Biodiversity restoration and conservation of inland water ecosystems for environmental and human well-being

BioReset

BiodivRestore-406

2020 - 2021 Joint Call

Joint COFUND Call on "Conservation and restoration of degraded ecosystems and their biodiversity, including a focus on aquatic systems"

Deliverable 2.1.1

Optimized procedures to obtain activated carbonaceous biosorbents

Lead Beneficiary	Work package	Delivery month
UVIGO	**2**	**15**

1. Executive Summary

BioReset proposes to advance treatment processes (chemical, physical, biological and their combination) to promote ecosystem recovery and conservation and to develop assessment strategies. Diatoms will be used to model ecosystem conservation and restoration since their communities show high levels of biodiversity. The diatoms will provide an expeditious method to compare different recovery strategies and water treatment processes, allowing to address timescale and key conservation/restoration questions. The full environmental, economic, and social viability of the upgraded and innovative treatment technologies will be assessed. Based on this knowledge, scale-up studies in geographically different sites (Portugal and Spain) will be performed to ascertain the technical and economic feasibility at a larger scale and recommended action guidelines will be issued.

BioReset also envisages the creation of a representative space-time picture of the presence of emerging contaminants in inland waters and its correlation to effects on diatom communities. For this, powerful analytical techniques, such as gas- and liquid chromatography, will be used. Besides these methods, and to obtain real-time information, miniaturized analytical platforms that can perform fast and on-site monitoring will also be employed.

Thus, an important point here is the high need for technologies to improve wastewater (WW) treatment, creating the necessary water quality to nurture ecosystem recovery. **Deliverable 2.1.1** is intended to provide the details of the work developed for Work Package (WP) 2, within **BioReset**. Additional information regarding communication and academic works within the WP is outlined in this report.

2. Task description

WP2 regards improving the effectiveness and upscaling of WW treatments. Within this, Task 2.1 – "Advanced oxidation processes (AOPs) with simultaneous adsorption" a concentration-degradation-purification strategy was developed by combining adsorption and AOPs to achieve the removal of emerging contaminants (EC) and improvement of water quality. Eco-innovative technologies were developed to produce biosorbents with high adsorption capability and selectivity for the target ECs. This was achieved by means of the recovery and use of industrial wastes, turning them into valuable and useful raw materials for the synthesis of biosorbents by thermal and hydrothermal processes. After the concentration of the EC onto the biosorbents optimal AOPs to regenerate and recycle them are being developed. In this process, the sensors developed in Task 1.2 will be used to determine the evolution of EC degradation and the effect of the operational conditions to reduce energy consumption while keeping a high efficiency.

Deliverable 2.1.1 is focused on two subtasks: **i)** valorisation of wastes by their thermal conversion to carbonaceous materials, **ii)** hydrochar modification by physical or chemical activation and assessment of their properties.

3. WP2 – Task 2.1 team members

The Team members in WP2, Task 2.1, are:

Name	Organization	Role	Name	Organization	Role
M. Ángeles Sanromán Braga	UVIGO	Task coordinator	Manuela Correia	REQUIMTE	Researcher
Marta Pazos Currás	UVIGO	Researcher	Valentina Domingues	REQUIMTE	Researcher
Emilio Rosales Villanueva	UVIGO	Researcher	Sónia Figueiredo	REQUIMTE	Researcher
Aida Diez Sarabia	UVIGO	Researcher	Olga Freitas	REQUIMTE	Researcher
Cristina Delerue-Matos	REQUIMTE	Project coordinator			

4. Developed activities

Concerning this deliverable, several wastes were selected, and their physical and chemical properties were evaluated. Based on this information and the knowledge of the project team, several strategies were developed to obtain different adsorbents with high adsorption capacity. The different activities are shown below.

Collection and selection of various agro-industrial wastes

Collaboration with local companies is integral to developing effective waste management strategies and contributing to the growth of a more circular and environmentally friendly economy. In our pursuit of promoting a circular economy, we have successfully contacted and obtained waste materials from several companies in Galicia (Spain), however, based on the possible composition of the wastes we decided to work with the wastes supplied by Aceites Abril, Coren, Freshcut, and Ence. This activity serves as the basis for the development of this WP2 and was done by two doctoral students (S. Escudero and B. Lomba) from the University of Vigo (Spain).

Pre-treatment process and characterization of wastes for conversion into biosorbents

By subjecting these waste materials to carefully tailored pre-treatment procedures, we can optimize their composition and properties, ensuring that they are well-suited for subsequent thermal treatment. In general, all wastes were cleaned, dried and cutting into small pieces prior to their carbonization. These pretreated wastes contain a substantial amount of organic matter, predominantly consisting of varying proportions of cellulose, hemicellulose, and lignin, and inherent physicochemical properties that confirm their use of starting materials for the production of biosorbent with different properties. Both activities were done in the scope of a traineeship for the graduation in Industrial Chemical Engineering of students from the University of Vigo (Spain).

Development of protocols for the valorisation of wastes by their thermal conversion to carbonaceous materials

The focus of this endeavour is to establish efficient and environmentally friendly protocols for converting various types of waste materials into valuable hydrochar and biochar. Biochar was produced by slow-pyrolysis of waste and hydrochar was obtained by hydrothermal carbonization, where the wastes are treated with hot compressed water instead of drying. It was determined that the thermal decomposition by slow-pyrolysis of waste materials is influenced by several key variables that play a significant role in the yield, quality, and properties of the resulting biochar. Some of the main studied variables were the temperature, heating and cooling rate, residence time, or particle size. These factors were optimized for each selected agro-industrial wastes in order to improve their adsorption capacity. In hydrothermal carbonization, upon completion of the hydrolysis, dehydration, decarboxylation, aromatization, and recondensation reactions take place, and a solid product, hydrochar, and a liquid product are obtained. Thus, the relationship was established between hydrochar properties and several factors in its production process such as temperature, residence time, or solid-liquid ratio. In addition to assessing their application as adsorbents, these carbonaceous materials were also tested as catalysts in different AOPs in order to explore their application as biosorbents and catalysts in the concentration-degradation-purification strategy. Based on the knowledge gained, a review article has been published in the journal Foods. This activity was performed by several junior researchers from the University of Vigo (Spain) in their traineeship for graduation in Industrial Chemical Engineering and by a PhD student (A. Puga) whose thesis that will be defended in early 2024.

Modification by physical or chemical activation to improve the properties of carbonaceous materials

Chars produced by both processes exhibit significantly different physiochemical properties that affect their potential applications. The analysis of surface properties was carried out to study the surface morphology, structural defects, the chemical structure, surface composition, and the chemical state of the activated carbonaceous materials. Biochars are characterized by large a specific surface area, however, the hydrochars have a significant abundance of functional groups on their surface. Novel approaches were developed to modify both chars and to boost their adsorption capacity for selected EC. Thus, by capitalizing on the straightforward one-step, one-pot synthesis and the versatile range of modification possibilities offered by the hydrothermal carbonization approach, a nitrogen grafting modification was executed, resulting in a high-capacity, versatile, and selective hydrochar. For example, alperujo (oil waste supplied by Aceites Abril) was used to produce an N-doped hydrochar which demonstrated significantly enhanced adsorption capabilities, achieving an approximate 1500% increase in adsorption capacity. This remarkable improvement can be attributed to the emergence of novel amide functional groups through tailored modification. In addition, Metal Organic Framework (MOF) and more specifically Fe-based MOFs are known for their large surface area, high porosity, ample adsorption sites, and easy exchange counterions, however, several weaknesses, such as poor electrical conductivity and poor chemical stability in water, limit their use as a potential biosorbent or catalysts. For this reason, several MOFs were synthesised with the objective to obtain composites in which the MOF is incorporated on the hydrochar surface composite by solvothermal method. In this scope, various alternative iron-based materials were considered such as nano-zero particles which experimental work was performed in collaboration with the REQUIMTE (Portugal) group. In addition, based on the studies with different AOPs, it is remarkable the high potential of the

integration of these carbonaceous materials with other compounds such as titanium dioxide, graphitic carbon nitride (g-C_3N_4) or to obtain composite materials that improve the adsorptive properties, with upgraded photocatalytic properties and allowing the mineralization of adsorbed contaminants. The g-C_3N_4 alone and several doped materials were synthesised and evaluated for this approach. Finally, several bionanocomposites were synthesised during a stay of a PhD student from Izmir Institute of Technology (Turkey) in UVIGO lab which are tested as effective candidates for remediation of the environmental media contaminated with dibutyl phthalate, diethyl hexyl phthalate and other phthalic acid esters. The work was performed by Silvia Escudero during her PhD thesis that will be defended in the University of Vigo in November 2023. It is important to highlight the collaboration of several students of Chemical Engineering of the University of Vigo and the work carried out by the PhD student contracted with funds from the **BioReset** project and the postdoctoral researcher A. Díez in her stay in the REQUIMTE lab. In addition, several short stays were performed by Drs Á. Sanroman, M. Pazos (UVIGO) and S. Figueiredo (REQUIMTE), under Erasmus+ call, to collaborate in the production of tailored or engineered biomaterials.

5. Results

The integration of the work performed provides an assessment of recent advancements in the valorization of different agro-industrial wastes in the form of biochar and hydrochar. One of the main results is that, through the customization of engineering techniques and the optimization of production conditions, these char materials can acquire a versatile porous structure, remarkable electrochemical properties, and an increased surface area. In addition, we are exploring synergistic combinations of different functional groups and materials for developing char composites, hybrid composites, with enhanced properties, such as increased surface area, porosity, and selectivity for specific pollutants. Their use as a biosorbent of the different synthetised carbonaceous materials was confirmed. In addition, different engineering materials exhibited the requested properties to be considered as versatile biosorbent/catalyst in the concentration-degradation-purification strategy. The promising results obtained show a clear trend towards engineering materials to overcome the barriers to their future industrial application, however, future research will be focused on scaling up their production and evaluating their performance in real-world scenarios. More detail in the results obtained are disclosed in the different communications in conferences and in several journal articles (see section 6).

6. Associated indicators

The associated indicators are the same as those for Deliverable 2.1.2 since in all cases, after to study of procedures for obtaining biosorbents, their adsorption capacity was assessed.

Publications

1. Escudero-Curiel, S., Giráldez, A., Pazos, M., Sanromán, Á. (2023). *From Waste to Resource: Valorization of Lignocellulosic Agri-Food Residues through Engineered Hydrochar and Biochar for Environmental and Clean Energy Applications - A Comprehensive Review*. Foods 12 (19), 3646. doi: 10.3390/foods12193646.
2. Díez, A.M., Cruz Fernandes, V., Moreira, M.M., Pazos, M., Sanromán, M.A., Albergaria, T., Delerue-Matos, C. (2023). *Nano-zero-valent particles synthesized with agroindustry wastes for pesticide degradation under real conditions*. Process Safety and Environmental Protection 176, 1089-1100. doi: 10.1016/j.psep.2023.06.089.
3. Puga, A., Rosales, E., Pazos, M., Sanromán, M.A. (2023). *Application of Deep Eutectic Solvents (DES) for the Synthesis of Iron Heterogeneous Catalyst: Application to Sulfamethoxazole Degradation by Advanced Oxidation Processes*. Catalysts 13 (4), 679. doi: 10.3390/catal13040679.
4. Escudero-Curiel, S., Pazos, M., Sanromán, A. (2023). *Facile one-step synthesis of a versatile nitrogen-doped hydrochar from olive oil production waste, "alperujo", for removing pharmaceuticals from wastewater*. Environmental Pollution 330, 121751. doi: 10.1016/j.envpol.2023.121751.
5. Balci, E., Rosales, E., Pazos, M., Sofuoglu, A., & Sanromán, M.A. (2023). *Immobilization of esterase from Bacillus subtilis on Halloysite nanotubes and applications on dibutyl phthalate degradation*. Environmental Technology and Innovation 30 103113. doi: 10.1016/j.eti.2023.103113.
6. Fdez-Sanromán, A., Lomba-Fernández, B., Pazos, M., Rosales, E., Sanromán, A. (2023). *Peroxymonosulfate Activation by Different Synthesized CuFe-MOFs: Application for Dye, Drugs, and Pathogen Removal*. Catalysts 13 (5), 820. doi: 10.3390/catal13050820.
7. Díez, A.M., Núñez, I., Pazos, M., Sanromán, M.Á., Kolen'ko, Y.V. (2022). *Fluoride-Doped TiO_2 Photocatalyst with Enhanced Activity for Stable Pollutant Degradation*. Catalysts 12 (10), 1190. doi: 10.3390/catal12101190.
8. Balci, E., Rosales, E., Pazos, M., Sofuoglu, A., Sanroman, M.A. (2022) *Continuous treatment of diethyl hexyl and dibutyl phthalates by fixed-bed reactor: comparison of two esterase bionanocomposites*. Bioresource Technology 363, 127990. doi: 10.1016/j.biortech.2022.127990.

Book chapters

1. Escudero-Curiel, S., Pazos, M., Sanromán, A. (2023). Bio-Adsorbent based Integrated System. In: Biodegradation of Toxic and Hazardous Chemicals (CRC Press, Taylor & Francis Group. *in press*). ISBN: 9781032453705.l

Communications

1. Escudero-Curiel, S., Pazos, M., Sanromán, A., *Modification strategies on the hydrochar synthesis from agro-industrial wastes for sustainability application for removing pharmaceuticals from aqueous media*, X IBA-IFIBiop 2022. October 27-30, 2022, NKUST, Kaohsiung, Taiwan. (Oral presentation, Invited lecture)
2. Escudero-Curiel, S., Pazos, M., Sanromán, A., *Strategies for producing hydrochars as engineering adsorbents from agro-industrial wastes*, International Conference on Biotechnology for Sustainable Bioresources and Bioeconomy (BSBB-2022). December, 7-11 2022, Guwahati, India. (Oral presentation, Plenary lecture)
3. Lomba-Fernández, B., Fdez-Sanromán, A., Pazos, M., Rosales, E., Sanromán, M.A., *Application of different CuFe-MOFs for reduction of the environmental and sanitary impact of hospital effluents*, 14th International Chemical and Biological Engineering Conference (CHEMPOR 2023), September 12-15, 2023, Bragança, Portugal. (Poster presentation)
4. Fdez-Sanromán, A., Lomba-Fernández, B., Pazos, M., Rosales, E., Sanromán, M.A., *Influence of FeCu-MOF morphologies on peroxymonosulfate activation for Rhodamine B degradation*, 14th International Chemical and Biological Engineering Conference (CHEMPOR 2023), September 12-15, 2023, Bragança, Portugal. (Poster presentation)
5. Escudero-Curiel, S., López Rodríguez, X., Díez-Sarabia, A., Pazos, M., Sanromán, M.A., *Valorization of agro-industrial wastes by hydrothermal carbonization: synthesis, nitrogen functionalization, and evaluation as carbocatalysts in water treatment*, 14th International Chemical and Biological Engineering Conference (CHEMPOR 2023), September 12-15, 2023, Bragança, Portugal. (Oral presentation)
6. Lomba-Fernández, B., Bernárdez, N., Rosales, E., Pazos, M., Sanromán, M.A., *Optimización de parámetros, diseño y escalado de un reactor para tratamiento electro-Fenton de contaminantes recalcitrantes*, XLIII Reunión del Grupo Especializado de Electroquímica de la RSEQ (GERSEQ43), July 3-5, 2023, Ciudad Real, Spain. (Poster presentation)
7. Bernárdez, N., Rosales, E., Pazos, M., Sanromán, M.A., *Adsorption capacity of two synthesized biochars and their application in pharmaceuticals removal*, 5th Doctoral Congress in Engineering, June 15-16, 2023, Porto, Portugal. (Poster presentation)
8. Lomba-Fernández, B., Fdez-Sanromán, A., Pazos, M., Rosales, E., Sanromán, M.A., *Development of different CuFe-MOF/PMS systems for selective treatment of wastewater pollutants*, 5th Doctoral Congress in Engineering, June 15-16, 2023, Porto, Portugal. (Poster presentation)
9. Escudero-Curiel, S., López Rodríguez, X., Pazos, M., Sanromán, M.A., *Hydrothermal carbonization for agro-industrial waste valorization: synthesis of Nitrogen-doped hydrochars as carbocatalysts for efficient removal of pharmaceuticals in water treatment*, 5th Doctoral Congress in Engineering, June 15-16, 2023, Porto, Portugal. (Oral presentation)
10. Poza-Nogueiras, V., Bernárdez, N., Lomba-Fernández, B., Pazos, M., Sanromán, M.A., *Combined adsorption and electrochemical treatments for the remediation of water containing sulfamethoxazole*, 5th Doctoral Congress in Engineering, June 15-16, 2023, Porto, Portugal. (Poster presentation)

Graduation reports

1. Shirley Rivas González. *Valorización de residuos da industria hortofrutícola: Deseño e simulación dunha planta de produción de antioxidantes*. Industrial Chemical Engineering, University of Vigo, Spain, 23/11/2022.
2. Xacobe Martín López Rodríguez. *Valorización de residuos agroindustriais por carbonización hidrotermal: Síntese e e avaliación contra a contaminación acuosa*. Industrial Chemical Engineering, University of Vigo, Spain, 26/04/2023.
3. Sergio Fernández Davila. *Descontaminación da auga por inmobilización de material carbonoso en estruturas xeradas por impresión 3D*. Industrial Technologies Engineering, University of Vigo, Spain, 26/04/2023.
4. Verónica Laíño Rodríguez. *Claro coma a auga: unha nova vida para os residuos agroindustriais deseñada á descontaminación de fármacos en augas residuais mediante adsorción e posterior degradación dos contaminantes*. Industrial Chemical Engineering, University of Vigo, Spain, 22/06/2023.
5. María Bolaños Vázquez. *Síntese, caracterización e aplicación de biochar e hidrochar como catalizadores na producción de hidróxeno*. Industrial Chemical Engineering, University of Vigo, Spain, 14/09/2023.

PhD thesis to be defended in less than six months

1. Silvia Escudero-Curiel. *Application of Biomaterials in Aquatic Contaminated Environments*. University of Vigo, Spain (Estimated date of defense: November 2023).
2. Anton Puga Pazo. Combination of Advanced Oxidation Technologies and Selective Adsorption for the Treatment of Micro-contaminants. University of Vigo, Spain (Estimated date of defense: February 2024).