SCIENTIFIC AND TEHNICAL REPORT

(1.07.2022-29.11.2024)

Project PCE : Bio-based porous materials for hydrogen storage and environmental applications

(BIOPOROMAT)

PN-III-P4-PCE-2021-1455, Contract no. PCE 118/2022

Website: http://www.cercetare.icpm.tuiasi.ro/proiecte/BIOPOROMAT/2022_en/default.html

Coordinator: Gheorghe Asachi Technical University of Iaşi (TUIaşi)

Project manager: Professor Irina Volf

I. Short description

Summary of the activities carried out in the framework of this project:

The purpose of this project was to design and obtain hybrid materials based on carbon micro/nano structures (CMNS), resulting from the conversion of biomass waste, embedded in polymer matrices (natural or synthetic), with environmental and energy storage applications.

A summary of the main results obtained is presented herein further.

O1 focused on the evaluation and analysis of the availability and types of biomass waste, through the chemical, morphological and structural characterization of some lignocellulosic waste in order to achieve a realistic evaluation of the valorization potential as well as the establishment of their pretreatment and conversion techniques. The biomass wastes (spruce bark, vine wood and wheat straw), the necessary pretreatments (physical) as well as the thermochemical conversion techniques (slow pyrolysis at 550°C and hydro thermolysis at 260°C) were defined and their optimized protocols have been developed. CMNS have been extensively investigated.

O2 aimed at porosity tailoring for the obtained CMNS. Obtaining data through numerous experimental tests and evaluations, the activities resulted in the validation of three working protocols for the adaptation of the porosity/functionalization of the CMNS in direct correlation with the targeted applications. Two types of polymer gels were designed as matrices for embedding CMNS: (i) a hydrogel based on a natural polymer (gellan); (ii) a cryogel based on Poly(2-hydroxyethyl methacrylate) (p-HEMA) and one based on poly-acrylic alcohol (PAA) physically cross-linked with poly-vinyl alcohol (PVA), where carbon structures were embedded successfully; (iii) two configurations of hybrid materials based on CMNS functionalized for energy storage and bacterial immobilization (bioremediation) applications.

O3: The carried-out studies showed that the gels based on gellan and CMNS present an affinity for dyes (Crystal Violet and Methylene Blue) with better adsorption capacities at equilibrium than other gels reported in the literature. Also, removal rates of 70-97% were obtained for Pb(II) ions and emerging organic pollutants (diclofenac). One of the proposed configurations represents a remarkable protective support for bacterial immobilization that increases by 4 times the survival rate of Pseudomonas bacteria, and by 30% the bioremediation capacity of wastewater polluted with plasticizer agents (diethyl phthalate). In the alternative forms of energy storage, the supercapacitor characteristics of the hybrid carbon material were validated, as well as the ability to retain some gases (H_2, N_2, CO_2) of the hybrid cryogels obtained within the project. Some of the proposed composite configurations could represent a good protective film for H_2 storage containers, reducing the possibility of embrittlement of the metal ferrule.

III. Results indicators

Deliverables of the project.

Nr. crt.	Indicatori de rezultat	Accomplished	Expected
1.	Articles published in ISI ranked journals (Q1 şi Q2)	**7**	5
2.	Article submitted to ISI Conference Proceeding	**1**	0
3.	Patent requests	**3**	1
4.	Articles published in international data bases journals	**2**	0
5.	Research stages abroad	**5**	0
6.	Communications at international conferences	**9**	2
7.	Conference Awards	**1**	0
8.	Doctoral theses defended by young researchers, project members	**1**	0
9.	Kick-off meetings	**2**	0
10.	Web site	**1**	1

A. Articles submitted to ISI journals

1. Tincu C., Hacerencu M., Secula M.S., Stan C.S., Albu C., Popa M., **Volf I***., 2024, A natural Carbon Encapsulated In Gellan-Based Hydrogel Particles designed for Environmental Challenges, Gels,10, 713, https://doi.org/10.3390/gels10110713, **(Q1, FI 5)**

2. Armanu G.E., Secula M.S., Tofanica B.M., **Volf I*.,** 2024, The Impact of Biomass Composition Variability on the Char Features and Yields Resulted through Thermochemical Processes, Polymers, 16, 2334. https://doi.org/10.3390/polym16162334 **(Q1 FI 4.7)**

3. Hristea G., Iordoc M., Lungulescu E.M., Bejenari I. and Volf I.*, 2024, A sustainable bio-based char as emerging electrode material for energy storage applications, Scientific Reports, *14(1*), 1095. https://doi.org/10.1038/s41598-024-51350-x **(Q1, FI 4.6)**

4. Mikhailidi A., Ungureanu E., Belosinschi D., Tofanica B.M.* and Volf I.* , 2023, Cellulose-Based Metallogels - Part 3: Multifunctional Materials, Gels, 9(11), 878. **(Q1, FI 5),** https://doi.org/10.3390/gels9110878

5. Ciuperca O.T., Ionescu E., Secula M.S., Volf I.*, 2023, Microwave-Assisted Extraction of Condensed Tannins from Branches of *Prunus spinosa* L.: Response Surface Modeling and Optimization, Processes, 11, 2024, https://doi.org/10.3390/pr11072024 **(Q2, FI 3.5).**

6. Stan L., **Volf I.*,** Stan C.S.*, Albu C., Coroabă A., Ursu L.E., Popa M., 2023, Intense Blue Photo Emissive Carbon Dots Prepared through Pyrolytic Processing of Lignocellulosic Wastes, Nanomaterials, 13 (1), 131, https://doi.org/10.3390/nano13010131 **(Q1, FI 5.719)**

7. Ungureanu G., Bejenari I., Hristea G., **Volf I.*,** 2022, Carbonaceous materials from forest waste conversion and their corresponding hazardous pollutants remediation performance, Forests, 13, 2080. https://doi.org/10.3390/f13122080 **(Q1 FI 3.282).**

B. Article submitted to ISI Conference Proceeding

1. Armanu G.E., Secula M.S., Heipieper H.J., Volf I., 2024, *Pseudomonas canadensis* immobilized on a carbonaceous material enhance plasticizer biodegradation, paper submitted to Conference Proceedings (ISSN 1314-2704) indexed by ISI Web of Science – Clarivate.

C. Patent requests

1. Stan C.S., Albu C., Volf I., 2024, A lignocellulosic waste valorisation path into a new porous polimeric composite material designed for wastewater treatment**, A/00677 din 10.11.2023**.

2. Hristea G., Iordoc M.N., Volf I., 2024, An electroactive carbon material based on lignocellulosic waste for supercapacitors and production process, **A /00139 din 28.03.2024**.

3. Volf I., Armanu G.E., Secula M.S., 2024, A natural sustainable carrier for bacterial immobilization used in bioremediation, **A /00606 din 11.10.2024**.

D. Articles published in international data bases journals (BDI):

1. Toma A.C., Volf I., 2023, A short review on urban air pollution and innovative bio-remedial approaches, Bulletin of Polytechnic Institute of Iasi, Chemistry and Chemical Engineering section, 69 (73), 3, 87-101, doi.105281/zenodo.10072450.

2. Armanu G.E., Volf I., 2022, Natural carriers for bacterial immobilization used in bioremediation, Bulletin of Polytechnic Institute of Iasi, Chemistry and Chemical Engineering section, 68 (72), 3, 109-122.

E. Communications:

1. Armanu G.E., Tofanica B., Volf I**., 2022,** „Measurement of key compositional parameters in three type of biomass wastes in order to define the appropriate feedstock for thermochemical conversion**" ,** *The 6th International Conference on Chemical Engineering ICCE2022, Advanced Materials and Processes for a Sustainable Development*: http://www.cercetare.icpm.tuiasi.ro/conferinte/ICCE2022/pdf/ICCE2022-program.pdf

2. Armanu G.E., Tofanica B., Secula M.S., Mamaliga I., Volf I*., 2022*, **"**Predictive carbonaceous materials yields resulted from carbonization in relation with the main components of the feedstock", *SICHEM 2022 Hydrogen the future energy and chemical engineering vector:*

https://sicr.ro/wp-content/uploads/2022/11/SICHEM_Program_2022_v12.pdf

3. Asoltanei A.M., Iacob Tudose E.T., Secula M.S., Mamaliga I., 2022, Effective diffusivity in porous spherical and cylindrical particles, *SICHEM 2022, Hydrogen the future energy and chemical engineering vector*
https://sicr.ro/wp-content/uploads/2022/11/SICHEM_Program_2022_v12.pdf

4. Armanu G.E., Secula M.S., Volf I., 2023, Eco-efficient hydrochar for immobilization of P*seudomonas species*, The 12th International Conference on Environmental Engineering and Management ICEEM 12, Circular Economy and Sustainability, https://www.iceem.tuiasi.ro/wp-content/uploads/ICEEM12_Program-04.09.2023_f.pdf

5. Armanu G.E., Bertoldi S., Chauhan Z., Eberlein C., Nikolausz M., Shmidt M., Heipieper H.J., Volf I., 2023, Biodegradation of phthalic acid esters using immobilized bacteria on a natural carbonaceous porous material, Annual International Conference of the Association for General and Applied Microbiology, VAAM 2023, Göttingen, https://vaam.de/aktivitaeten/jahrestagung/archiv-der-jahrestagungen/

6. Armanu G.E., Secula M.S., Cimpoeşu N., Volf I., 2024, A biobased nano/micro-structured material for microorganisms immobilization, XXIVth International Multidisciplinary Scientific GeoConference: Surveying, Geology and Mining, Ecology and Management – SGEM 2024, 29 Jun - 8 Jul, https://www.sgem.org/index.php/dates-deadlines/conference-plenary-programme.

7. Bejenari I., Secula M.S., Volf I., 2024, Integral valorization of biomass waste towards sustainable and value-added hybrid materials, PolyChar World Forum on Advanced Materials, 30th edition, September 11-13. https://icmpp.ro/polychar'30/program.php

8. Armanu G.E., Secula M.S., Heipieper H.J., Volf I., 2024, *Pseudomonas canadensis* immobilized on a carbonaceous material enhance plasticizer biodegradation, XXIVth International Multidisciplinary Scientific GeoConference: Surveying, Geology and Mining, Ecology and Management – SGEM 2024, 29 Jun - 8 Jul, https://www.sgem.org/index.php/dates-deadlines/conference-plenary-programme.

9. Armanu G.E., Bertoldi S., Eberlein C., Heipieper H.J., Secula M.S., **Volf I.,** 2024, Immobilized bacterial cells on a natural carbonaceous material for diethyl phthalate biodegradation, 7th International

Conference of the Doctoral School "Gheorghe Asachi" Technical University of Iasi, CSD 2024, May 15-17, https://conferinta-csd.tuiasi.ro/wp-content/uploads/2024/05/Program-CSD2024_full_Updated_12_mai_cover-1.pdf

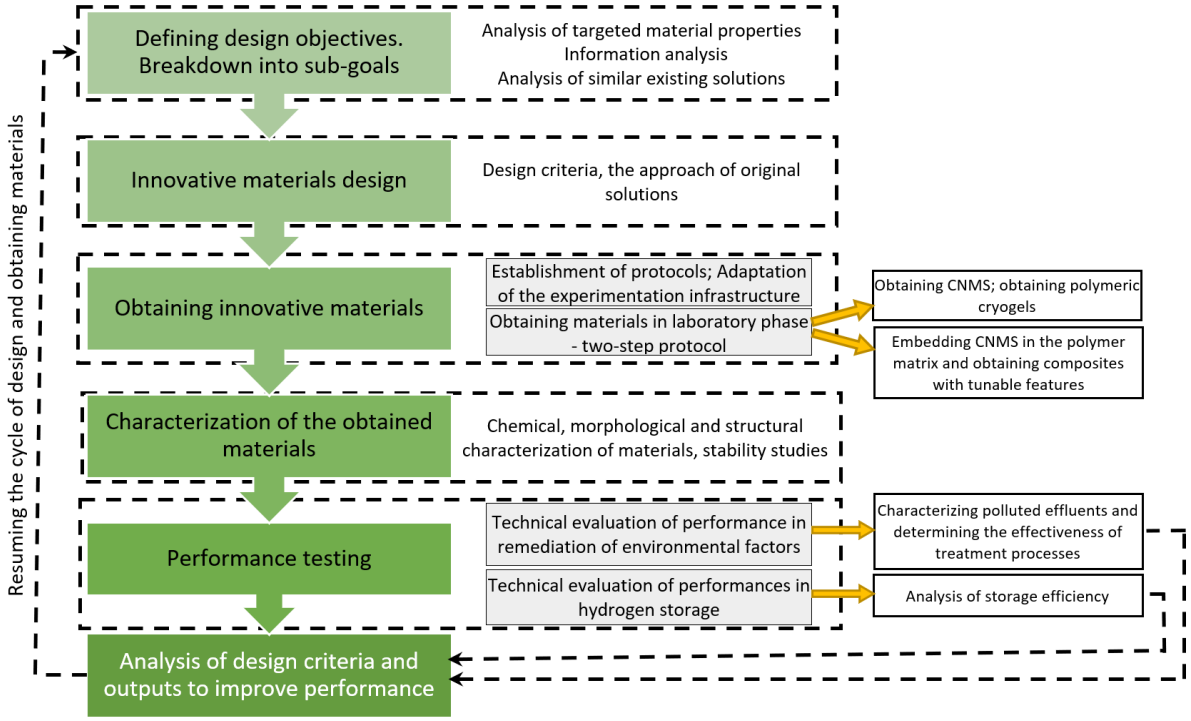
F. Workshop (11.07.2023 and 10.06.2024).

E. Webpage: http://www.cercetare.icpm.tuiasi.ro/proiecte/BIOPOROMAT/2022_en/default.html

II. Research activities in the 1st stage of the project

Act 1.1 - Experimental studies on proximate and ultimate analyses of feedstock and identification of suitable ones for CNMSs assembly. Assessment of the optimal pre-treatment techniques.
Act 1.2 - A.1.2. Preparation of micro/nanostructures by pyrolytic and hydrothermal processes.
Act 1.3 - Experimental study on the obtaining of CNMSs from biomass with a laser heat processing system.
Act 1.4 - Morpho-structural investigation of nano/ micro carbon structures obtained from biomass.
Act 1.5 – Lab scale studies on porosity tailoring and functionalization of prepared nano/ micro carbon structures.

Project concept:



The details of the project's achievement indicators can be found in Annex 1 to the scientific and technical report, on the web page dedicated to the project and on the UEFISCDI EvoC platform.

The activities of the project were carried out in full and within the assumed deadline, leading to the fulfillment of the three assumed objectives as well as to the achievement of the project indicators.

The estimated impact of the obtained results

The implementation of the project PCE 1455/2021 represented a challenge for the research team. Also, it was a great opportunity to explore and bring together apparently divergent research directions: the conversion of biomass waste with the proposal of optimal operating parameters for maximum efficiency, minimal costs and impact on the environment, the generation of new natural micro-

and nanostructured carbon materials (CMNS) with remarkable properties and applications in energy storage and environment remediation, the generation of new hybrid composites (polymer matrices and CMNS), also with a major role in gas storage applications and the remediation of environmental factors.

Multidisciplinary experimental research generated a significant volume of data and distinct results, some of which were not anticipated in the project proposal.

Thus, three types of polymer gels were designed as matrices for the inclusion of CMNS: (i) a hydrogel based on a natural polymer (gellan); (ii) a cryogel based on Poly(2-hydroxyethyl methacrylate) (p-HEMA) and a cryogel based on poly-acrylic alcohol (PAA) physically cross-linked with poly-vinyl alcohol (PVA) in which the structures were successfully embedded of carbon obtained from biomass waste as well as (iii) two configurations of hybrid materials based on CMNS functionalized for energy storage and bacterial immobilization applications for bioremediation of waste water.

The studies carried out showed that the gels based on gellan and CMNS show an affinity for dyes (Crystal Violet and Methylene Blue) with better adsorption capacities at equilibrium compared to other gels reported in literature. Also, removal degrees of 70-97% were obtained for Pb(II) ions and priority organic pollutants (diclofenac). One of the proposed configurations represents a remarkable protective support for bacterial immobilization that increases by 4 times the survival rate of Pseudomonas bacteria, and by 30% the bioremediation capacity of wastewater polluted with plasticizing agents (diethyl phthalate).

In the storage of alternative forms of energy, the supercapacitor characteristics of the hybrid carbon material were demonstrated, as well as the ability to retain some gases (H2, N2, CO2) of new cryogels based on poly-acrylic alcohol (PAA) physically cross-linked with poly-alcohol vinyl (PVA) where the carbon structures were successfully embedded. For the PAA/PVA-CMNS cryogel, 4 times higher values of the BET surface area and the total pore volume were obtained compared to those of the polymer matrix. Also, the volume of nanopores smaller than 0.7nm is 2 times larger, which favors the retention of hydrogen molecules in the porous structure. The increase in the volume of pores with dimensions located in the nanometric range can be achieved in the phase of obtaining the cryogel by increasing the concentration of PAA/PVA and CMNS in the initial aqueous solution.

The obtained results generated significant impacts. Impact on knowledge: through the integrated approach, the obtained results open future research directions in the field of obtaining hydride composite materials that incorporate biomass waste. Also, these new types of materials represent a development basis for a very wide range of applications that can be transferred and implemented in an economic environment (photovoltaic panels, medical imaging, etc.). Impact on the career of the members of the research team: a research group was consolidated that brought together three teams (Integrated Resource Management and Sustainable Design, Polymer Science, Chemical Engineering). The innovative results obtained led to permanent employment (2 post docs), to participation in international research internships (2 Ph.D.s and 1 post doc), to the completion of the doctoral program (2 Ph.D.s) and therefore to the consolidation of the professional career of the members the team. Impact on the scientific community: the project led to the identification of partners in the country (ICPE-CA) and abroad (UMR7272 and UMR7374/ICMN, France, and Istanbul University Cerrahpasa, Turkey) interested in deepening aspects of knowledge generated by the project. The achieved project indicators (7 ISI Q1 and Q2 works) contribute to increasing the visibility of the project team members as well as the entire scientific community in which this project was implemented. Environmental and industrial impact: the application of sustainable design principles (recycling, recovery) promoted by the project will lead to a major decrease in environmental impacts through the gradual replacement in industrial activities of carbon materials obtained through very expensive and polluting chemical synthesis.

Project Manager,

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