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 2.3.2

Microplastic removal using colloidal systems

Lead Beneficiary	Work package	Delivery month
UNIOVI	**2**	**24**

1. Executive Summary

BioReset is a transnational project that aims to improve wastewater treatment in order to reduce emerging contaminants, including microplastics, and thereby support the restoration and conservation of freshwater ecosystems. Within this framework, Deliverable 2.3.2 focuses on the development and testing of experimental systems to better understand and enhance microplastic removal from water.

In this deliverable, model waters contaminated with microplastics are first prepared from several common plastics using controlled fragmentation procedures to obtain particles in the micrometer range. These model waters are then treated using two complementary, sustainable approaches: size-controlled colloidal systems (emulsions) and biodegradable gelatin-based sponges incorporating additional biopolymers. For both technologies, formulation and operating conditions are optimized, and their performance is evaluated in terms of microplastic removal efficiency.

2. Task description

Work Package (WP) 2 is aimed at enhancing the efficiency and scalability of water treatment processes by focusing on exploring new technologies for microplastics (MP) removal. In this context, Task 1 focuses on the preparation of model water containing MPs generated through two different methodologies. The first one is based on the physical degradation of plastic and involves its mechanical fragmentation using a ball mill. The second one is based on exposing macroplastics to an aqueous medium at moderate-to-high temperatures to induce their physicochemical degradation and the MP generation.

Task 2 focuses on the formulation and optimization of size-controlled colloidal systems for an efficient MP removal from water. To achieve this, preparation and optimization of emulsions based on vegetable oils and different stabilizers is required. Upon contact with MP-contaminated water and after the phase separation, this emulsion promotes the transfer of MP to the organic phase due to their hydrophobic properties. Additionally, biodegradable sponges based on biopolymers are formulated and optimized. The main characteristics of these sponges are investigated, and the optimal formulation is employed as an adsorbent material for microplastics in water.

A set of analytical techniques are used to characterize the MP generated and their concentration in water (before and after the treatment). These include turbidity measurements, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and dynamic light scattering (DLS).

3. WP2 team members

The Team members in WP2, task 2.3, regarding microplastic removal using colloidal systems, were:

Name	Organization	Role
Susana Luque Rodríguez	UNIOVI	Task coordinator
José Ramón Álvarez Saiz	UNIOVI	Task coordinator
María Matos González	UNIOVI	Task coordinator
Gemma Gutiérrez Cervelló	UNIOVI	Task coordinator
Mª del Carmen Blanco López	UNIOVI	Task coordinator
Olvido C. Iglesias Huelga	UNIOVI	Task coordinator
Irene García Fernández	UNIOVI	Junior researcher

4. Developed activities

Preparation of Model Waters Containing Microplastics

This Task aims to generate MP through two different methodologies. Then, model water samples are prepared with known MP concentrations and size. Five different types of plastic are used in this process: polyethylene terephthalate (PET), polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polyvinyl chloride (PVC). All of them are supplied by ONLYPLAST (a company specialized in plastic recycling) and have an average particle size from 3 to 10 mm.

Physical method: milling using a ball mil

An initial pre-grinding step is carried out using a grinder mill alternating 1 min of milling with 5 min of rest to avoid equipment overheating and plastic melting. These pretreated plastic samples are processed in a ball mill to reduce their size until micrometric size. Several process parameters are optimized: the type of ball mill (and hence the type of motion), the potential addition of auxiliary solvents, and the number of milling intervals (1 interval = 3 minutes of milling followed by 6 minutes of rest). The generated MP were characterized using DLS, SEM and TEM.

Physicochemical method: plastic degradation in a water bath

The larger plastics are introduced in an aqueous medium under constant stirring at 80ºC for 8h and 50ºC for 16h. This cycle is repeated 4 times and then larger plastic fragments are removed, leaving the aqueous medium contaminated with the generated MPs. The addition of an organic solvent (such as acetone) is studied in order to increase the polymer degradation. The generated MP were characterized using DLS, SEM and TEM.

Formulation and Preparation of Size-Controlled Colloidal Systems

A preliminary study is conducted to prepare colloidal systems using three hydrophobic surfactants (Span20, Span60 and Span80) and oils of different nature in order to check their affinity with the different types of plastic. The combination showing the highest interaction with the polymers is used for the emulsion formulation. Quinoa starch is also studied as a natural stabilizer in order to obtain a more sustainable colloidal system.

Emulsions are prepared using the selected optimal oils and surfactants and process parameters (mechanical stirring speed and time) are optimized. The aim is to get two distinct size distributions (100 µm y 10 µm) to study the effect of droplet size on the interaction with MP.

The optimized emulsions are brought into contact with the previously prepared model MP-contaminated water samples and different volumetric ratios of emulsion/water are studied. After phase separation, the MP concentration in the water phase is determined.

Formulation and Preparation of Biodegradable Sponges

Gelatin-based sponges incorporating pea starch and chitosan for the removal of MP from water are formulated and optimized. Sponges are prepared with different volumetric ratios 1:1, 2:1 and 4:1, where the first value corresponds to gelatin and the second to the starch/chitosan phase. Density, porosity and swelling ratio of each type of sponge are studied. Thermal behaviour is assessed by TGA/DSC analysis. SEM imaging is performed on the sponges before to contact with water and after MP adsorption. Finally, the removal efficiency of MP is evaluated by bringing the sponges into contact with the previously prepared model waters and determining the MP concentration in the water after an optimized contact time.

Characterization

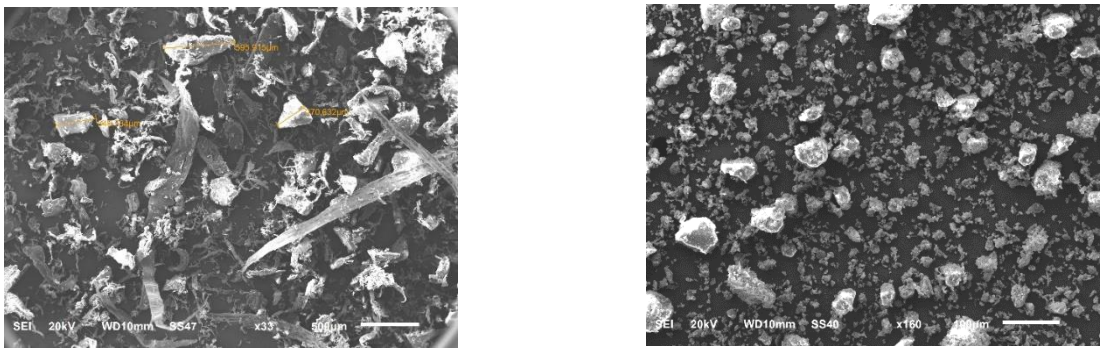
As it is previously mentioned, generated MP are characterized using DLS, SEM and TEM. The emulsions are characterized based on their droplet size of the dispersed phase (oil) within the continuous phase (water), using laser diffraction. A Malvern Mastersizer S Long Bench is used.

The concentration of MP in water is determined by turbidity measurements, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). In addition, this determination is cross-validated by filtering the aqueous phase, weighing the filter, and performing microscopic analysis.

5. Results

Preparation of Model Waters Containing Microplastics

After pre-trituration with the grinder mill, MP are obtained with an average size ranging from 100 to 500 µm for all the five types of plastic. Figure 1 shows the SEM images obtained for PET and PVC.



PET PVC

Figure 1. SEM image after pre-trituration.

These MP are triturated with the ball mill and the different process parameters are studied in order to optimize the methodology. The use of a mixer ball mill or a planetary ball mill, the addition of ethanol and the comparison of a continuous process or an interval process are the main variables studied. An interval means 3 min of milling and 6 min of rest.

Combining all these parameters, a sample after 40 intervals (and the equivalent continuous milling time) is taken for the size distribution analysis. It is concluded that using a mixer ball mill, without ethanol and an interval process achieve the smaller and more monodispersed size. This process optimization is carried out with PET and Figure 2 shows the TEM image obtained in optimal conditions.

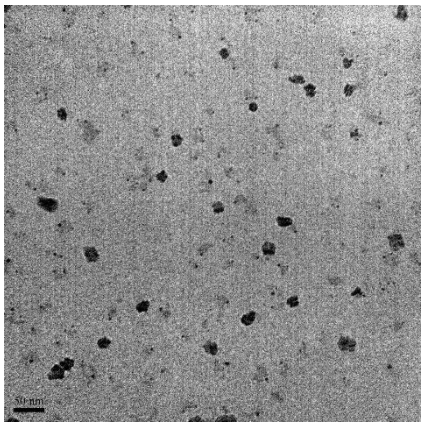


Figure 2. TEM image for PET after ball milling.

Also, DLS is used to determine the particle size distribution. Due to the density of the different polymers, the MP do not easily remain suspended in water. Therefore, the addition of surfactants to the medium is necessary to carry out the analysis. Two different surfactants (Tween 20 and Tween 80) are evaluated, along with a range of MP concentrations in water from 0.5% to 5%. It is determined that a suspension containing 1% Tween 80, 0.5% plastic, and 24 h of agitation results in a stable MP dispersion suitable for DLS measurement.

The results obtained show that more than 99% of PET MP generated have an average size on the order of 10nm. This represents a significant achievement as working with nanoplastics (NP) is considerably more challenging than with MP. NP are a great environmental problem due to their particular size and properties (such as their capacity to cross biological barriers). Their identification, detection, and quantification remain a major challenge for the scientific community. Therefore, this methodology not only allows the generation of MP but also produces NP, which can be employed for the study of removal methodologies. Additionally, samples are taken and analysed every 10 intervals to determine the optimal point. This is found to be 40 intervals in the case of PET.

With all the variables optimized, the particle size distribution is analysed for the remaining four plastics at 40 intervals. The results show that for PP and HDPE, over 90% of the particles have an average size of 10 nm, while for LDPE this percentage decreases to 70%. In the case of PVC, after 40 intervals, a final particle size of 578 nm is achieved. So, it can be concluded that the optimized process for PET is fully applicable to all the types of plastic.

However, to complete the study the number of intervals is optimized for each different polymer using the criteria of achieving at least more than 90% of the particles on the order of 10nm. For PP, 30 intervals are required, and for HDPE, 40 intervals are the optimum. In the case of LDPE, this percentage is not reached, but the minimum particle size is achieved with 80 intervals. The same applies to PVC, for which 80 intervals are also determined as optimal, resulting in a particle size of 275 nm.

Regarding the MP generated through physicochemical degradation, TGA and DSC analyses conclude that the addition of acetone is not necessary for the degradation of the plastics. The size distributions obtained by DLS range between 150 and 400 nm in all cases, except for LDPE, where most particles reach an average size of 10 nm. Figure 3 shows the size distributions obtained for the five plastics by the two methods studied, highlighting the size differences discussed above.

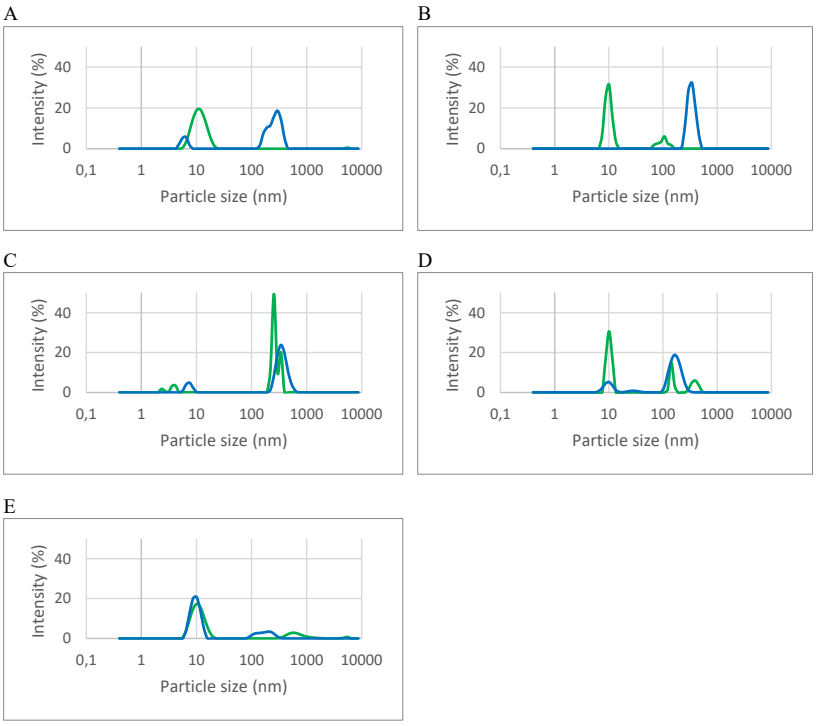


Figure 3. Comparison between sizes obtained using ball mill (green) and bath (blue). A: PET, B: PP, C: PVC, D: HDPE, E: LDPE. Green line: ball mill. Blue line: heated bath.

Therefore, it can be concluded that the generation of MP and NP using ball milling is a versatile approach that can be extrapolated to different types of plastics. This represents a breakthrough compared to other methods that focus solely on a specific plastic type.

Formulation and Preparation of Size-Controlled Colloidal Systems

The type of oil, oil-to-water ratio, type of stabilizer, stabilizer-to-emulsion ratio and process parameters (mixing time and speed) are optimized. As a result, different emulsions are formulated using a conventional surfactant (Span80) and a biodegradable stabilizer (Quinoa Starch). The optimal oil content is 40% and Miglyol and Miglyol-Cinnamon Oil mixture are selected as possible dispersed phases.

Figures 4 and 5 show the Mastersizer's size distribution obtained. It can be observed that it is possible to formulate emulsions with a distribution size according to the prefixed range for both types of stabilizers and both types of oil. So, the influence in the MP removal of these two parameters can be studied by bringing into contact with model water contaminated with MP at a concentration of 1.5 g/L.

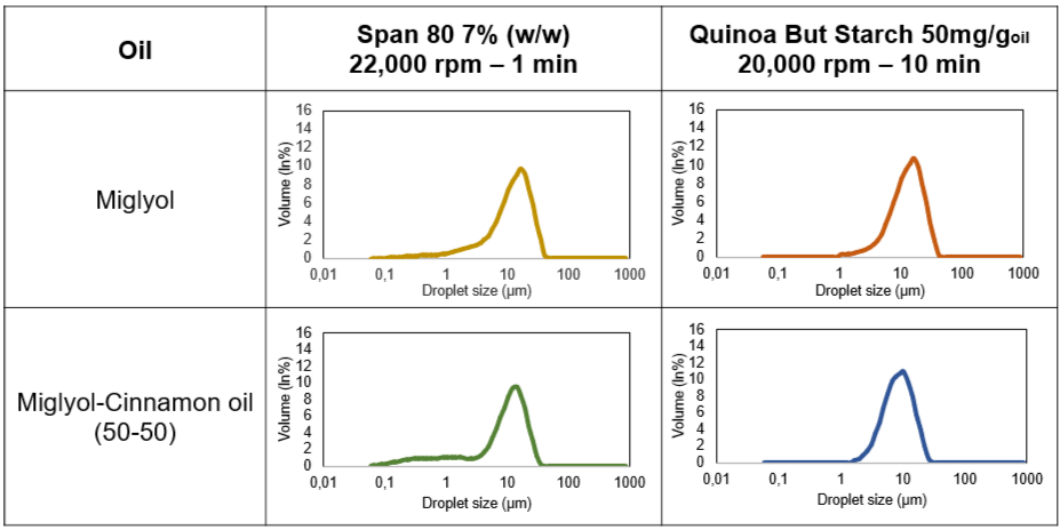


Figure 4. Size distribution for the small droplets (10 µm).

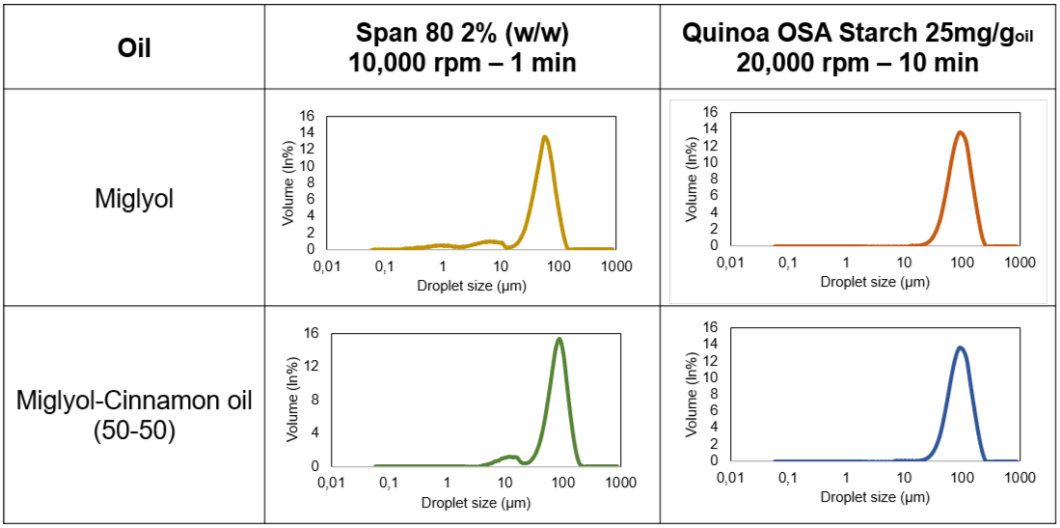


Figure 5. Size distribution for the big droplets (100 µm).

The emulsion-to-contaminated-water ratio was optimized for the emulsion stabilized with 2% Span 80 (100 µm). Figure 6 shows that the removal efficiency is strongly affected from an emulsion dilution of 1/10 onwards in the case of LDPE. The same study was carried out for all plastics, yielding similar trends, although the removal efficiency was also found to depend on the type of polymer, with values ranging between 65% and 90%

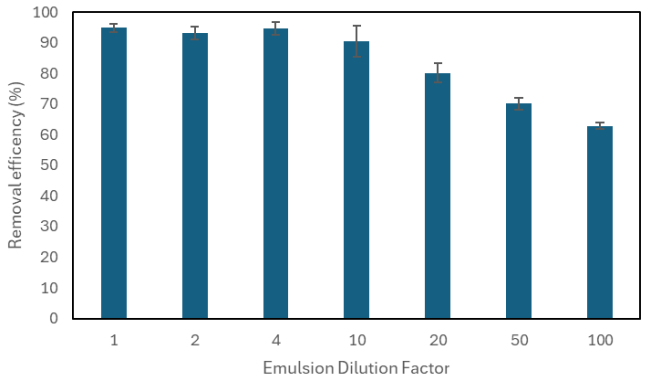


Figure 6. Removal efficiency for LDPE using an emulsion of 100 µm (Span 80) at different emulsion dilution factors.

Using the optimized dilution factor, the remaining emulsions were evaluated to assess the effect of droplet size and type of stabilizer. Figure 7 shows that droplet size does have an influence, with 10 µm emulsions being more effective for low-density polymers and 100 µm emulsions being more effective for high-density polymers. This behaviour can be explained by considering the Stokes settling velocity of both the microplastics and the droplets. In addition, emulsions stabilized with quinoa starch showed slightly lower removal efficiencies in all cases, so further formulation optimization will be studied in order to enable the use of these more sustainable emulsions.

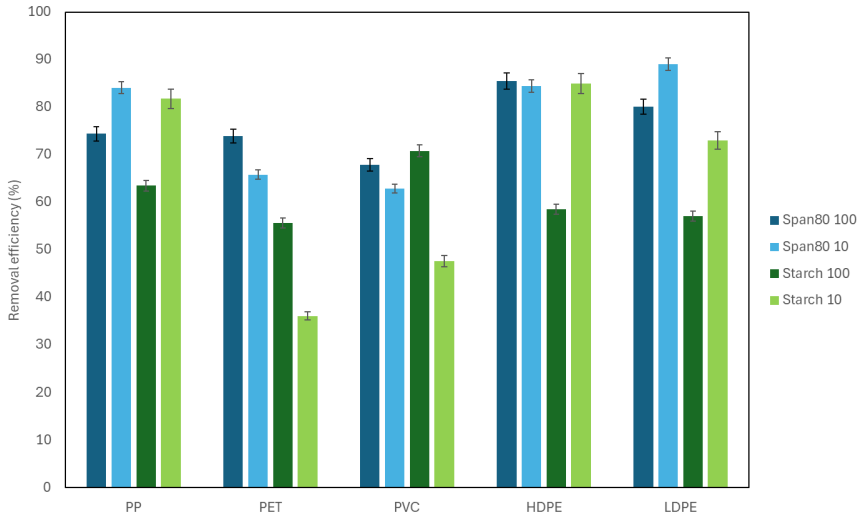


Figure 7. Removal efficiency for Emulsion Dilution Factor 10.

Additionally, combinations of polymers of different nature were studied to better simulate more realistic contaminated waters. A slight decrease in removal efficiency (<5%) was observed compared to the expected value, indicating that interactions between the polymers themselves occur, which affect their affinity for the oil phase.

Finally, the effect of the type of oil will be investigated in order to maximize the removal efficiency, particularly for those polymers that currently exhibit lower efficiencies

Formulation and Preparation of Biodegradable Sponges

Six different sponges were formulated with ratios of 1:1, 2:1 and 4:1, keeping gelatin as the base component in all of them and replacing chitosan with starch. All formulated sponges exhibited very similar properties in terms of porosity and density. However, clear differences were observed in terms of swelling ratio. For the same contact time with water, chitosan-based sponges absorbed less water than starch-based ones, which implies that, over prolonged use or multiple operation cycles, the latter are more likely to weaken, as the absorbed water may affect their internal structure.

Regarding the gelatin-to-starch/chitosan ratio, the 4:1 formulation was identified as the most robust and water-resistant sponge type. Using this formulation, the removal efficiency of three different polymers was evaluated by bringing the sponge into contact with model contaminated water for an optimized contact time. Figure 8 shows the removal efficiencies obtained in each case, and it can be observed that starch-based sponges exhibit a higher microplastic adsorption capacity in all cases.

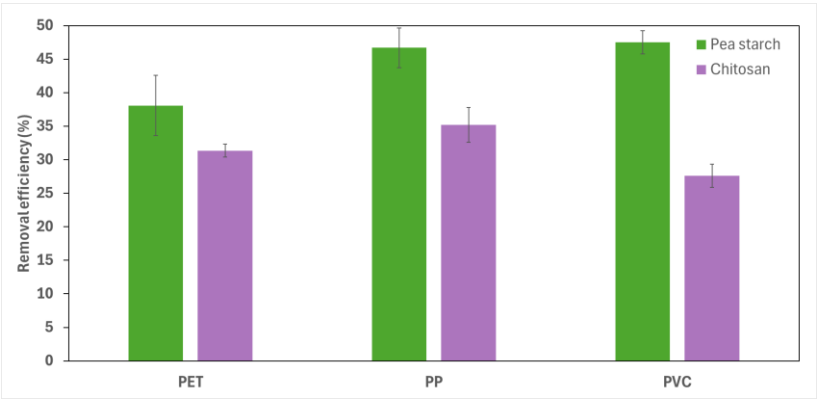


Figure 8. Removal efficiency for 4:1 sponges.

6. Associated indicators

Publications

1. García, I., Reynes, J.F., Gutiérrez, G., Matos, M., García, F., Luque, S., Nanoplastics obtention by mechanochemical degradation. (manuscript in preparation)
2. García, I., Gutiérrez, G., Matos, M., Using an oil-water emulsion to remove microplastics form water. (manuscript in preparation)

Communications

1. García, I., Reynes, J.F., Gutiérrez, G., Matos, M., García, F., Luque, S. Nanoplastics obtention by mechanochemical degradation. II PhD Multidisciplinary Chemical Congress. Poster Presentation, March 14-15, 2024, Gijón, Spain.
2. García, I., Reynes, J.F., Gutiérrez, G., Matos, M., García, F., Luque, S. Synthesis of model water containing micro- and nanoplastics (Poster). XV Congreso Español de Tratamiento de Aguas. Poster Presentation, June 19-21, 2024, A Coruña, Spain
3. García, I., Gutiérrez, G., Matos, M. (2025). Using an oil-water emulsion to remove microplastics form water. 14th International Colloids Conference. Poster Presentation, June 15-18, 2025, San Sebastián, Spain.

Master Theses

1. García, I. (2024). Estudio de procesos de generación y eliminación de microplásticos y nanoplásticos. MSc in Chemical Engineering, University of Oviedo (Spain).

PhD grants awarded

1. García, I. (2024) (ongoing). Estudio de nuevos procesos de eliminación de micro y nanoplásticos en corrientes acuosas. PhD in Chemical, Environmental and Biofood Engineering, University of Oviedo (Spain). Universidad de Oviedo-Banco Santander grant (PAPI-24-TESIS-15) from 15/10/2024 to 01/09/2025. Principado de Asturias: Programa de Ayudas “Severo Ochoa” para la formación en investigación y docencia del Principado de Asturias grant (NAC-AT-PUB-ASV-2025BP24-125) from 01/09/2025 to present.