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 2.1.2

Sorption behaviour of the developed 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 2.1.2** 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 2.1.2 is focused on one subtask: **iii)** evaluation of the sorption capacity of the different synthetized biosorbents by conventional adsorption or electro-adsorption.

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 biosorbents developed from agro-industrial wastes, described in **Deliverable 2.1.2**, were tested in the presence of the selected ECs in the **BioReset** project. Initially, their physical and chemical characteristics were assessed in order to understand the adsorption mechanisms. A comparative study of the conventional and innovative technologies was performed to improve and overcome the limitations of the adsorption process. Among these innovative strategies, the use of biosorbents as electrodes in the electrosorption process is worth noting. As was mentioned above one of the objectives is to use the sensors developed in Task 1.2 to determine the evolution of EC degradation. This work is performed under the supervision of Dr E. Romero in the University of Vigo (Spain) and Dr V. Pozas member of UVIGO BIOSUV group during her current postdoctoral stay in REQUIMTE's (Portugal) facilities. The task was carried out in the different activities are shown below:

Physical and chemical characterization of the synthetized adsorbents

The efficiency of the adsorption process is highly affected by the type of adsorbent, adsorbate properties, and the compositions of the waste stream. For this reason, chemical characterization of the different adsorbents was performed: elemental analysis -C,H,O,N and S- (Elemental analyser, Fisons Carlo Erba EA1108); mineral content previous sample digestion (ICP-MS, Thermo-Finnigan Neptune), and water-extractable ions (Ion chromatography, Thermo Fisher Scientific Dionex ICS-3000). Textural properties such as specific surface area, total pore volume and BJH pore size were evaluated by the single point Brunauer, Emmett and Teller (BET) method from N_2 adsorption-desorption isotherm at 77 K using a Micromeritics ASAP 2020. Their surface morphology was examined with SEM-EDS (JEOL JSM6010LA with EDS Oxford AZtecOne SEM) and FT-IR (Nicolet 6700, Thermo Fisher Scientific Inc.). X-ray diffraction (XRD) analysis was made on a Siemens D5000 diffractometer. Individual element obtained from XPS measurement was analysed (qualitative and quantitative). The electrochemical measurements of materials were performed by a potentiostat (Metrohm Autolab PGSTAT204). This activity serves as a basis for understanding the adsorption mechanism and designing the removal process based on the properties of the ECs present in the wastewater. All the equipment mentioned in this section belongs to the Centro de Apoio Científico-Tecnolóxico á Investigación (C.A.C.T.I.) from the University of Vigo (Spain) and were used by all UVIGO team members.

Adsorption tests

The assessment and optimization of the adsorption process with different biochar, hydrochar, and composites developed in the previous subtasks (i and ii, see **Deliverable 2.1.1**) were carried out in flask and column tests. Based on the information provided by AdCL (Portugal) different ECs were selected: Antipyrine, Fluoxetine, Cefazolin, Venlafaxine, Trazodone, Methylparaben, Sulfamethoxazole, Sulfamethizole, or Diclofenac. It was determined that the adsorption mechanisms of the pollutants onto pristine adsorbents may involve pore-filling, hydrophobic interaction, partitioning, electrostatic interaction, π-π, or hydrogen bonds. To evaluate the synthesised adsorbents for further use in a high-scale and real scenario, the kinetics and the equilibrium adsorption isotherms were determined in order to establish the interactions between solute and adsorbent. Once the monocomponent adsorption process was studied, the mixture behaviour (when the effluent contains several ECs) was evaluated and compared with individual adsorption. Fixed-bed column adsorption experiments using single and multicomponent mixtures of ECs were performed. The obtained profiles were represented by well-known breakthrough models (Thomas, Yoon-Nelson and Yan models). Finally, the evaluation of the different biosorbents behaviour, operating with (real) wastewater spiked with different mixtures of ECs, was performed. In general, it was determined that the presence of inorganic or organic compounds in the wastewater (e.g. carbonates) can act as competitive adsorbates. For this reason, a decrease in the column efficiency was observed in the experimental uptake reached in the column, which is quite similar to that obtained in the batch assays. It is worth noting that the predicted uptake by the breakthrough models and the experiments are fairly similar, but they are significantly lower than those attained for the synthetic wastewater. This activity was performed by several junior researchers from the University of Vigo in their traineeship for graduation in Industrial Chemical Engineering and two PhD students (S. Escudero and A. Puga) whose thesis will be defended within six months.

Development of electrosorption process

Electrosorption refers to a process that takes place when a current or polarization potential is applied, and the charged ions are adsorbed by the oppositely charged electrodes, allowing the occurrence of charge separation, and converting in an efficient water purification technique. After electrode saturation, a desorption step takes place by short-circuiting or reversing the electric field which could restore the electrodes sorption capacity. Initially, it was studied the effect on sorption properties of the biosorbents as a function of the potential drop in the liquid-solid interface. It was established that the application of low potential (<1.4V) did not lead to redox reactions, resulting in shifts in equilibrium between charged and uncharged molecules. However, as a result of high external voltage, electrochemical redox reactions that lead to Faradaic currents also occur. Consequently, it was possible to oxidize or reduce the adsorbed molecules and transform them into others. This topic is being developed in the next subtasks (iv and v) and will be reported in **Deliverable 2.1.3**. It was found that the effectiveness of electrosorption depends on factors like the electrode material and its properties, applied voltage, and the characteristics of the electrolyte solution (pH, concentration, electric conductivity,..). As the electrode material properties play a crucial role in the electrosorption process, the potential of the synthetised carbonaceous materials was analysed. In addition, it was determined that the use of metals and N-doped porous carbon from agro-industrial wastes improves the selective removal of pollutants. The presence of iron promotes charge transfer, for this reason, the use of these materials as cathodes exhibited remarkable removal efficiency of ECs from wastewater by electrosorption/desorption cycles. These studies were performed in a two-dimensional (2D) reactor, however, to overcome the scale-up limitations, a three-dimensional (3D) particle electrode was designed. In this configuration, the third electrode is composed of synthetised carbonaceous materials, causing a remarkable expansion of its specific surface area enhancing mass transfer in fixed-bed or fluidized-bed reactors, providing a large electroactive surface area. The work was performed by a PhD student (A. Puga) whose thesis that will be defended in early 2024. It is important to highlight the collaboration of several students of Chemical Engineering of the University of Vigo and the experiments carried out by the PhD student (B. Lomba) contracted with funds from the **BioReset** project.

5. Results

The physical and chemical properties (internal microstructural features, shape and size of particles, porosity, density, surface area, chemical composition, and distribution of the elements) of the different porous carbonaceous materials synthetised using agro-industry residues as starting point (biochars, hydrochars, engineering chars and composites) were reported. The comparison of the properties of pristine chars and modified materials allow to explain the different behaviour detected in different adsorption tests. Equilibrium and kinetic batch adsorption experiments were performed, and their evaluation provided the most viable option material for the removal of the ECs, individually and combined. The multicomponent system exhibited different synergetic behaviour when compared to the single and multicomponent systems in synthetic and real wastewater previously evaluated in batch assays. Different fixed-bed column adsorptions were performed, and the breakthrough curves were modelled to simulate their scale-up. In parallel, it was verified that the electric field is a useful tool to improve the poor adsorption of ECs on carbonaceous materials. The effect of key parameters that directly affect the process (voltage, electrolyte concentration, or distance between electrodes) were determined. Thus, by the increase of the voltage from 0 to 1.1 V, the ECs removal was accelerated due to the intensive electric field force, however at voltage over 1.1 V, the detected electrolytic reaction of water causes the decline in the electro-adsorption capacity of biosorbents. Based on the mechanism responsible for the electrosorption, the reverse process was carried out by changing the polarity, achieving the desorption of the adsorbed species in a simple way. The results confirmed the feasibility of this strategy in 2D and 3D cell configurations, maintaining the efficiency with no structural changes in the biosorbent after several cycles, so the electrosorption/desorption of ECs on carbonaceous materials is a promising technology. 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).