Cod proiect PN-III-P2-2.1-PED-2021-1870

Nr contractului 646PED/2022

Titlul proiectului (în română) ECOTECHNOLOGIE DE OBȚINERE A UNOR FITOINGREDIENTI INCAPSULATI IN HIDROGEL PE BAZA DE COMPLECSI BIOACTIVI IMOBILIZATI IN MATRICE DE HIDROXIZI DUBLI LAMELARI

Titlul proiectului (în engleză)

ECOTECHNOLOGY FOR OBTAINING PHYTOINGREDIENTS ENCAPSULATED IN HYDROGEL BASED ON BIOACTIVE COMPLEXES IMMOBILIZED IN A LAYER DOUBLE HYDROXIDE MATRIX

Acronimul proiectului DUACTIVMER

Valoare totală contract: 658.675,00 lei

Din care :

Sursa 1 de la bugetul de stat : 598.795,00 lei

Sursa 2 - din alte surse atrase: 59.880,00 lei
(cofinanțare)
Durata contractului: **24 luni**

REPARTIZAREA SUMELOR PE ANII BUGETARI

ANUL	Sursa 1 (lei)	Sursa 2 (lei)	TOTAL(lei)
2022	146.765,00	13.430,00	160.195,00
2023	345.176,00	46.450,00	391.626,00
2024	106.854,00	0,00	106.854,00
TOTAL	598.795,00	59.880,00	658.675,00

ORGANIZAȚIILE PARTENERE ÎN PROIECT

Denumirea organizației participante în proiect	Acronim organizație	Tip organizație	Rolul organizației în proiect (Coordonator/Partener)
(CO) Universitatea din Bucuresti	UB	UNI	Coordonator
(P1) Institutul Național de Cercetare-Dezvoltare pentru Chimie si Petrochimie ICECHIM	INCDCP ICECHIM	INCD	Partener P1
(P2) CENTRUL DE CERCETARE SI PRELUCRARE A PLANTELOR MEDICINALE PLANTAVOREL SA	PLV	Întreprindere Mică	Partener P2

Repartizarea fondurilor pe parteneri

	2022		2023		2024		TOTAL	
	Finanțare de la bugetul de stat	Finanțare din alte surse atrase(contribuț ie financiară proprie)	Finanțare de la bugetul de stat	Finanțare din alte surse atrase(contribuție financiară proprie)	Finanțare de la bugetul de stat	Finanțare din alte surse atrase(contribuție financiară proprie)	Finanțare de la bugetul de stat	Finanțare din alte surse atrase(contribuție financiară proprie)
CO	57972	0	121313	0	57239	0	236524	0
P1	49166	0	101815	0	49615	0	200596	0
P2	39627	13430	122048	46450	0	0	161675	59880
Total	146765	13430	345176	46450	106854	0	598795	59880

Abstract: Proiectul urmărește dezvoltarea unor eco-tehnologii integrate validate (TRL4) cu dublu scop: 1) de obținere a ingredientelor bioactive încapsulate în hidrogel pe baza fitocomplecşilor din 2 plante medicinale (Rhamnus frangula L (RfL) şi Helianthus tuberosus L (HtL) cu biocompatibilitate crescută care sunt protejate contra degradării prin imobilizarea într-o

matrice de hidroxid dublu lamelar (LDH) si 2) de valorificare a resturile vegetale ramase dupa extractie, ca adsorbant ieftin al poluanților din ape reziduale. Conceptul de bază al tehnologiei (TRL2) pornește de la rezultatele preliminare obținute de partenerii din consorțiu în i) extracția fitocomplecşilor din RfL şi HtL, ii) imobilizarea anionilor organici în matrici Mg/Al-LDH şi Zn/Al-LDH, iii) obținerea hidrogelurilor hibride cu fitoextracte bioactive din Rosa Canina şi Hypericum Perforatum L imobilizate in zeoliți naturali şi iv) tratarea apelor reziduale poluate cu metale grele şi poluanți organici. Proiectul extinde aplicarea fitoextractelor dublu-protejate la noi sisteme bazate pe fitoextracte RfL şi HtL incorporate în matrici Mg,Ca/Al,Fe-LDH şi încapsulate apoi în hidrogeluri. Tehnologia integrată, cu producere minimă de deșeuri va permite utilizarea ingredientelor active obținute în suplimente alimentare cu efecte benefice în reglarea unui tranzit intestinal lent prin aportul constant de glucofranguline din RfL şi de electroliți precum Mg/Ca si Fe, având totodată şi efectul benefic de prebiotic, îmbunătăţind absorbția mineralelor şi scăderea colesterolului datorită HtL. Se vor obține si beneficii în tratarea apelor reziduale. Folosirea produselor obținute la suplimente alimentare este benefică pentru bunăstarea oamenilor, scăzând efectele negative ale stilului de viața haotic, cu prea multe ore de muncă, stres continuu şi decizii greșite în ce privește alimentația, care toate conduc la repercusiuni grave asupra sănătăţii sistemului digestiv.

Abstract: The project aims the development of integrated validated eco-technologies (TRL4) with double action: 1) obtaining hydrogel encapsulated bioactive ingredients based on phytocomplexes from 2 medicinal plants (e.g. Rhamnus frangula L (RfL) and Helianthus tuberosus L (HtL)) with increased biocompatibility and protected from degradation by

immobilization in a layer double hydroxide (LDH) matrix, and 2) valorization of spent vegetal after extraction as cheap adsorbent of pollutants from wastewaters. The basic concept of the technology (TRL2) lays on preliminary results obtained by consortium partners in: i) extraction of RfL and HtL phytocomplexes; ii) immobilization of different organic anions in Mg/Al-LDH and Zn/Al-LDH matrices, iii) obtaining of hybrid hydrogels containing bioactive phytoextracts from Rosa Canina and Hypericum Perforatum L immobilized in natural zeolite and iv) treatment of wastewaters polluted with heavy metals and organic pollutants. This project extends the application of double-protected bioactive phytoextracts to new systems based on RfL and HtL phytoextracts incorporated in Mg,Ca/Al,Fe-LDH matrices and further encapsulated into hydrogels. The integrated technology ensuring minimum waste production, will allow the further utilization of obtained active ingrediends in food supplements with benefic effects for improving a lazy intestinal transit due to a constant low apport of glucofrangulins brought by RfL along with electrolytes such as Mg/Ca and Fe, while acting also as prebiotic and promoter of mineral absorption and cholesterol-lowering due to HtL. A benefit for wastewater treatment would also be brought. The use of the obtained products in food supplements could be benefic to people well-being, by reducing the negative effects of their chaotic lifestyle, with too many working hours, continuous stress and most important, poor dietary decisions, all leading to tremendous repercussions on the health of the digestive system.

Obiectivul proiectului:

Obiectivele științifice ale proiectului sunt: 1) selectarea modalității de extracție adecvate a complecșilor activi din Rhamnus frangula L (RfL) și Helianthus tuberosus L (HtL) pentru obținerea de extracte bogate compatibile pentru încapsularea în LDH; 2) selectarea parametrilor

operaționali necesari imobilizării cantității maxime de fitocomplecși în matrici de tip LDH (ce conțin Mg/Ca/Al/Fe); 3) selectarea tipului de hidrogel și a celei mai adecvate metode de sinteză pentru încapsularea eficientă a fitocomplecșilor imobilizați în matrice LDH (RfL-LDH; HtL-LDH) în scopul obținerii HYG-RfL-LDH și HYG- HtL-LDH; 4) determinarea capacității de adsorbție a deșeurilor vegetale rămase după extracția fitocomplecșilor bioactivi pentru reținerea poluanților metale grele (Fe, Ni, Cu, Cr) și coloranților organici (indigo carmin) din ape reziduale în scopul minimizării deșeurilor și dezvoltării unei tehnologii cu dublă acțiune; 5) evaluarea influenței pH-ului la eliberarea in vitro a ingredientelor active din RfL-LDH; HtL-LDH; 6) proiectarea celor două tehnologii de laborator pentru obținerea: a) HYG-RfL-LDH și b) HYG-HtL-LDH și valorificarea resturilor vegetale ca adsorbanți ai poluanților; 7) optimizarea parametrilor operaționali care guvernează extracția fitocomplecșilor activi din RfL și HtL; 8) punerea la punct a celor două tehnologii de laborator optimizate, cu dublă acțiune, aplicate la obținerea fitocomplecșilor în matrice LDH încapsulați în hidrogel; 9) evaluarea influenței pH-ului asupra capacității de eliberare a ingredientelor active din HYG-RfL-LDH and HYG-HtL-LDH in vitro, după optimizare, în vederea determinării cantităților adecvate de compozite care pot fi utilizate în formularea suplimentelor alimentare; 10) demonstrarea funcționalității celor două tehnologii; 11) validarea celor două tehnologii menționate anterior (TRL4). Obiectivele indirecte ale proiectului sunt: a) creșterea calității și diversității suplimentelor alimentare; b) scăderea efectelor secundare negative ale fitocomplecșilor concentrați; c) creșterea competitivității produselor românești pe piața internațională; d) îmbunătățirea vizibilității științifice pe plan național și internațional.

Obiectivul proiectului

(în engleză)

The scientific objectives of the project are: 1) the selection of the adequate extraction route of the active phytocomplexes from Rhamnus frangula L (RfL) and Helianthus tuberosus L (HtL) in order to obtain rich extracts compatible to their incorporation in LDH; 2) the selection of the operational parameters required for the immobilization of the highest amount of these phytocomplexes in LDH-type matrices (containing Mg/Ca/Al/Fe); 3) the selection of the hydrogel type and of the most adequate synthesis route required for an efficient encapsulation of the phytocomplexes immobilized in the LDH-matrix (RfL-LDH; HtL-LDH) yielding HYG-RfL-LDH and HYG- HtL-LDH; 4) the determination of the adsorption capacity of the vegetal residue remained after the extraction of bioactive phytocomplexes for the retention of heavy metals pollutants (Fe, Ni, Cu, Cr) and organic dyes (indigo carmine) from wastewaters aiming to minimize the wastes while achieving a dual action technology; 5) the assessment of the pH influence on active ingredients in vitro release from RfL-LDH; HtL-LDH; 6) the design of the 2 laboratory technologies (TRL3) for the obtaining of a) HYG-RfL-LDH and b) HYG-HtL-LDH and the valorization of the spent vegetal materials as pollutants adsorbents; 7) the optimization of the operational parameters governing the extraction of the active phytocomplexes from RfL and HtL; 8) setting up the two optimized double action laboratory technologies applied for the obtaining of hydrogel encapsulated phytocomplexes imobilised in LDH matrix; 9) the post optimality assessment of the active ingredients in vitro release from HYG-RfL-LDH and HYG-HtL-LDH depending on the pH in order to determine the appropriate amounts of composites that could be utilized in the formulation of food supplements; 10) the demonstration of the functionality of the two technologies; 11) the validation of the above mentioned technologies (TRL4). Other indirect objectives are: a) increasing the quality and diversity of food

supplements; b) decreasing the adverse side effects of concentrated phytocomplexes; c) increasing the competitiveness of the Romanian products on the international market; d) improving the scientific visibility at national and international level.

Rezultatele estimate

(în română)

Model experimental pentru tehnologia 1 HYG-RfL-LDH

Model experimental pentru tehnologia 2 HYG-HtL-LDH

Tehnologie de laborator 1 HYG-RfL-LDH

Tehnologie de laborator 2 HYG-HtL-LDH

Raport de demonstrare si documente de validare (TRL4) tehnologie 1 HYG-RfL-LDH

Raport de demonstrare si documente de validare (TRL4) tehnologie 2 HYG-HtL-LDH

4 comunicari

2 articole trimise spre publicare

2 cereri de brevet.

Rezultatele estimate

(în engleză)

Experimental model of technology 1 HYG-RfL-LDH

Experimental model of technology 2 HYG-HtL-LDH

Laboratory technology 1 HYG-RfL-LDH

Laboratory technology 2 HYG-HtL-LDH

Demonstration report and validation document (TRL4) for technology 1 HYG-RfL-LDH

Demonstration report and validation document (TRL4) for technology 2 HYG-HtL-LDH

4 communications

2 articles submitted for publication

2 applications for patent

Raport stiintific etapa 1

SURSA DE FINANȚARE – UEFISCDI Programul PNIII
Cod proiect - PN-III-P2-2.1-PED-2021-1870 –
Nr. Contract 646PED/2022

Titlu proiect:
Ecotechnologie de obținere a unor fitoingredienţi încapsulaţi în hidrogel pe baza de complecşi bioactivi imobilizaţi în matrice de hidroxizi dubli lamelari –
Acronim - DUACTIVMER
Consorțiu:
Coordonator (CO) - Universitatea din București – Director de proiect Conf. Dr. Rodica Zăvoianu
Partener 1 (P1) - INCDPC-ICECHIM București – Responsabil proiect partener 1 - Dr. Ing. Andrei Sârbu
Partener 2 (P2) - Centrul de cercetare și prelucrare a plantelor medicinale Plantavorel SA (P2) – Responsabil proiect Partener 2 – Dr. Ing. Carmen Țebrencu

Stadiul de implementare al proiectului
Etapa 1 -2022 CERCETARE INDUSTRIALĂ ASUPRA CONCEPTULUI FORMULAT AL TEHNOLOGIEI 1 ȘI DEZVOLTAREA MODELULUI EXPERIMENTAL

Durata 21 iunie 2022-31.12.2022
Finanțare etapa 1 – 160195,00 lei
Sursa 1 – buget de stat -146765,00 lei
Sursa 2 – cofinanțare – 13430,00 lei

REZUMAT RAPORT ȘTIINȚIFIC

În cadrul primei etape a proiectului PN-III-P2-2.1-PED-2021-1870-DUACTIVMER în perioada iunie-decembrie 2022 s-au efectuat o serie de activități de **cercetare industrială** în vederea **dezvoltării modelului experimental al ecotehnologiei 1 HYG-RfL-LDH de obținere a unor fitoingredienţi din *Rhamnus Frangula L* (RfL) încapsulaţi în hidrogel pe baza de complecşi bioactivi imobilizaţi în matrice de hidroxizi dubli lamelari (LDH).**

La **activitatea 1.1., P2** a efectuat **30** de experimente pentru a elabora **modelul experimental** tehnologic și analitic **privind modulul a_1 al ecotehnologiei de extracție a fitocomplecșilor din RfL** prin 2 metode de extracție neconvenționale (a_{11}- extracție asistată de microunde (MAE) și a_{12} – extracție asistată de ultrasunete (UAE)) și **a livrat la CO o șarjă de soluție extractivă RfL obținută prin MAE** în vederea imobilizării fitocomplexului extras în diverse matrici LDH (**pentru dezvoltarea modulului b_1 al ecotehnologiei**) **și o șarjă de material vegetal epuizat** în vederea testării capacității de adsorbție a diferiților poluanți (**pentru modulul d_1 al ecotehnologiei**). **În vederea dezvoltării modulului b_1 al ecotehnologiei, CO** a efectuat sinteza a **8** compuși LDH, care au fost calcinați înainte de a fi folosiți la imobilizarea fitoextractului RfL prin metoda reconstrucției și care au fost caracterizați prin difracție de raze X, DRIFT, spectroscopie DR-UV-Vis și analiză termică diferențială (TG-DTA) și a predat la P1 un număr de **16** probe LDH precursor și LDH-RfL pentru a fi utilizate la elaborarea **modulului c_1 al ecotehnologiei**. **P1** a evaluat posibilitatea incorporării compușilor LDH precursori și LDH-RfL în două tipuri diferite de hidrogel efectuând **10** experimente cu hidrogel pe bază de polimer natural biocompatibil și **18** experimente cu hidrogel compozit biocompatibil în scopul **dezvoltării modulului c_1 al ecotehnologiei**.

La **activitatea 1.2**., **CO** a efectuat **39** experimente pentru **evaluarea tehnico-științifică și testarea capacității de adsorbție a resturilor vegetale epuizate după extracția fitocomplecșilor din RfL** prin metoda MAE pentru 4 poluanți din ape reziduale: indigo carmin, Cr, Ni și Fe. Capacitatea de adsorbție a materialului vegetal epuizat a fost determinată în urma dozării prin spectrofotometrie UV-Vis

a poluanților rămași în apă la sfârșitul testelor. **Rezultatele obținute au permis elaborarea modelului experimental pentru modulul d_1 al ecotehnologiei**.

Prin urmare, la finalizarea activităților 1.1. și 1.2 s-a putut elabora integral modelul experimental pentru ecotehnologia 1 HYG-RfL-LDH urmând ca acesta să fie perfecționat în cadrul etapei următoare a proiectului.

P2 a efectuat **activitatea 1.3.** de cercetare industrială premergătoare pentru elaborarea modulului a_2 al modelului experimental al ecotehnnologiei 2 **de obținere a unor fitoingredienţi din *Helianthus tuberosus L* (HtL) încapsulaţi în hidrogel pe baza de complecşi bioactivi imobilizaţi în matrice de hidroxizi dubli lamelari (LDH).** S-au testat 4 modalități de inactivare enzimatică a tuberculilor HtL care au fost apoi supuși procedurii de extracție a fitocomplecșilor biologic activi prin 3 metode convenționale diferite ca număr de etape (în două trepte de extracție, într-o treaptă de extracție cu prelucrarea soluției extractive și într-o singură treaptă de extracție de lungă durată). Atât solidele cât și soluțiile extractive rezultate au fost caracterizate fitochimic.

Activitatea 1.4. a constat în diseminarea rezultatelor după cum urmează:

2 articole ISI

1. I. E. Neblea, A.-M. Gavrilă, T. V. Iordache, A. Zaharia, P. O. Stănescu, I. C. Radu, S. G. Burlacu, G. Neagu, A.L. Chiriac,* A. Sârbu*, Interpenetrating networks of bacterial cellulose and poly (ethylene glycol) diacrylate as potential cephalexin carriers in wound therapy, J. Polymer Research (2022) 29: 406 https://doi.org/10.1007/s10965-022-03250-9, (IF 3,097, zona galbena)
2. R. Zăvoianu, M. Tudorache, V.I. Pârvulescu, B. Cojocaru, O.D. Pavel, New MgFeAl-LDH Catalysts for Claisen–Schmidt Condensation, Molecules, 2022, 27, 8391. https://doi.org/10.3390/molecules27238391. (IF 4,972, zona galbena)

3 Comunicări orale la Conferința Nationala de Chimie ediția XXXVI, Călimănești-Caciulata Vâlcea, 4-7 oct. 2022 (autori de la CO, P1 și P2)

a) Beads based on sodium alginate and titania composites for heavy metals removal from simulated waste waters, A. Miron, A.L. Neagu, S. Dolana, A. Zaharia, A.-M. Gavrilă, A. Sârbu, T.-V. Iordache, A.-L. Chiriac (P1)

b) Molecularly imprinted supermacroporous cryogels for Penicillin G adsorption, M. V. Dumitru, T.-V. Iordache, I. E. Neblea, E. B. Stoica, T. Sandu, A. Sârbu, A.-M. Gavrilă, A.L. Chiriac (P1)

c) Removal of indigo carmine from wastewater by adsorption on vegetal wastes, O.D. Pavel (CO), R. Zăvoianu (CO), D. Buha, E.M. Ungureanu, A. Cruceanu (CO), A. Tîrșoagă (CO), O.T. Apreutesei (P2)

2 postere; i) A non-traditional perspective in the synthesis of Fe-LDH type materials, O. D. Pavel, R. Zăvoianu, A. Tîrșoagă, A. Cruceanu, B. Cojocaru, R. Bîrjega, V. I. Pârvulescu **la Conferința Nationala de Chimie** ediția XXXVI (autori CO) ; **ii)** Hydrogels based on natural polymers dopped with LDH and phytoextract – M. V. Dumitru, T. V. Iordache, A. L. Neagu, A. Zaharia, R. Zăvoianu, O. Pavel, S. Teodor, A. Sârbu, SICHEM 2022, Universitatea Politehnica Bucuresti, 17-18 noiembrie 2022 (autori P1 și CO)

Abstractele pentru comunicările și posterele prezentate sunt atașate la finalul acestui document.

În cadrul **activității 1.5.** trei membri din echipa CO au făcut o vizită de lucru la P2 pentru a prelua probele de extract și material vegetal uzat și a se instrui cu privire la protocoalele de lucru pentru controlul analitic al fitocomplecșilor extrași din RfL.

Pe baza celor prezentate mai sus se poate considera că toate obiectivele propuse pentru această etapă au fost atinse și chiar depășite în ceea ce privește diseminarea la care erau prevăzute doar 2 comunicări în această etapă.

International Chemical Engineering and Material Symposium, SICHEM 2020, 17-18 September 2022, ISSN 2537-2254

Hydrogels based on natural polymers dopped with LDH and phytoextract

Marinela V. Dumitru[1], Tanta Verona Iordache[1], Ana L. Neagu[1], Anamaria Zaharia[1], Rodica Zavoianu[2], Octavian Pavel[2], Sandu Teodor[1], Andrei Sarbu[1]*

[1]National Research-Development Institute for Chemistry and Petrochemistry-ICECHIM, Splaiul Independentei 202, district 6, 060021, Bucharest, Romania
[2] University of Bucharest, 050663 Bucharest, Romania

Abstract: ***N****ew composite hydrogels based on Chitosan and hydrotalcite dopped with phyoextracts were prepared with the aim of possible slow release of bioactive substances.*
Key words: Chitosan, hydrogels, LDH, phytoectract

Introduction: Lately, with the rapid development of industry, hydrogels have attracted more and more attention due to their large specific surface area and unique structure. Hydrogels are three-dimensional network-structured polymer formed by a polymer main chain and a hydrophilic functional group through covalent bonds, hydrogen bonds, or physical winding cross-linking [1-2]. Hydrogels have been used for many years in controlled drug delivery, water purification (for heavy metals, dyes, antibiotics) tissue regeneration, etc. Natural polymers (chitosan alginate, biocelulose) are the most attractive materials used to replace synthetic materials [3]. In this work, new hydrogels based on chitosan (CS) were successfully prepared by adding layered double hydroxides (hydrotalcite-LDH) and LDH dopped with phytoextract during the process of CS hydrogel preparation.

Experimental and Modelling: For the development of the aimed hydrogels two polymers were needed: chitosan (CS) and poly(vinylalcohol) (PVA). Two solutions of these polymers were prepared and mixed, followed by the addition of hydrotalcites (LDH) and LDH with a phytoextract and, at the end, the crosslinker was introduced.

Results and discussions: In order to highlight the new developed hydrogels, the samples were characterized using various modern techniques such as FTIR, swelling degree. FTIR spectra confirmed the occurrence of characteristic bands for the involved raw materials**.**

Conclusions: The aimed hydrogels based on natural polymers were succesfully developed and characterized by FTIR and also their swelling degree capacity was studied in time.

Aknowledgement: The study was funded by the Ministry of Education and Research through Ececutive Unit for Financing Higher Education, Research, Development and Innovation (UEFISCDI), grant. No. 646 PED/2022 DUACTIVMER and grant no. 15PFE/2021 NeXT-BExcel.

References:

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[3]. R. Jayakumar et al., Biomedical applications of chitin and chitosan-based nanomaterials—A short review, Carbohydrate Polymers, 82,2010, p. 227-232.

A NON-TRADITIONAL PERSPECTIVE IN THE SYNTHESIS OF Fe-LDH TYPE MATERIALS

Octavian Dumitru Pavel[1], Rodica Zăvoianu[1], Alina Tîrşoagă[1], Anca Cruceanu[1], Bogdan Cojocaru[1], Ruxandra Bîrjega[2], Vasile I. Pârvulescu[1]

[1] University of Bucharest, Faculty of Chemistry, Sos. Panduri No. 90-92, S5, Bucharest, Romania

[2]National Institute for Lasers, Plasma and Radiation Physics, 409 Atomistilor Street, PO Box MG-16, 077125, Magurele, Romania

The aim of this work was the obtaining of Fe modified layered double hydroxides (LDH) materials (Mg,Fe/Al=3 and Mg/Fe=1 molar ratio) using two non-traditional approaches in LDH synthesis: *i)* the mechano-chemical method and *ii)* the use of an organic base (tetramethylammonium hydroxide - TMAH) as precipitation agent.[1]For comparison, Fe-LDH was also prepared by the traditional method: co-precipitation at pH of 10 in the presence of inorganic alkalis ($NaOH/Na_2CO_3$).Fe-LDH materials were subsequently calcined at 460 °C for 18 h to obtain the corresponding mixed oxides. The mixed oxides were then rehydrated with distilled water to reconstruct the layered structure of the parent LDH based on the memory effect.All materials were characterized by XRD, IR and UV-Vis spectroscopy, N_2 adsorption-desorption isotherms and basic sites determination by irreversible adsorption of organic molecules with different pK_a. Thus, a higher purity was remarkable for the compounds obtained by co-precipitation compared to those obtained by the mechano-chemical method regardless of the nature of the base.The presence of impurities in Fe-LDH obtained by both routes is related to the presence ofFe_3O_4diffraction lines in the XRD patterns.The contaminating Fe_3O_4phase is preserved even after the reconstruction of the layered structure. The catalytic activity in Claisen-Schmidt condensation between cyclohexanone and benzaldehyde followed the same order as the basicity of the samples: mixed oxides > reconstructed> dried, regardless thepreparation method.

Acknowledgement: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CCCDI - UEFISCDI, project number PN-III-P2-2.1-PED-2021-1870, within PNCDI III. 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-2020-2207, within PNCDI III.

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BEADS BASED ON SODIUM ALGINATE AND TITANIA COMPOSITES FOR HEAVY METALS REMOVAL FROM SIMULATED WASTE WATERS

Andreea Miron[12], Ana-Lorena Neagu[1], Sorin Dolana[1], Anamaria Zaharia[1], Ana-Mihaela Gavrila[1], Andrei Sarbu[1], Tanta-Verona Iordache[1], Anita-Laura Chiriac[1*]

[1] *National Institute for Research & Development for Chemistry and Petrochemistry- ICECHIM Bucharest, Spl. Independentei 202, sector 6, ROMANIA*

[2] *University Politehnica of Bucharest, 011061 Bucharest, Romania*

**Correspondence: anita-laura.radu@icechim.ro*

One of the major environmental issues is heavy metal pollution, hence new techniques must be developed to minimize the effects on the aquatic environment [1]. Sodium alginate (SA) is a natural polymer that is frequently used in wastewater treatment due to the remarkable properties in heavy metals absorption [1-2]. Titanium dioxide (TiO_2) presents good compatibility and mechanical properties, thermal stability and efficiency in removal of heavy metal [2].

Hybrid inorganic-organic composites can be used as innovative additive for beads and can act as effective sorbents for the removal of numerous pollutants, particularly for heavy metals. The most significant benefit of inorganic-organic hybrids is combining properties in a single material. An efficient and inexpensive method to obtain composites materials is host-guest polymerization.

Therefore, the aim of this study is the obtaining of sodium alginate beads based on inorganic-organic composites/or titanium oxide as reference for the removal of heavy metals from simulated waters. The composites synthesis process is very straightforward and assumes impregnation of the inorganic host into a solution containing a monomer and a polymerization initiator, after which template polymerization of the monomer in the inorganic pores is conducted. For this part of the research a TiO_2 obtained by hydrothermal process was used as an inorganic matrix and a vinyl monomer, acrylonitrile, as an organic host [3]. In order to evaluate the adsorption properties of adsorbents, modern techniques were used. Physical, morphological and textural properties were performed using X-Ray fluorescence (XRF), Brunauer-Emmett-Teller (BET) analysis and Scanning Electron Microscopy (SEM). Ultraviolet-visible spectroscopy (UV-Vis) was used to determine the metals retention over time. The effect of the parameters varied during the synthesis of beads upon the final properties were investigated through Fourier-Transform Infrared Spectroscopy (FTIR) and Thermal Gravimetric Analysis (TGA). The results showed interesting adsorption performances of the new biocomposites material.

Acknowledgement: This work was supported by a grant of the Ministry of Research, Innovation and Digitization - UEFISCDI, project number 646PED/2022 - DUACTIVMER and PN-III-Human Resources Programme-YOUNG RESEARCH TEAMS- PN-III-P1-1.1-TE-2021-0915, grant no. 135/2022 project – I-ON-MEM.

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MOLECULARLY IMPRINTED SUPERMACROPOROUS CRYOGELS FOR PENICILLIN G ADSORPTION

MarinelaVictoria Dumitru[1,2], Tanta-Verona Iordache[1], Iulia Elena Neblea[1], Elena Bianca Stoica[1], Teodor Sandu[1], Adrei Sarbu[1], Ana-Mihaela Gavrila[1], Anita Laura Chiriac[1]*

[1] National Research-Development Institute for Chemistry and Petrochemistry-ICECHIM, Splaiul Independentei 202, district 6, 060021, Bucharest, Romania

[2] University Politechnica of Bucharest, 011061 Bucharest, Romania

**Correspondence: anita-laura.radu@.icechim.ro*

Since their first appearance in the 1980s, interest in natural polymers has grown rapidly at worldwide level, especially in the medical field (tissue engineering, controlled drug delivery). Due to their outstanding properties such as high biocompatibility and low toxicity, this type of polymers can be used to obtain many types of materials for different applications[1]. Unfortunately, the water pollution became a problem for humans, and not only. Higher concentrations of antibiotics were found in all water sources[2]. Molecularly imprinted polymers (MIP) are polymeric materials based on the polymerization of a functional monomer/polymer and a cross-linking agent in the presence of a template molecule. After removing the molecule (template), an imprinted polymer with selective cavities and high affinity for the template molecule was obtained[3]. So, in order to solve the water pollution problem, this study was focused on using natural polymers to obtain molecularly imprinted supermacroporous cryogels for Penicillin G retention.

To develop the aimed molecularly imprinted supermacroporous cryogels, bacterial cellulose and two types of chitosan were used: commercial chitosan (CC) and laboratory prepared chitosan from commercial chitin (CCHC1). The cryogels were lyophilized and tested for their adsorption capacity towards PG.

To highlight the imprinting process and study the structure of supermacroporous cryogels, the samples were characterized through various modern techniques (FTIR, TGA, SD, UV-Vis). The characteristic bands for the involved raw materials and the obtained cryogels were confirmed through FTIR spectroscopy. The template molecule effect and the stability of the samples were studied by Thermogravimetric Analysis. The molecularly imprinted supermacroporous cryogels (**MIP1-MIP4**) were shown to exhibit greater thermal stability than their non-imprinted counterparts (**NIP1-NIP4**). The swelling behavior of the new cryogels revealed their high ability to absorb a large amount of water. Additionally, the UV-Vis results confirmed that supemacroporous cryogels were able to bind PG from aqueous solutions.

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REMOVAL OF INDIGO CARMINE FROM WASTEWATER BY ADSORPTION ON VEGETAL WASTES

Octavian Dumitru Pavel[1], Rodica Zăvoianu[1], Diana Buha[1], Elena Mihaela Ungureanu[1], Anca Cruceanu[1], Alina Tîrşoagă[1], Oana Teodora Apreutesei[2]

[1] University of Bucharest, Faculty of Chemistry, Sos. Panduri No. 90-92, S5, Bucharest, Romania

[2] Research and Processing Center for Medicinal Plants Plantavorel SA, Cuza Vodă 46, Piatra Neamț, Neamț County, Romania

Lately there is an increased trend to find bio-derived cheap adsorbents.[1] This research evaluates the adsorption capacity of vegetal wastes originating from the processing of sea-buckthorn (*Hippophaes rhamnoides*) and topinambur (*Helianthus tuberosus L*) for indigo carmine (IC) dye pollutant from wastewater. Two different vegetal waste adsorbents were recovered after the juice extraction from fresh sea-buckthorn berries: A1Hr – solid separated after the mechanical cold pressing and A2Hr – solid deposit after the centrifugation of the extracted juice at 4000 rpm for 20 min. Two other vegetal waste adsorbents were collected after inulin extraction from topinambur bulbs, i.e. A1HtL (after extraction in water under stirring) and A2HtL-US (after ultrasound extraction in water). All solids were dried at 90^{o}C for 24 h before the adsorption tests which were performed at 25^{o}C in brown tapered bottles under mild stirring (150 rpm) using synthetic wastewater samples having an initial concentration of IC (14 mg/L) and various adsorbent concentrations in the range of 0.1 - 5 g/L. Wastewater samples were analyzed by UV-Vis spectrometry at 1 h time intervals until 6 h and also after 24 h and 48 h. The adsorbents were characterized before and after the tests by DRIFTS and DR-UV-Vis. The correlation of the adsorption tests results and the characteristics of the solids revealed by DRIFTS and DR-UV-Vis indicated that IC adsorption depended on the aromatics content in the vegetal waste. Richer in aromatics HtL-adsorbents showed higher adsorption capacity than sea-buckthorn-derived ones, e.g. A2HtL-US (9.9 mgIC/g) > A2HtL (8.8 mgIC/g) > A2Hr (7.4 mgIC/G) > A1Hr (5.2 mgIC/g). The resulting spent adsorbents may be further used as additives in colored wrapping paper manufacture.

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FINANCING SOURCE – UEFISCDI Program PNIII
Project Code - PN-III-P2-2.1-PED-2021-1870 –
Contract No. - 646PED/2022

Project Title:
Ecotechnology for obtaining hydrogel encapsulated phytoingredients based on bioactive complexes immobilised in layered double hydroxides matrices
Acronim - DUACTIVMER
Consortium:
Coordinator (CO) – University of Bucharest – Project Manager Conf. Dr. Rodica Zăvoianu
Partner 1 (P1) - INCDPC-ICECHIM Bucharest – Project responsible for partner 1 - Dr. Ing. Andrei Sârbu
Partener 2 (P2) – Research and Processing Center for medicinal plants Plantavorel SA (P2) – Project responsible for Partner 2 – Dr. Ing. Carmen Țebrencu

The implementation status of the project:

Stage 1 -2022 INDUSTRIAL RESEARCH ON THE FORMULATED CONCEPT OF THE TECHNOLOGY 1 AND THE DEVELOPMENT OF THE EXPERIMENTAL MODEL

Period: 21 June 2022-31 December 2022
Stage 1Financing – 160195,00 lei
Source 1 – buget -146765,00 lei
Sursa 2 – cofinancing – 13430,00 lei

SUMMARY OF THE SCIENTIFIC REPORT

In the first step of the project PN-III-P2-2.1-PED-2021-1870-DUACTIVMER, during the period June-December 2022, according to the project implementation plan, the consortium formed by the research teams of the **University of Bucharest (CO)**, **INCDPC-ICECHIM Bucharest (P1) and the Center for research and processing of medicinal plants Plantavorel SA (P2)** carried out a series of industrial research activities to **develop the experimental model of eco-technology 1 consisting in the obtaining of phytoingredients from *Rhamnus Frangula L* (RfL) encapsulated in a hydrogel containing bioactive complexes immobilized in layered double hydroxides (LDH) matrices**.

At **activity 1.1., P2** carried out **30** experiments to develop the **experimental technological and analytical model** regarding **module a_1 of the eco-technology of extracting phytocomplexes from RfL** through 2 non-conventional extraction methods (a_{11}- microwave-assisted extraction (MAE) and a_{12} – extraction assisted by ultrasound (UAE)) and delivered to CO a batch of RfL extractive solution obtained by MAE to immobilize the extracted phytocomplex in various LDH matrices (**for the development of module b_1 of the eco-technology**) and a batch of exhausted plant material to test the capacity of adsorption of different pollutants (**for module d_1 of eco-technology**). **To develop module b_1 of the eco-technology**, **CO** synthesised **8** LDH-type compounds, which were calcined before being used to immobilize the RfL phytoextract by the reconstruction method and further characterized by X-ray diffraction, DRIFT, DR-UV-Vis spectroscopy and differential thermal analysis (TG-DTA). **CO** provided to P1 **16** LDH-precursor materials and LDH-RfL samples to be used in developing **the c_1 module of eco-technology**. For the further development of module c_1 of the eco-technology, P1 evaluated the possibility of incorporating the LDH-precursor materials and the LDH-RfL compounds into two different types of hydrogel by performing **10** experiments with biocompatible natural polymer hydrogel and **18** experiments with biocompatible composite hydrogel.

At **activity 1.2., CO** performed **39** experiments for the technical-scientific evaluation and testing of the adsorption capacity of plant residues exhausted after the extraction of phytocomplexes from RfL by the MAE method for 4 pollutants from wastewater, namely: indigo carmine, Cr, Ni and Fe. The

adsorption capacity of the spent plant material was determined by dosing the pollutants remaining in the water at the end of the tests and analyzing them using UV-Vis spectrophotometry. The obtained results allowed the development of the experimental model for the $\mathbf{d_1}$ module of eco-technology.

Therefore, by fulfilling the tasks in activities 1.1 and 1.2, the experimental model for the eco-technology 1 HYG-RfL-LDH was fully developed and it will be further optimized in the next stage of the project implementation.

P2 has performed **activity 1.3**, which was the preliminary industrial research needed for developing module a_2 of the experimental model of eco-technology 2 consisting in obtaining some phytoingredients from Helianthus tuberosus L (HtL) encapsulated in hydrogel based on bioactive complexes immobilized in the layered double hydroxide (LDH) matrices. Four ways of enzymatic inactivation of HtL tubers were tested, which were further subjected to the extraction procedure of the biologically active phytocomplexes by using 3 conventional methods having different numbers of stages (in two extraction stages, in one extraction stage followed by the analysis of the extractive solution and in one long extraction step). Both the solids and the resulting extractive solutions were phytochemically characterized.

Activity 1.4. consisted of disseminating the results as it follows

2 ISI publications

1. I. E. Neblea, A.-M. Gavrilă, T. V. Iordache, A. Zaharia, P. O. Stănescu, I. C. Radu, S. G. Burlacu, G. Neagu, A.L. Chiriac,* A. Sârbu*, Interpenetrating networks of bacterial cellulose and poly (ethylene glycol) diacrylate as potential cephalexin carriers in wound therapy, J. Polymer Research (2022) 29: 406 https://doi.org/10.1007/s10965-022-03250-9, (IF 3,097, yellow zone) authors from P1

2. R. Zăvoianu, M. Tudorache, V.I. Pârvulescu, B. Cojocaru, O.D. Pavel, New MgFeAl-LDH Catalysts for Claisen–Schmidt Condensation, Molecules, 2022, 27, 8391. https://doi.org/10.3390/molecules27238391. (IF 4,972, yellow zone) authors from CO

3 oral presentations at the XXXVI Edition of the National Conference of Chemistry Călimănești-Caciulata Vâlcea, 4-7 oct. 2022 (authors froma CO, P1 and P2)

a) Beads based on sodium alginate and titania composites for heavy metals removal from simulated waste waters, A. Miron, A.L. Neagu, S. Dolana, A. Zaharia, A.-M. Gavrilă, A. Sârbu, T.-V. Iordache, A.-L. Chiriac (P1)

b) Molecularly imprinted supermacroporous cryogels for Penicillin G adsorption, M. V. Dumitru, T.-V. Iordache, I. E. Neblea, E. B. Stoica, T. Sandu, A. Sârbu, A.-M. Gavrilă, A.L. Chiriac (P1)

c) Removal of indigo carmine from wastewater by adsorption on vegetal wastes, O.D. Pavel (CO), R. Zăvoianu (CO), D. Buha, E.M. Ungureanu, A. Cruceanu (CO), A. Tîrșoagă (CO), O.T. Apreutesei (P2)

2 posters; i) A non-traditional perspective in the synthesis of Fe-LDH type materials, O. D. Pavel, R. Zăvoianu, A. Tîrşoagă, A. Cruceanu, B. Cojocaru, R. Bîrjega, V. I. Pârvulescu **at the XXXVI Edition of the National Conference of Chemistry** (authors CO) ; **ii)** Hydrogels based on natural polymers dopped with LDH and phytoextract – M. V. Dumitru, T. V. Iordache, A. L. Neagu, A. Zaharia, R. Zăvoianu, O. Pavel, S. Teodor, A. Sârbu, SICHEM 2022, University Politehnica Bucharest, 17-18 november 2022 (authors P1 and CO)

The abstracts for the above mentioned oral presentations and posters are attached at the end of this document.

Within **activity 1.5.**, three team members of CO made a work visit to P2 to collect the extract samples and the spent plant material and train on the working protocols needed for the analytical control of phytocomplexes extracted from RfL.

Based on the above information, it can be considered that all the objectives proposed for the current stage have been reached and even exceeded in terms of dissemination which targeted initially only 2 communications.

International Chemical Engineering and Material Symposium, SICHEM 2020, 17-18 September 2022, ISSN 2537-2254

Hydrogels based on natural polymers dopped with LDH and phytoextract

Marinela V. Dumitru[1], Tanta Verona Iordache[1], Ana L. Neagu[1], Anamaria Zaharia[1], Rodica Zavoianu[2], Octavian Pavel[2], Sandu Teodor[1], Andrei Sarbu[1]*

[1]National Research-Development Institute for Chemistry and Petrochemistry-ICECHIM, Splaiul Independentei 202, district 6, 060021, Bucharest, Romania
[2] University of Bucharest, 050663 Bucharest, Romania

Abstract: ***N****ew composite hydrogels based on Chitosan and hydrotalcite dopped with phyoextracts were prepared with the aim of possible slow release of bioactive substances.*
Key words: Chitosan, hydrogels, LDH, phytoectract

Introduction: Lately, with the rapid development of industry, hydrogels have attracted more and more attention due to their large specific surface area and unique structure. Hydrogels are three-dimensional network-structured polymer formed by a polymer main chain and a hydrophilic functional group through covalent bonds, hydrogen bonds, or physical winding cross-linking [1-2]. Hydrogels have been used for many years in controlled drug delivery, water purification (for heavy metals, dyes, antibiotics) tissue regeneration, etc. Natural polymers (chitosan alginate, biocelulose) are the most attractive materials used to replace synthetic materials [3]. In this work, new hydrogels based on chitosan (CS) were successfully prepared by adding layered double hydroxides (hydrotalcite-LDH) and LDH dopped with phytoextract during the process of CS hydrogel preparation.

Experimental and Modelling: For the development of the aimed hydrogels two polymers were needed: chitosan (CS) and poly(vinylalcohol) (PVA). Two solutions of these polymers were prepared and mixed, followed by the addition of hydrotalcites (LDH) and LDH with a phytoextract and, at the end, the crosslinker was introduced.

Results and discussions: In order to highlight the new developed hydrogels, the samples were characterized using various modern techniques such as FTIR, swelling degree. FTIR spectra confirmed the occurrence of characteristic bands for the involved raw materials**.**

Conclusions: The aimed hydrogels based on natural polymers were succesfully developed and characterized by FTIR and also their swelling degree capacity was studied in time.

Aknowledgement: The study was funded by the Ministry of Education and Research through Ececutive Unit for Financing Higher Education, Research, Development and Innovation (UEFISCDI), grant. No. 646 PED/2022 DUACTIVMER and grant no. 15PFE/2021 NeXT-BExcel.

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A NON-TRADITIONAL PERSPECTIVE IN THE SYNTHESIS OF Fe-LDH TYPE MATERIALS

Octavian Dumitru Pavel[1], Rodica Zăvoianu[1], Alina Tîrşoagă[1], Anca Cruceanu[1], Bogdan Cojocaru[1], Ruxandra Bîrjega[2], Vasile I. Pârvulescu[1]

[1] University of Bucharest, Faculty of Chemistry, Sos. Panduri No. 90-92, S5, Bucharest, Romania

[2]National Institute for Lasers, Plasma and Radiation Physics, 409 Atomistilor Street, PO Box MG-16, 077125, Magurele, Romania

The aim of this work was the obtaining of Fe modified layered double hydroxides (LDH) materials (Mg,Fe/Al=3 and Mg/Fe=1 molar ratio) using two non-traditional approaches in LDH synthesis: *i)* the mechano-chemical method and *ii)* the use of an organic base (tetramethylammonium hydroxide - TMAH) as precipitation agent.[1]For comparison, Fe-LDH was also prepared by the traditional method: co-precipitation at pH of 10 in the presence of inorganic alkalis ($NaOH/Na_2CO_3$).Fe-LDH materials were subsequently calcined at 460 °C for 18 h to obtain the corresponding mixed oxides. The mixed oxides were then rehydrated with distilled water to reconstruct the layered structure of the parent LDH based on the memory effect.All materials were characterized by XRD, IR and UV-Vis spectroscopy, N_2 adsorption-desorption isotherms and basic sites determination by irreversible adsorption of organic molecules with different pK_a. Thus, a higher purity was remarkable for the compounds obtained by co-precipitation compared to those obtained by the mechano-chemical method regardless of the nature of the base.The presence of impurities in Fe-LDH obtained by both routes is related to the presence ofFe_3O_4diffraction lines in the XRD patterns.The contaminating Fe_3O_4phase is preserved even after the reconstruction of the layered structure. The catalytic activity in Claisen-Schmidt condensation between cyclohexanone and benzaldehyde followed the same order as the basicity of the samples: mixed oxides > reconstructed> dried, regardless thepreparation method.

Acknowledgement: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CCCDI - UEFISCDI, project number PN-III-P2-2.1-PED-2021-1870, within PNCDI III. 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-2020-2207, within PNCDI III.

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BEADS BASED ON SODIUM ALGINATE AND TITANIA COMPOSITES FOR HEAVY METALS REMOVAL FROM SIMULATED WASTE WATERS

Andreea Miron[12], Ana-Lorena Neagu[1], Sorin Dolana[1], Anamaria Zaharia[1], Ana-Mihaela Gavrila[1], Andrei Sarbu[1], Tanta-Verona Iordache[1], Anita-Laura Chiriac[1*]

[1] *National Institute for Research & Development for Chemistry and Petrochemistry- ICECHIM Bucharest, Spl. Independentei 202, sector 6, ROMANIA*

[2] *University Politehnica of Bucharest, 011061 Bucharest, Romania*

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[1] University of Bucharest, Faculty of Chemistry, Sos. Panduri No. 90-92, S5, Bucharest, Romania

[2] Research and Processing Center for Medicinal Plants Plantavorel SA, Cuza Vodă 46, Piatra Neamț, Neamț County, Romania

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[1] PATEL, S., Rev Environ Sci Biotechnol., **11**, 2012, p.365–380.

SURSA DE FINANȚARE – UEFISCDI Programul PNIII
Cod proiect - PN-III-P2-2.1-PED-2021-1870 –
Nr. Contract 646PED/2022

Titlu proiect:
Ecotechnologie de obținere a unor fitoingredienţi încapsulaţi în hidrogel pe baza de complecşi bioactivi imobilizaţi în matrice de hidroxizi dubli lamelari –
Acronim - DUACTIVMER
Consorțiu:
Coordonator (CO) - Universitatea din București – Director de proiect Conf. Dr. Rodica Zăvoianu
Partener 1 (P1) - INCDPC-ICECHIM București – Responsabil proiect partener 1 - Dr. Ing. Andrei Sârbu
Partener 2 (P2) - Centrul de cercetare și prelucrare a plantelor medicinale Plantavorel SA (P2) – Responsabil proiect Partener 2 – Dr. Ing. Carmen Țebrencu

Stadiul de implementare al proiectului
ETAPA 2/2023 – ELABORAREA ECOTEHNOLOGIILOR DE LABORATOR INTEGRATE HYG-RfL-LDH ŞI HYG-HtL-LDH

Durata 3 Ianuarie 2023-29.12.2023
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REZUMAT RAPORT ȘTIINȚIFIC

ETAPA 2/2023 – ELABORAREA ECOTEHNOLOGIILOR DE LABORATOR INTEGRATE HYG-RfL-LDH ŞI HYG-HtL-LDH

În cadrul etapei 2 a proiectului PN-III-P2-2.1-PED-2021-1870-DUACTIVMER în perioada ianuarie-decembrie 2023 consorțiul format din echipele de cercetători **Universitatea din Bucureşti (CO), INCDPC-ICECHIM București (P1) și Centrul de cercetare și prelucrare a plantelor medicinale Plantavorel SA (P2),** conform planului de realizare al proiectului**,** a efectuat o serie de activități de **cercetare industrială** în vederea: **dezvoltării modelului experimental al ecotehnologiei HYG-HtL-LDH** de obținerea unor fitoingredienţi din *Helianthus tuberosus L* (HtL) încapsulaţi în hidrogel pe baza de complecşi bioactivi imobilizaţi în matrice de hidroxizi dubli lamelari (LDH) **(**activitățile **2.1, 2.2, 2.3); elaborarea tehnologiei de laborator HYG-RfL-LDH pentru obținerea** unor fitoingredienţi din *Rhamnus frangula L* (RfL) încapsulaţi în hidrogel pe baza de complecşi bioactivi imobilizaţi în matrice de hidroxizi dubli lamelari (LDH) **(**activitatea **2.4) și elaborarea tehnologiei de laborator HYG-HtL-LDH (activitatea 2.5). Partenerul P2** a efectuat activitățile de **cercetare industrială 2.6** pentru caracterizarea fitochimică completă și stabilirea caracteristicilor extractelor HtL și **2.7** pentru **verificarea funcționalității modulului (a_1)** al tehnologiei de extracție a fitocomplecșilor din RfL și stabilirea caracteristicilor acestora și activitățile de **dezvoltare experimentală 2.8** pentru **demonstrarea și validarea modulului (a_1) al tehnologiei HYG-RfL-LDH** și activitatea **2.9.** pentru **demonstrarea și validarea modulului (a_2) al tehnologiei HYG-HtL-LDH.**

Pentru a elabora **modelul experimental al ecotehnologiei HYG-HtL-LDH** cercetările privind **modulul a_2** al ecotehnologiei în vederea extracției fitocomplecșilor din HtL au fost efectuate de **P2** care a evaluat 5 surse de materie primă vegetală dintre care a selectat materialul cu concentrația cea mai mare de inulină și a efectuat **30** de experimente de extracție prin 2 metode neconvenționale (extracție asistată de ultrasunete (UAE) și extracție asistată microunde de (MAE)). În urma testelor s-a selectat soluția extractivă (SE) cea mai bogată în inulină (SE-MAE) care a fost livrată la CO în vederea imobilizării

inulinei în diverse matrici LDH (pentru dezvoltarea **modulului b_2** al ecotehnologiei) împreună cu două șarje de material vegetal epuizat (A1HTl-US, A2-HTL-MAE) (pentru **modulul d_2** al ecotehnologiei). Pentru **modulul b_2** al ecotehnologiei, **CO** a sintetizat **6** compuși LDH în care a incorporat SE-MAE prin metoda reconstrucției – probele R2-I, R3-I, R4-I și prin metoda coprecipitării probele P2-I, P3-I, P4-I. Solidele au fost caracterizate prin DRX, DRIFT, spectroscopie DR-UV-Vis și analiză termică diferențială (TG-DTA) și a efectuat teste de eliberare la pH-controlat a inulinei din solid. S-au a predat la P1 un număr de **9** probe LDH precursor (H2,H3,H4) și cele 6 probe cu inulină pentru a fi utilizate la elaborarea modulului c_2 al ecotehnologiei. **Modulul c_2 al ecotehnologiei**. a fost elaborat de **P1** care a evaluat posibilitatea incorporării compușilor LDH precursori și LDH-HtL în două tipuri diferite de hidrogel efectuând **9** experimente cu hidrogel pe bază de polimer natural biocompatibil și **9** experimente cu hidrogeluri compozite semi-interpenetrate. După analizarea compozitelor prin determinarea gradelor de gonflare, comportării reologice și SEM, s-au selectat 6 probe care au fost transmise la CO pentru testele de eliberare la pH-controlat a inulinei din solid. **Modulul d_2** al tehnologiei a fost realizat de **CO** care a efectuat **54** experimente pentru determinarea capacității de adsorbție a resturilor vegetale epuizate A1HTl-US (15 teste), A2-HTL-MAE (39 teste) pentru 5 poluanți din ape reziduale: indigo carmin (IC), Cr, Cu, Fe și Ni.. S-a constatat capacitatea de adsorbție mai mare a A2-HTL-MAE pentru IC și selectivitatea acestuia pentru adsorbția Fe.

Elaborarea tehnologiei de laborator **HYG-RfL-LDH** s-a efectuat pe baza modelului experimental propus în etapa 1, și a experimentelor suplimentare efectuate de CO pentru eliberarea controlată a fitocomplexului *RfL* din compușii *RfL*-LDH și hidrogelurile corespunzătoare acestora și a testelor suplimentare pentru adsorbția Cu din apele reziduale pe materialul vegetal epuizat. Tehnologia cuprinde **4 module**: **(a_1)** extracția complecșilor bioactivi din *Rhamnus Frangula L (RfL)* realizat de P2, **(b_1)** – imobilizarea complecșilor bioactivi din *RfL* în matrici LDH realizat de **CO**; (c_1) încapsularea în hidrogel a complecșilor bioactivi din *RfL* imobilizați în matrici LDH realizat de **P1**; **(d_1)** valorificarea materialului vegetal epuizat după extracția compușilor bioactivi din *RfL* ca material adsorbant pentru poluanți din ape. P2 a demonstrat și validat modulul (a_1) cu ajutorul metodei de validare prospectivă efectuând o serie de 3 experimente.

Tehnologia de laborator **HYG-HtL-LDH** s-a dezvoltat pe baza modelului experimental descris mai sus. Demonstrarea și validarea modulului a_2 al tehnologiei a fost realizată de P2 conform metodei aplicate și la tehnologia **HYG-RfL-LDH**

Activitatea 2.10. Diseminarea s-a materializat în:

participări cu 4 prezentări orale, 1 conferință invitată și 3 postere la conferințe:

i) 18th INTERNATIONAL CONFERENCE ON CHEMISTRY AND THE ENVIRONMENT (ICCE 2023) Venice Italy 11 -16 June 2023 R. Zăvoianu, A.-E. Stamate, O.D. Pavel, A. Cruceanu, R. Bîrjega, I.A. Brezeștean, A. Ciorîtă, Efficient Removal of AB74 Dye from Wastewater Using Hybrid Catalysts: Comparative Studies on Ce-LDH-GO and Mo-LDH-GO Composites Prezentare orală (OP107)

ii) 15th European Congress on Catalysis Prague Czech Republic 27 August-1 September 2023 O.D. Pavel, B.-C. Jurca, R. Zăvoianu, R. Bîrjega, B. Cojocaru, V.I. Pârvulescu, Organic alkalis as an alternative for eco-friendly mechano-chemical synthesis of Layered Double Hydroxides-type catalysts

iii) International Conference „Clean Nature For Health“ 10 - 13 September 2023, Velingrad, Bulgaria A. Sârbu, T. V. Iordache, A. M. Gavrilă, E. B. Stoica, B. Tsyntsarski, S. Teodor, G. Georgiev, I. Stoycheva, Molecularly Imprinted Polymers Preparation and their Use for Environment and Health- Own Result, invited lecture

iv) The Days of Technical Sciences Academy of Romania, Brasov, Romania, 5-6 October 2023; A. Sârbu, S. Teodor, A. L. Chiriac, T. V. Iordache, F. Yardim, A. Sirkecioglu, N. Petrov, B. Tsintsarski, R. Zăvoianu, Polymer bioactive membranefor the treatment of waste waters from hotels. Prezentare orală

v) PRIORITIES OF CHEMISTRY FOR A SUSTAINABLE DEVELOPMENT PRIOCHEM-XIXth Edition, 11-13 octombrie 2023; A.-Lorena Neagu, A. Zaharia, M. V. Dumitru, I. E. Neblea, S. Dolana, T.V. Iordache, C. E. Țebrencu, R. Zăvoianu, O. D. Pavel, A. Tîrșoagă, A. Sârbu, Drug-Release System

Based onBiocompatible Hydrogel Charged With Layered Double Hydroxide Containing Encapsulated *Rhamnus Frangula* L. Phytoextract, prezentare orală

vi). 3 rd International Conference on Bioengineering and Polymer Science, Bucharest, June 7-11,2023 ROMANIA; A. Zaharia, A. L. Neagu, O. D. Pavel, A. Tîrşoagă, I. E. Neblea, S. V. Dolana, T. V. Iordache, R. Zăvoianu, A. Sârbu, Layered Double Hydroxides - Polyethylene Glycol Diacrylate Composite Hydrogels for the Controlled Release of Rhamnus Frangula L Phytoextract- poster

vii) 18th INTERNATIONAL CONFERENCE ON CHEMISTRY AND THE ENVIRONMENT (ICCE 2023) Venice Italy 11 -16 June 2023 A. Tirșoagă, R. Zăvoianu, O.D. Pavel, A. Cruceanu, O.T. Apreutesei, C. Țebrencu, Using lignocellulosic vegetal wastes as adsorbents for transition metals from wastewaters - poster

viii) 5th Euro-Mediterranean Conference for Environmental Integration (EMCEI-2023), 2-5octombrie 2023, A. Zaharia, I. E. Neblea, A.-L. Chiriac, A.-M. Gavrilă, S. Dolana, A. L. Neagu, B. Trică, A. Sârbu, F.-X. Perrin, T.-V. Iordache, Polyethylene glycol diacrylate nanogels - a versatile sys-tem for themolecularly imprinting of biomolecules – poster

Publicarea unui articol într-o revistă ISI (Q1): A.-L. Neagu, A. Zaharia, O. D. Pavel, A. Tîrșoagă, I. E. Neblea, S. V. Dolana, C. E. Țebrencu, T.-V. Iordache, A. Sârbu, R. Zăvoianu, Synergistic Sustained Drug Release System based on immobilized Rhamnus Frangula Lphytoextract into Layered Double Hydroxide covered by Biocompatible Hydrogel, Pharmaceutics, 2023, 15(7), 1888; https://doi.org/10.3390/pharmaceutics15071888.

Publicarea unui articol într-o revistă ISI (Q2): O.D. Pavel, A.E. Stamate, R. Zăvoianu, A. Cruceanu, A. Jurca, R.Birjega, I.A. Brezestean, A. Ciorîță, D.C. Culiță, A.P.S. Dias, Mo-LDH-GO Hybrid Catalysts for Indigo Carmine Advanced oxidation, Materials, 2023, 4, 3205, doi: 10.3390/ma16083025

Depunerea a două cereri de brevet la OSIM:

1. Sârbu A., Zăvoianu R., Pavel O. D., Zaharia A., Neagu A. L., Jurca A., Tebrencu C., Apreutesei O. T., Dumitru M. V., Sandu T., Iordache T. V., Hidrogeluri compozite biocompatibile, conţinând hidroxizidublu lamelari, pentru eliberarea controlată a substanţelor bioactive din fitoextracte de cruşin şi procedeu de obţinere, A 2023 -00108/07.03.2023.
2. Sârbu A., Zăvoianu R., Zaharia A., Pavel O. D., Dumitru M. V., Sandu T., Jurca A., Țebrencu C. E., Stamate A. E., Iordache T. V., Chiriac A. L., Gavrilă A.-M., Hidrogeluri cu reţele semi-interpenetrate, conţinând hidroxizi dubli lamelari, pentru eliberarea controlată de inulină şi procedeu de obţinere.

În cadrul **activității 2.11.** trei membri din echipa CO au făcut o vizită de lucru la P2 pentru discutarea rezultatelor obținute la demonstrarea și validarea modulului (a_1) al tehnologiei HYG-RfL-LDH și la demonstrarea și validarea modulului (a_2) al tehnologiei HYG-HtL-LDH..

Pe baza celor prezentate mai sus se poate considera că obiectivele propuse pentru această etapă au fost atinse și chiar depășite în ceea ce privește diseminarea.

In English

FINANCING SOURCE – UEFISCDI Program PNIII
Project Code - PN-III-P2-2.1-PED-2021-1870 –
Contract No. - 646PED/2022
Project Title:
Ecotechnology for obtaining hydrogel encapsulated phytoingredients based on bioactive complexes immobilised in layered double hydroxides matrices
Acronim - DUACTIVMER
Consortium:
Coordinator (CO) – University of Bucharest – Project Manager Conf. Dr. Rodica Zăvoianu
Partner 1 (P1) - INCDPC-ICECHIM Bucharest – Project responsible for partner 1 - Dr. Ing. Andrei Sârbu
Partener 2 (P2) – Research and Processing Center for Medicinal Plants Plantavorel SA (P2) – Project responsible for Partner 2 – Dr. Ing. Carmen Țebrencu

The implementation status of the project:

Stage 2 -2023 SETTING UP OF THE INTEGRATED LABORATORY ECOTECHNOLOGIES HYG-RfL-LDH AND HYG-HtL-LDH
Period: 1 January 2023-31 December 2023
Stage 2 Financing – 391626,00 lei
Source 2 – budget -345176,00 lei
Sursa 2 – cofinancing – 46450,00 lei

SUMMARY OF THE SCIENTIFIC REPORT
STAGE 2/2023 – SETTING UP OF THE INTEGRATED LABORATORY ECOTECHNOLOGIES HYG-RfL-LDH AND HYG-HtL-LDH

During the second stage of the project PN-III-P2-2.1-PED-2021-1870-DUACTIVMER from January to December 2023 the consortium made by joining the research teams from **University of Bucharest (CO), INCDPC-ICECHIM Bucharest (P1) and the Research and Processing Center for Medicinal Plants SA (P2),** according to the realisation plan of the project**,** performed a series of **industrial research activities** aimed to: set up the **experimental model of the ecotechnology HYG-HtL-LDH** for the obtaining of hydrogel encapsulated fitoingredients from *Helianthus tuberosus L* (HtL) based on bioactive complexes immobilised in layered double hydroxides matrices (LDH) **(**activities **2.1, 2.2, 2.3); the development of the laboratory technology HYG-RfL-LDH for the obaining** of hydrogel encapsulated fitoingredients from *Rhamnus frangula L* (RfL) based on bioactive complexes immobilised in layered double hydroxides (LDH) **(**activity **2.4) and the development of the laboratory technology HYG-HtL-LDH (activity 2.5). Partner P2** performed the **industrial research activities 2.6** for the full phytochemical characterization and the setting up of the HtL extracts characteristics and **2.7** for the **functionality checking-up of the module (a_1)** of the technology for the extraction of RfL phytocomplexes and the setting up of their characteristics as well as the **experimental development activities 2.8** to **demonstrate and validate the module (a_1) of the technology HYG-RfL-LDH** and the activity **2.9.** to **demonstrate and validate the module (a_2) of the technology HYG-HtL-LDH.**

In order to set up the **experimental model of the ecotechnology HYG-HtL-LDH,** the researches related to the **module a_2** of the ecotechnology targeting the extraction of the phytocomplexes from HtL were perfomed by **P2** who evaluated 5 sources of vegetal raw material in order to select the one with the highest concentration of inulin and carried out **30** extraction tests using 2 nonconventional methods (ultrasound assisted extraction (UAE) and microwave assisted extraction (MAE)). Following the tests, the extractive solution (SE) having the highest concentration of inulin (SE-MAE) was selected and

delivered to CO in order to be immobilised in different LDH matrices (for setting up the **module b_2** of the ecotechnology) along with two batches of vegetal spent material (A1HTl-US, A2-HTL-MAE) (to be utilized in the **module d_2** of the ecotechnology). For the **module b_2** of the ecotechnology, **CO** synthesized **6** LDH compounds Into which SE-MAE was incorporated by reconstruction– samples R2-I, R3-I, R4-I and by co-precipitation samples P2-I, P3-I, P4-I. The resulting solids were characterized by XRD, DRIFT, ATR-FTIR, DR-UV-Vis spectroscopy, thermodifferential analysis (TG-DTA) and inulin release tests under controlled pH. CO delivered to P1 a number of **9** LDH samples, 3 samples of reference LDH precursors (H2,H3,H4) and the six samples containing inulin]n order to be utilized for setting up the modulule c_2 of the ecotechnology. The **module c_2 of the ecotechnology** was set up by **P1** who evaluated the possibility to incorporate of the LDH precursors and LDH-HtL compounds in two different types of hydrogels by performing **9** experiments with a hydrogel based on a natural biocompatible polymer and **9** experiments with semi-interpenetrated composite hydrogels. After analysing the composites by determining the swelling degree, the reologcal behaviour and SEM, 6 samples were selected and delivered to CO for the inulin release tests under controlled pH. The **module d_2** of the technology was set up by **CO** who performed **54** experiments to determin the adsorbtion capacity of the spent vegetal materials A1HTl-US (15 tests), A2-HTL-MAE (39 tests) for 5 polutants from waste waters: indigo carmin (IC), Cr, Cu, Fe and Ni. The obtained results indicated a higher adsorption capacity of A2-HTL-MAE for IC and its selectivity for Fe adsorption.

The setting up of the laboratory technology **HYG-RfL-LDH** was based on the experimental model proposed in the first stage of the project and the supplementary experiments performed by CO for the controlled release of *RfL* phytocomplex from *RfL*-LDH compounds and the corresponding hydrogels as well as the supplementary tests for Cu adsorption from waste water onto the spent vegetal material. The technology consists of **4 modules**: **(a_1)** the extracion of bioactive complexes from *Rhamnus Frangula L (RfL)* realised by P2, **(b_1)** – immobilization of bioactive complexes from *RfL* into LDH matrices realized by **CO**; (c_1) hydrogel encapsulation of the bioactive complecxes from *RfL* immobilized into LDH matrices LDH realized by **P1**; **(d_1)** valorisation of the spent vegetal material after the extraction of the bioactive compounds from *RfL* as adsorbant for water pollutants. P2 demonstrated and validated the module (a_1) using the prospective validaton method by performing a series of 3 experiments.

The laboratory technology **HYG-HtL-LDH** was developed based on the above described experimental model. The demonstration and validation for the module a_2 of the technology was realized by P2 according to the same method applied for the technology **HYG-RfL-LDH.**

Activity 2.10. The dissemination consisted in:

participations with 4 oral presentations, 1 invited lecture and 3 poster presentations at conferences:

i) 18th INTERNATIONAL CONFERENCE ON CHEMISTRY AND THE ENVIRONMENT (ICCE 2023) Venice Italy 11 -16 June 2023 R. Zăvoianu, A.-E. Stamate, O.D. Pavel, A. Cruceanu, R. Bîrjega, I.A. Brezeștean, A. Ciorîtă, Efficient Removal of AB74 Dye from Wastewater Using Hybrid Catalysts: Comparative Studies on Ce-LDH-GO and Mo-LDH-GO Composites Oral Presentation (OP107)

ii) 15th European Congress on Catalysis Prague Czech Republic 27 August-1 September 2023 O.D. Pavel, B.-C. Jurca, R. Zăvoianu, R. Bîrjega, B. Cojocaru, V.I. Pârvulescu, Organic alkalis as an alternative for eco-friendly mechano-chemical synthesis of Layered Double Hydroxides-type catalysts

iii) International Conference „Clean Nature For Health“ 10 - 13 September 2023, Velingrad, Bulgaria A. Sârbu, T. V. Iordache, A. M. Gavrilă, E. B. Stoica, B. Tsyntsarski, S. Teodor, G. Georgiev, I. Stoycheva, Molecularly Imprinted Polymers Preparation and their Use for Environment and Health- Own Result, invited lecture

iv) The Days of Technical Sciences Academy of Romania, Brasov, Romania, 5-6 October 2023; A. Sârbu, S. Teodor, A. L. Chiriac, T. V. Iordache, F. Yardim, A. Sirkecioglu, N. Petrov, B. Tsintsarski, R. Zăvoianu, Polymer bioactive membranefor the treatment of waste waters from hotels. Oral Presentation

v) PRIORITIES OF CHEMISTRY FOR A SUSTAINABLE DEVELOPMENT PRIOCHEM-XIXth Edition, 11-13 octombrie 2023; A.-Lorena Neagu, A. Zaharia, M. V. Dumitru, I. E. Neblea, S. Dolana, T.V. Iordache, C. E. Țebrencu, R. Zăvoianu, O. D. Pavel, A. Tîrșoagă, A. Sârbu, Drug-Release System

Based onBiocompatible Hydrogel Charged With Layered Double Hydroxide Containing Encapsulated *Rhamnus Frangula* L. Phytoextract, Oral Presentation

vi). 3 rd International Conference on Bioengineering and Polymer Science, Bucharest, June 7-11,2023 ROMANIA; A. Zaharia, A. L. Neagu, O. D. Pavel, A. Tîrşoagă, I. E. Neblea, S. V. Dolana, T. V. Iordache, R. Zăvoianu, A. Sârbu, Layered Double Hydroxides - Polyethylene Glycol Diacrylate Composite Hydrogels for the Controlled Release of Rhamnus Frangula L Phytoextract- poster

vii) 18th INTERNATIONAL CONFERENCE ON CHEMISTRY AND THE ENVIRONMENT (ICCE 2023) Venice Italy 11 -16 June 2023 A. Tirșoagă, R. Zăvoianu, O.D. Pavel, A. Cruceanu, O.T. Apreutesei, C. Țebrencu, Using lignocellulosic vegetal wastes as adsorbents for transition metals from wastewaters - poster

viii) 5th Euro-Mediterranean Conference for Environmental Integration (EMCEI-2023), 2-5octombrie 2023, A. Zaharia, I. E. Neblea, A.-L. Chiriac, A.-M. Gavrilă, S. Dolana, A. L. Neagu, B. Trică, A. Sârbu, F.-X. Perrin, T.-V. Iordache, Polyethylene glycol diacrylate nanogels - a versatile sys-tem for the molecularly imprinting of biomolecules – poster

Publication of a paper in ISI journal (Q1): A.-L. Neagu, A. Zaharia, O. D. Pavel, A. Tîrșoagă, I. E. Neblea, S. V. Dolana, C. E. Țebrencu, T.-V. Iordache, A. Sârbu, R. Zăvoianu, Synergistic Sustained Drug Release System based on immobilized Rhamnus Frangula L phytoextract into Layered Double Hydroxide covered by Biocompatible Hydrogel, Pharmaceutics, 2023, 15(7), 1888; https://doi.org/10.3390/pharmaceutics15071888.

Publication of a paper in ISI journal (Q2): O.D. Pavel, A.E. Stamate, R. Zăvoianu, A. Cruceanu, A. Jurca, R.Birjega, I.A. Brezestean, A. Ciorîță, D.C. Culiță, A.P.S. Dias, Mo-LDH-GO Hybrid Catalysts for Indigo Carmine Advanced oxidation, Materials, 2023, 4, 3205, doi: 10.3390/ma16083025

2 Applications for national patents at OSIM:

1. Sârbu A., Zăvoianu R., Pavel O. D., Zaharia A., Neagu A. L., Jurca A., Tebrencu C., Apreutesei O. T., Dumitru M. V., Sandu T., Iordache T. V., Biocompatible composite hydrogels containing layered double hydroxides, for the controlled release of the bioactive substances from alder buckthorn phytoextracts and obtaining procedure, A 2023 -00108/07.03.2023.
2. Sârbu A., Zăvoianu R., Zaharia A., Pavel O. D., Dumitru M. V., Sandu T., Jurca A., Țebrencu C. E., Stamate A. E., Iordache T. V., Chiriac A. L., Gavrilă A.-M., Hidrogels with semi-interpenetrated networks containing layered double hydroxides for the controlled release of inulin and obtaining procedure. A 2023 -00795/05.12.2023.

Within **activity 2.11.**, three team members of CO made a work visit to P2 to discuss the results obtained at the demonstration and validation of the module (a_1) of the technology HYG-RfL-LDH and the demonstration and validation of the module (a_2) of the tehnology HYG-HtL-LDH.

Based on the above information, it can be considered that all the objectives proposed for the current stage have been reached and even exceeded in terms of dissemination which targeted initially only 2 communications and 1 paper submitted for publication.