, phytopathogen, volatiles, essential oil***

**Introduction** The application of essential oils (EO) as antifungals has several advantages: they are of natural origin, do not affect the environment, and present low risk of inducing resistance in phytopathogens, given the variety of phytoconstituents as active substances. EO can help increase the protection of foods and feeds and can improve their shelf life [1]. Thymol is the major constituent of some thyme varieties, like *T. vulgaris and Thymus zigi* [1]. Thymol has some important bioactivities: antioxidant, antimicrobial, antitumor, anti-inflammatory, analgesic, antipyretic, etc. [2] [3] The aim of this study was to evaluate the possibility of using thyme essential oil (TEO) for seed disinfection.

**Materials and methods**: The fungal strains used in this study were *F. graminearum* CBS 454.97, *R. solani* anastomosis group AG-4, *P. ultimum* DSM 62987 *and B. allii* DSMZ 62081. The antifungal assays were performed by biofumigation using filter paper discs soaked with corresponding TEO volume and applied on the inner surface of plate lid. The minimal fungistatic dose (MFsD) was the dose with zero fungal growth. The minimal fungicidal dose (MFcD) was determined by transferring the mycelium discs incubated at FsD > MFsD to fresh PDA to assess their viability. The effect of TEO on plant seeds was determined for *Sorghum saccharatum, Lepidium sativum, and Sinapis alba* by two methods: biofumigation and direct contact between TEO and seeds.

**Results**: The growth of all the strains tested was inhibited by TEO, but the inhibitory dose was dependent on fungal species. The most resistant strain was *P. ultimum* (MFsD 0.244 µL /cm$^3$) and the least resistant was *R. solani* (MFsD 0.054 µL /cm$^3$). MFcD was from much higher (20x higher MFcD than MFsD in the case of *B. allii*) to identical to MFsD (*R. solani* and *P. ultimum*), with intermediate difference between MFsD and MFcD for *F. graminearum*. The highest MFsD (*P. ultimum*) was 4*x* higher than the lowest MFsD (*R. solani*) and the highest MFcD (*B. allii*) was almost 40x higher than the lowest MFcD (*R. solani*). The direct contact of seeds with TEO showed a lack of selectivity by partially inhibiting the germination and more significantly (> 80%) the root and shoot development. Biofumigation improved selectivity.

**Conclusions**: The most sensitive fungal specie to TEO was *R. solani*. TEO has the potential to reduce inoculum of soilborne plant pathogens by reducing the soil inoculum by fumigation, but the phytotoxicity of TEO must be reduced. One solution could be TEO formulation that would slowly release the volatile components and would reduce their side-effects.

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# STUDY AND OPTIMIZATION OF ULTRASOUND ASSISTED EXTRACTION OF LIPIDS AND CAROTENOIDS FROM MICROALGAE VIA SURFACE RESPONSE METHODOLOGY

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***Keywords: Chlorella vulgaris, Porphyridium purpureum, lipids, ultrasound assisted process***

**Introduction**: Microalgae have become recently more widely used in food supplements and products due to their high content of beneficial biocompounds such as polyunsaturated fatty acids, proteins and antioxidants, to name a few, being considered a source of essential fatty acids for vegan based diets. While several methods have been investigated for the extraction of biocompounds from microalgae, from the conventional Soxhlet extractions to the more innovative technologies centred around assisted processes via microwaves or ultrasound, most studies involve the use of a single solvent or binary systems, such as dichloromethane-methanol and chloroform-methanol [1].

The aim of this work is the study and optimization by Surface Response Methodology, of ultrasound assisted extraction of lipids and pigments, specifically carotenoids, from two species of microalgae, *Chlorella Vulgaris* and *Porphyridium purpureum*.

**Materials and methods**: For this study, three solvents with different polarities have been used: water, ethanol and hexane and experiments have been carried out in a Sonorex DigiPlus DL255 H Bandelin ultrasonic bath, coupled with an external cooling device. For the optimization process, 4 parameters were proposed as variables and studied, specifically the intensity setting on the ultrasonic bath (60-100%), the aqueous ethanol concentration (25% to 70% v/v of water), ratio of ethanol solution to hexane (1:2, 2:1 and 1.25:1 v/v) and the ratio of biomass to solvent expressed in w/v. Carotenoid concentration was determined from each of the two phases in the extraction solvent (aqueous and organic), by spectrophotometric analysis and quantified following existing methodologies in published literature. The total lipids were obtained from the hexane extract by sulfo-phospho-vanillin colorimetric analysis, while the fatty acids profile was obtained by GC-MS [2],[3].

**Results**: By analysing the fatty acid distribution between the two non-miscible phases after ultrasound assisted extraction, in both species of microalgae, a concentration of polyunsaturated fatty acids in the ethanolic phase was observed for optimal extraction conditions, while the saturated fatty acids accumulated in the hexane phase. The extraction conditions for which the highest yields were obtained, in both carotenoid (6.4 mg/g) and lipids (29 mg/g), are 70% ultrasonic intensity, 1:4 biomass to solvent ratio, ethanol concentration of 60% and ethanol solution to hexane ratio of 2:1.

**Conclusions**: This work evaluated the one step ultrasound assisted extraction of carotenoids and lipids from two species of microalgae, and identified the optimum parameters for increased yield in both compounds, by experimental design. Results obtained show the selective extraction of saturated and polyunsaturated fatty acids, using food grade solvents which allows for a wide array of applications in the food industry. Additionally, the presence of antioxidants, in the form of carotenoid extracts, increases the shelf life of the total extract by preserving polyunsaturated fatty acids.

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