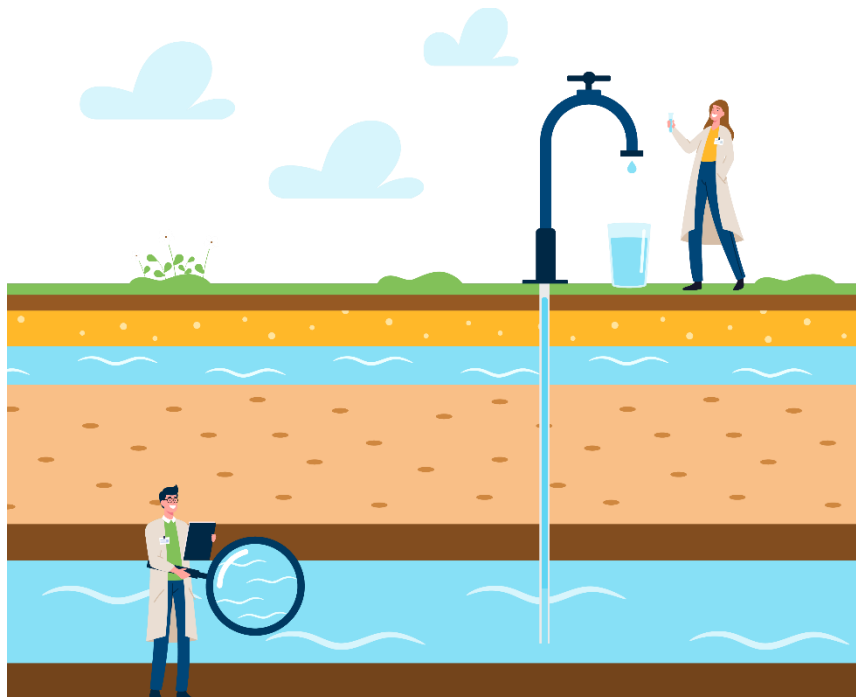




MAR2
PROTECT

D2.2 Report of functionalised biomaterials

NOVA FCT, PORTUGAL



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SU	STELLENBOSCH UNIVERSITY, SOUTH AFRICA
UNIBO	UNIVERSITY OF BOLOGNA, ITALY

ABBREVIATION / ACRONYM:

ACs: Activated carbons	10
BET: Specific surface area.....	21
BPA: Bisphenol A.....	20
Caco-2: Human colon carcinoma cells.....	9
DES: Deep Eutectic Solvents.....	11
DMSO: Dimethyl sulfoxide.....	21
EDS: Energy Dispersive Spectrometry	21
FAA: 3-(2-furyl) acrylic acid).....	16
FILs: Fluorinated Ionic Liquids	9
FTIR: Fourier Transform Infrared	21
HBA: Hydrogen-bond acceptor	11
HBD: Hydrogen-bond donor.....	11
HEMA: 2-Hydroxyethyl methacrylate.....	12
HepG2: Human hepatocellular carcinoma cells.....	9
ILs: Ionic liquids.....	9
MIP: Molecularly imprinted polymer.....	14
ND: carbon nanodots.....	14
NIP: Non-molecularly Imprinted Polymer	14
OFX: Ofloxacin.....	20
OH: Hydroxyl groups.....	21
PFAS: Perfluoroalkylated and polyfluoroalkylated substances.....	11
PFBS: Perfluorobutanesulfonic acid	13
PFOA: Perfluorooctanoic acid.....	13
PFPeA: Perfluoropentanoic acid	13
PIM: Polymer of intrinsic microporosity	14
SEM: Scanning Electron Microscopy	21
TGA: Thermogravimetric analysis.....	10
THF: Tetrahydrofuran.....	21
XRD: X-ray diffraction analysis.....	21

Executive Summary

The following document is a public Deliverable 2.2 “*Report of functionalised biomaterials*” of the MAR2PROTECT project, funded by the European Union’s Horizon Europe research and innovation programme under grant agreement Number 101082048. The preparation and characterisation of functionalised biomaterials are reported in this document while their application in technologies is reported in Deliverable 2.4 “*Report of the preliminary assessment of WP2 technology performances for upscale to TRL5*”. The corresponding sensitive versions of these deliverables are Deliverable 2.1 “*Functionalized biomaterials*” and Deliverable 2.3 “*Preliminary assessment of WP2 technology performances for upscale to TRL5*”.

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1 Introduction

The development of technologies to tackle challenges in the water management area and increase the quality and quantity of groundwater in the scope of climate and global change is a crucial aspect of MAR2PROTECT. Managed Aquifer Recharge is a promising water management approach. However, several research and development challenges must be addressed to successfully apply this strategy. The technologies tested in MAR2PROTECT such as adsorption and biodegradation are widely studied. Nevertheless, their implementation is often hindered due to high costs, lack of selectivity and operational challenges. Large-scale removal processes of various micropollutants have also been hampered due to the regeneration cost, toxicity, and poor biodegradability of the materials used in these processes. Therefore, MAR2PROTECT focused on the design & functionalisation of cost-effective, selective, biocompatible and biodegradable (bio)materials which will be applied to develop innovative technologies & sensors to be validated on pilot-scale applications of several demo sites in the scope of this project.

For this task, four consortium partners of MAR2PROTECT developed innovative selective functionalised (bio)materials and molecularly imprinted polymers, using biocompatible materials and sustainable processes with low-cost and environmentally friendly regeneration processes to ensure stable long-term operation under real operational conditions. Different biomass wastes (available in each demo site area) were used to prepare (bio)materials. Additionally, some biomaterials were also prepared for the GHG removal released by WWTP bioreactors.

The materials developed in the scope of Task 2.1 are:

- **6 Fluorinated Ionic Liquids (FILs)** for **emerging contaminants (PFAS) absorption (NOVA)**.
- **16 biomaterials** prepared from **corn cob, coconut shell** and two **biomasses from Lima River estuary** for **sorption of emerging contaminants, in particular pharmaceuticals and PFAS (NOVA & CIIMAR)**.
- **36 Deep Eutectic Solvents (DES)** were used in the preparation of 48 “eutectogels” soft ionic materials with 5 biocompatible acrylate polymer networks. 6 membranes with the same proportions were found suitable and the best membrane was selected for the preparation of **sensing layers and sorption materials for PFAS (NOVA)**.
- **Molecularly imprinted polymer (MIP)** and Non-molecularly Imprinted Polymer (NIPs) for the **selective sorption of PFAS (NOVA)**.
- **MIPs targeting pharmaceuticals** - diclofenac, ibuprofen, carbamazepine, and clarithromycin (**UNIBO**).
- **Biochars from agricultural waste** (Palm leaves, Artichoke leaves, Eggshells) for the **adsorption of diclofenac, bisphenol A and ofloxacin (ISSBAT)**.

The full description of the preparation and characterisation of functionalised biomaterials are detailed in Deliverable 2.1 and their integration in the developed technologies is further described in Deliverable 2.3 Preliminary assessment of WP2 technology performances.

2 Preparation, functionalisation and characterisation of (bio)materials for pollutant removal and monitoring

2.1 Synthesis and Characterisation of Fluorinated Ionic Liquids – FILs (NOVA)

2.1.1 Introduction

Ionic liquids (ILs) are compounds characterised by organic cations paired with organic or inorganic anions, possessing melting points close to or below 100°C. In recent years, ILs have gained significant attention across various scientific disciplines including chemistry, chemical engineering, materials science, and environmental engineering, emerging as a promising multidisciplinary field for their industrial applications. Fluorinated Ionic Liquids (FILs) have emerged as environmentally favourable media for engineering applications, owing to their properties such as low volatility, tuneability and recyclability. These compounds exhibit distinct nanosegregated domains, each with unique behaviours, affording them the remarkable ability to simultaneously solubilize and interact with three different compounds. Consequently, FILs can function as versatile "3-in-1" solvents, enhancing the adaptability of traditional ionic liquids (Pereiro et al., 2013). FILs offer tailored solutions for specific pollutant removal processes through strategic manipulation of interactions and fluorinated domain sizes (Sosa et al., 2022). By carefully selecting constituents, the design of specialised FILs with optimal characteristics for eliminating pollutants from aqueous streams can be realised.

2.1.2 Results and Discussion

6 Fluorinated Ionic Liquids (FILs) of the family of phosphoniums were synthesised and characterised for the absorption of emerging pollutants. The ion exchange resin method was used to synthesise. FILs based on different alkyl-phosphonium cations with perfluorobutanesulfonate and perfluoropentanoate anions were previously characterised in our lab (Naranjo et al., 2022) to check their suitability to apply as engineering solvents. Thermophysical and thermal properties were determined and the molecular volumes, free volumes and the coefficients of isobaric thermal expansion were determined from experimental values of refractive index and density. Lastly, the Walden plot was used to evaluate the ionicity of the novel FILs. The cytotoxicity of these compounds was also determined using the human hepatocellular carcinoma cells (HepG2) and the human colon carcinoma cells (Caco-2) (Naranjo et al., 2022).

2.1.3 Conclusions

FILs synthesised in this work present adequate properties for their application in different industrial processes. As presented in section 2.1.2 of Deliverable 2.4, the removal of PFOA from aqueous solutions was assessed using these synthesised FILs. Most of these compounds are liquid at room temperature with high de-composition temperatures. All phosphonium-based FILs have lower densities than conventional ionic liquids and common organic solvents, and the viscosity depends directly on the selected anion. Furthermore, the ionicity of FILs based on the sulfonate anion is higher than those based on the carboxylate anion. Finally, the phosphonium-based FILs have no significant effect on cellular viability at lower concentrations (Naranjo et al., 2022).

2.2 Synthesis and characterisation of activated carbons from different biomass (NOVA & CIIMAR)

2.2.1 Introduction

In the specific family of solid porous materials, biomass-derived options present themselves as an attractive alternative due to their potential to valorise residues or by-products. Moreover, these biomaterials can undergo chemical or physical treatments to be finely tuned, resulting in materials boasting high surface areas, varied structural properties, and reduced carbon footprints. In various everyday scenarios, diverse sources of residual biomass can serve as raw materials for crafting solid porous carbons (Czerwinska et al., 2024; Dias et al., 2020). The lignocellulosic waste material holds promise as a suitable substrate for producing porous carbons endowed with commendable adsorption capabilities. In this project, activated carbons derived from different biomass sources have yielded a spectrum of structural characteristics, encompassing alterations in surface area and pore dimensions, thereby potentially augmenting the adsorption efficacy against emerging pollutants. Through strategic manipulation of these textural properties, this activity wants to tailor solutions for specific pollutant removal processes from aqueous streams.

2.2.2 Results and Discussion

The activated carbons (ACs) were prepared from different biomasses and chemically and physically activated using specific conditions. A total of 16 biomaterials were prepared and characterised from corn cob (3 biomaterials), coconut shell (3 biomaterials) and 2 biomasses of the Lima estuary (10 biomaterials) residual biomasses by physical activation and chemical activation.

The synthesised biomaterials were characterised by elemental analysis. Thermogravimetric analysis (TGA) was performed to study the weight loss of biomaterials with the increment of the temperature. Finally, the textural properties of the porous biomaterials (surface area, pore size distribution) were determined using the nitrogen adsorption-desorption isotherms. The results of the elemental analysis show that these biomaterials have a high carbon content, as expected for materials derived from biomass rich in cellulose, hemicellulose and lignin. The thermogravimetric analysis proved the thermal stability of the biomaterials studied in this work. The activated carbons obtained by chemical activation seem to be less stable than the carbon obtained by physical activation. The initial mass loss may be attributed to the water evaporation adsorbed in the carbon surface. This weight loss is much more pronounced for the biomaterials with chemical treatment, suggesting that these materials have a more hydrophilic nature, probably related to the functional groups present in these materials. The analysis of textural properties demonstrated that the chemical treatment of the biomaterials has an important influence on the textural properties. Although carbons have similar BET surface areas, the pores size distribution is quite different because some biomaterials presented a higher micropore volume and smaller micropores while other ones presented higher mesopore volume and larger micropores.

2.2.3 Conclusions

The main goal of this study is to recycle different biomass sources to prepare different solid porous biocarbons. Then, different activated carbons were synthesised from two different chemical activation processes (acidic and basic) and one physical activation process. The chosen chemical agents were selected to promote the porosity and increment the surface area of the solid porous biocarbons. As illustrated in section 2.1.2 of Deliverable 2.4, these materials were utilized in batch tests for removal of 3 different

pharmaceuticals (DCF, VAL and IOP) and PFAS (PFOA, PFPeA and PFBS). The results indicated a higher capacity for pharmaceuticals and PFAS removal from aqueous solutions, using biomaterials synthesised by NOVA than commercial Norit.

2.3 Synthesis of Deep Eutectic Systems - DES - “Eutectogels” (NOVA)

2.3.1 Introduction

Deep Eutectic Solvents (DES) represent a cutting-edge category of solvents, emerging as a distinct class within the broader realm of Ionic Liquids (ILs). DES amalgamate the advantageous characteristics associated with ILs, including thermal and chemical stability, non-flammability, minimal vapour pressure, and broad solute dissolution capability, while offering a more economical and facile preparation process than ILs (Tomé et al., 2020; Criado-Gonzalez et al., 2023). DES consist of a blend of a hydrogen-bond acceptor (HBA) and a hydrogen-bond donor (HBD), exhibiting significant self-association facilitated by hydrogen bonding. This characteristic results in a homogeneous liquid medium, presenting itself as a novel alternative solvent. Although few large-scale applications for DES currently exist, they are garnering considerable attention as a greener alternative in various domains such as organic synthesis, extraction of value-added products, biotransformation and materials synthesis and processing.

2.3.2 Results and Discussion

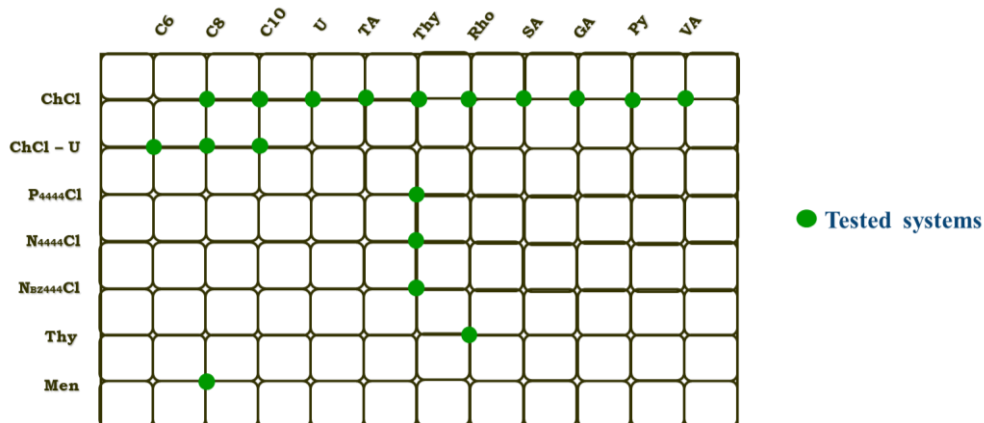
Regarding the development of sensing layers for real-time monitoring using optical sensors and (bio)materials used in adsorption processes, different deep eutectic solvents (DES) were prepared using 16 precursors selected from nature-inspired starting materials and/or compounds with functional groups highly sensitive to fluorescence and/or PFAS (perfluoroalkylated and polyfluoroalkylated substances). The precursors selected in this work are shown in Table 2.3.2.1.

Table 2.3.2.1 Starting materials used to prepare the different Deep Eutectic Solvents (DES) for Task 2.1.

Name and abbreviation	Acronym
Choline Chloride	ChCl
Tetrabutylphosphonium Chloride - (C ₄ H ₉) ₄ PCl	P₄₄₄₄Cl
Benzyltributylammonium Chloride - C ₁₉ H ₃₄ ClN	N_{B2444}Cl
Tetrabutylammonium Chloride - (C ₄ H ₉) ₄ NCl	N₄₄₄₄Cl
Hexanoic Acid - C ₆ H ₁₂ O ₂	C6
Salicylic Acid - C ₇ H ₆ O ₃	SA
Gallic Acid - C ₇ H ₆ O ₅	GA
Octanoic Acid - C ₈ H ₁₆ O ₂	C8
Decanoic Acid - C ₁₀ H ₂₀ O ₂	C10
Tannic Acid - C ₇₆ H ₅₂ O ₄₆	TA
Urea - CH ₄ N ₂ O	U
Pyrogallol - C ₆ H ₆ O ₃	Py
Vanillyl Alcohol - C ₈ H ₁₀ O ₃	VA

Thymol - $C_{10}H_{14}O$	Thy
Rhodamine B - $C_{28}H_{31}ClN_2O_3$	Rho
Menthol - $C_{10}H_{20}O$	Men

Based on these starting materials, the following DES were prepared:

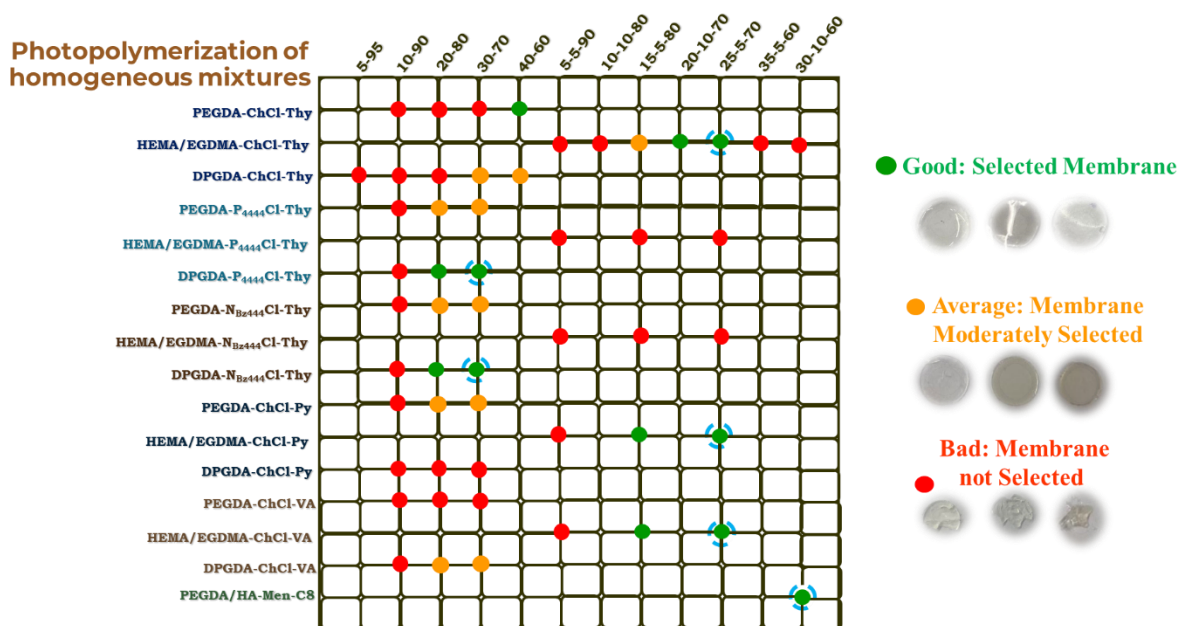


36 DES were prepared using different proportions of the starting materials selected in this work. Only the proportions that formed DES, a total of 15 binary systems, were selected to formulate “eutectogels” soft ionic materials with the following biocompatible acrylate polymer networks:

Table 2.3.2.2 Acrylate polymer structures used to prepare the “eutectogels” soft ionic materials.

Name and abbreviation	Acronym
Polyethylene glycol diacrylate - $C_5H_{10}O_4$	PEGDA
Dipropylene Glycol Diacrylate - $C_{12}H_{18}O_5$	DPGDA
2-Ethylhexyl Acrylate - $C_{11}H_{20}O_2$	HA
Octadecyl Acrylate - $C_{21}H_{40}O_2$	OA
2-Hydroxyethyl methacrylate - $C_6H_{10}O_3$ + Ethylene glycol dimethylacrylate - $C_{10}H_{14}O_4$	HEMA + EGDMA

The combination of the selected DES with the 6 different acrylate polymer networks generated 48 homogeneous liquid mixtures and 93 heterogeneous mixtures. Only homogeneous mixtures were selected and three types of membrane materials were obtained: 1) 12 good (membranes selected because they present interesting characteristics for these applications); 2) 11 average (membranes moderately selected because they are fragile and difficult to handle without broking); and 3) 30 bad (membranes not selected because they are not self-standing materials). From the 12 good membranes were selected 6 membranes with the same proportions, for sensing layers and sorption materials. A summary of the results is represented in the following matrix:



The prepared eutectogels were characterised in terms of their physico-chemical properties. The characterisation of eutectogels was carried out including contact angle, water absorption (swelling), ATR-FTIR, Differential Scanning Calorimetry and rheology. The chemical and physical characterisation was carried out for the 6 eutectogels selected for sensing layers and sorption materials.

The surface energy of the selected six membranes was calculated by contact angle measurement using different solvents. The results indicated the least hydrophilic membranes (small polar component) and therefore the most hydrophobic ones (large dispersive component). The water uptake measurements were in agreement with the surface energy results, where the most hydrophilic membranes almost completely lost the DES present in their formulation. In the case of hydrophobic membranes, they maintained their structure. The FTIR analysis confirmed the complete disappearance of the double bonds of the acrylates used as crosslinkers indicating the formation of the membrane. The spectra show the signals of the DES together with the crosslinker agents in all the cases indicating the formation of the eutectogels. DSC analysis was performed to study the thermal properties of the membranes. The membranes showed no melting temperature, confirming the amorphous nature of the membranes. For the rheological measurements, the 4 most stable membranes in water were selected and strain and frequency sweep measurements were performed. Strain and frequency sweep measurements indicate that all membranes have the storage modulus (G') above the loss modulus (G''). These results indicate that the materials are solid and do not flow.

The results obtained in the full characterisation reveal that 5 of the selected membranes cannot be used for sensing layers because they are not stable in water solutions. Then, one membrane was selected to be evaluated with different compounds highly sensitive to fluorescence and PFAS: carbon nanodots (synthesised in this work), a polymer of intrinsic microporosity, modified silica with rhodamine B and graphene oxide. The fluorescence response of the eutectogels was evaluated in contact with water, PFOA (perfluorooctanoic acid), PFPeA (perfluoropentanoic acid) and PFBS (perfluorobutanesulfonic acid). In the cases of modified silica with rhodamine B and graphene oxide, there was no fluorescence signal detected for any of the membranes when introduced to both water and PFAS solutions. The best

fluorescence responses were obtained with carbon nanodots (ND) and polymer of intrinsic microporosity (PIM). In these two cases, various parameters were optimised to establish the optimal conditions for fluorescence: the photoinitiator quantity, membrane thickness, the polymerisation time, the polymerisation energy, the optimal parameters for polymerisation, the amount of fluorescent compound (% filler) and the fluorescent spectrophotometer conditions. The optimal conditions for the selected membranes are reported in Deliverable 2.1 *Functionalized biomaterials*.

2.3.3 Conclusions

In this work, 36 deep eutectic solvents (DES) were prepared to formulate “eutectogels” soft ionic materials with biocompatible acrylate polymer networks. Only 6 homogeneous membranes were selected with the same proportions, for sensing layers and sorption materials. From the chemical and physical characterisation, one membrane was selected to be evaluated with 4 compounds highly sensitive to fluorescence and PFAS. The fluorescence response of this membrane was evaluated in contact with water, PFOA and PFBS. Various parameters were optimised to establish the optimal conditions for fluorescence. The best fluorescence responses were obtained polymer of intrinsic microporosity.

2.4 Molecular Imprinted Polymers - MIPs (NOVA)

2.4.1 Introduction

A molecularly imprinted polymer (MIP) is a polymer crafted through the molecular imprinting technique. In this technique, the polymer matrix is imbued with cavities possessing a specific affinity for a designated "template" molecule: in the case of demo site 3 (Frielas, Portugal), this template is pharmaceuticals or PFAS. The polymerisation of monomers is carried out in the presence of the template molecule, which is subsequently extracted, leaving behind voids that match the shape and chemical properties of the template (Ging et al., 2015; Cennamo et al., 2018). These innovative and novel polymers exhibit a strong affinity for the original molecule and find applications in diverse fields such as chemical separations, catalysis, and molecular sensing. One significant advantage of these artificial novel receptors over their naturally occurring counterparts lies in the freedom of molecular design they afford. Consequently, properties such as stability and flexibility can be readily tailored and tuneable to meet specific requirements. Additionally, synthetic compounds can also incorporate functional groups not found in nature. In order to improve the presence of the required functional groups and the formation of interactions between the material and the target molecules DES-based MIPs were prepared. It is known that the presence of DES could increase the selectivity of the materials due to their unique properties. MIPs could be prepared by different polymerisation methods. In this work, DES-based MIPs were prepared by radical polymerisation in bulk, where a radical initiator was employed for the synthesis of the materials. The radical initiator is decomposed when the temperature is increased and starts the polymerisation reaction to obtain the materials.

2.4.2 Results and Discussion

DES-based MIPs were prepared for the selective detection of PFOA and PFBS, together with their corresponding NIP (Non-molecularly Imprinted Polymer). The preparation of the materials was done by adding the DES, the crosslinker, a porogen, the thermal initiator and the target template.

In order to understand the chemical character that the materials need, a cationic, an anionic and a neutral DES were prepared. The MIPs with these three DES were synthesised. The uptake capacity and selectivity for the PFOA and PFBS of the MIPs and the NIPs prepared for PFOA and PFBS in Task 2.1 were determined. This screening was performed in solution with an initial concentration of each PFAS and respective material and was mixed for 48 h with constant agitation. The experimental results demonstrate that neutral MIP has a high capacity to sorb PFOA and is selective between PFOA and PFBS. These experimental results have been also compared with the polymer of intrinsic microporosity (PIM) which was the best material with high sensitivity to fluorescence and PFAS in the previous section. The cationic MIP has a high capacity to sorb PFAS but is not selective. Finally, the anionic MIP presents a lower PFAS sorption.

2.4.3 Conclusions

In Task 2.1, several MIPs and NIPs have been prepared for the selective sorption of PFAS in removal processes and for the preparation of sensing layers for the optical sensors used in real-time monitoring. Different materials with cationic, anionic or neutral character were prepared to understand the influence of chemical character on PFAS selectivity and sorption. The best results were obtained for MIPs with neutral character which showed a high sorption capacity for PFAS and selective for PFOA and PFBS synthetic samples. Furthermore, MIPs and NIPs for diclofenac were prepared for the preparation of the sensing layers of optical sensors used in WP3. These materials were synthesised following the protocol optimised by UNIBO. However, these MIPs and NIPs did not sorb diclofenac and were therefore not selected for the optical sensors of WP3.

2.5 Molecular Imprinted Polymers - MIPs (UNIBO)

2.5.1 Introduction

The molecular imprinting technique is an emerging technology where the subsequent removal of the template provides a material with memory sites able to selectively recognize and rebind the original template from a mixture. Recently, MIPs have been applied for the preconcentration and selective removal of pollutants for environmental purposes. Typically, the synthesis of MIPs involves different reagents: the template; the monomer, possessing functional groups which can interact with the template and form stable non-covalent interactions; the cross-linker, the principal constituent of the materials, which has a structural function, providing the stiffness to the polymer; the initiator, since most MIPs are prepared through radical polymerisation and finally the solvent/porogen, which supports the formation of pores.

The literature reports several methods for MIP preparation (Murdaya, 2022) (Sarpong, 2019), but the bulk and precipitation ones have been reported to be the most promising. In the present work, these two techniques have been tested. Moreover, different washing methods to remove the template and increase MIP adsorption capacities were evaluated. The pharmaceuticals investigated were selected from those predominantly found in the effluent of a water treatment plant in Emilia-Romagna. Specifically, two anti-inflammatory drugs (diclofenac and ibuprofen), an anticonvulsant (carbamazepine), and an antibiotic (clarithromycin) were chosen.

From the literature, the most commonly used monomers for the preparation of selective MIPs targeting diclofenac, ibuprofen, carbamazepine, and clarithromycin are methacrylic acid (MAA) and vinylpyridine (both regioisomers) (Olcer, 2017)

(Cantarella, 2019) (Mahmoudi, 2018). For this reason, preliminary tests were conducted using these monomers. Other monomers were also employed to evaluate the effects of different functional groups on the retention of target pharmaceuticals. Additionally, for carbamazepine, five innovative bio-based monomers were also tested. Regarding the cross-linker, a classical bifunctional cross-linker and a trifunctional cross-linker that should provide enhanced rigidity were employed. All the materials have been characterized by FT-IR to check the reaction evolution, by thermal gravimetric analysis (TGA) to evaluate thermal stability, by UV-vis spectrometry, UPLC-MS, and HPLC-UV-vis to establish the adsorption capacity (reported in Deliverable 2.3). The compression strength has been also investigated for the two best MIPs for diclofenac and carbamazepine as target pharmaceuticals.

2.5.2 Results and Discussion

For the bulk polymerisation, the materials were prepared by adapting the procedure reported by Cantarella et al (Cantarella, 2019). The template and porogen were mixed for a few min. Then, cross-linker and initiator were added. The reaction mixture was degassed with a flow of N₂, sealed and heated. Then, the template and the non-polymerized compounds were extracted by washing the polymer powders and the final material was dried. For the precipitation polymerisation, the materials were prepared using the same procedure previously outlined for bulk polymerisation, but a higher amount of solvent was employed. The protocol described was adapted from the method reported by Olcer et al (Olcer, 2017). A reference polymer, Non-Imprinted Polymer (NIP), was also synthesised for each type of polymerization. It was prepared with the same procedure and reaction conditions but without the addition of the template. The samples prepared were labelled indicating the pharmaceutical, the cross-linker, the monomer, and the polymerisation technique with the corresponding acronym. The list of all the samples prepared is provided in Table 2.5.2.1.

Table 2.5.2.1 List of all prepared samples.

Target pollutant	Sample	Polymerization method
Diclofenac	MIP_DCF_B_1	Bulk
	MIP_DCF_B_1	Precipitation 4h
	MIP_DCF_B_1	Precipitation 24h
	MIP_DCF_B_2	
	MIP_DCF_B_3	
	MIP_DCF_B_4	
	MIP_DCF_B_5	
	MIP_DCF_T_1	Bulk
	MIP_DCF_T_2	
	MIP_DCF_T_3	
	MIP_DCF_T_4	
	MIP_DCF_T_5	

	MIP_CBZ_B_1	
	MIP_CBZ_B_2	
	MIP_CBZ_B_3	
	MIP_CBZ_B_4	
	MIP_CBZ_B_5	
	MIP_CBZ_T_1	
	MIP_CBZ_T_2	
Carbamazepine	MIP_CBZ_T_3	Bulk
	MIP_CBZ_T_4	
	MIP_CBZ_T_5	
	MIP_CBZ_T_6	
	MIP_CBZ_T_7	
	MIP_CBZ_T_8	
	MIP_CBZ_T_9	
	MIP_CBZ_T_10	
Clarithromycin	MIP_CLA_B_11	
	MIP_CLA_B_4	
	MIP_CLA_B_1	Bulk
	MIP_CLA_T_11	
	MIP_CLA_T_4	
	MIP_CLA_T_1	
	MIP_IBU_B_1	
	MIP_IBU_B_2	
	MIP_IBU_B_3	
	MIP_IBU_B_4	
Ibuprofen	MIP_IBU_B_5	Bulk
	MIP_IBU_T_1	
	MIP_IBU_T_2	
	MIP_IBU_T_3	
	MIP_IBU_T_4	
	MIP_IBU_T_5	
Not imprinted	NIP_B_1	Bulk
	NIP_B_2	

NIP_B_3
NIP_B_4
NIP_B_5
NIP_T_1
NIP_T_2
NIP_T_3
NIP_T_4
NIP_T_5

For the MIP selective to CBZ, three washing techniques were studied. In the Buchner method, a simple vacuum filtration was applied using a Buchner. In the incubation method, the sample was stirred and then vacuum filtered (the procedure was repeated four times). In the sonication method, four sonication steps were applied. In all the techniques, a washing solution, composed of MeOH and AA, was employed. In the study of MIP selective to DCF, three methods were also compared but the solvent was changed.

The best synthetic strategy between the bulk and the precipitation polymerisation was evaluated by preparing a polymer selective to DCF, synthesised with 1 as a functional monomer and the bifunctional cross-linker. The two methods, as previously mentioned, differ in the amount of porogen used. In the precipitation polymerisation, an amount of porogen ten times higher was used. The use of other solvents reported in the literature (Sarpong, 2019) (Azizi, 2020), such as toluene or chloroform, was avoided due to their toxicity.

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA4000 apparatus. FTIR analysis was conducted using a Perkin Elmer Spectrum Three Spectrometer equipped with a Universal ATR Sampling Accessory. Kinetic adsorption tests for the MIP selective to DCF were conducted in a solution of DCF in deionised water. The adsorption capacity was evaluated using a UV-visible JASCO V-650 Spectrophotometer. Compression strength tests were performed at room temperature using a die-plunger test. Analyses were carried out using a Galdabini testing machine, adapting the international standard ISO 18591.

The polymerisation reactions were confirmed by FTIR analysis conducted on the final MIP samples by analysing the double bond disappearance, indicating the successful occurrence of the radical polymerisation reactions. The thermograms, characterised by TGA, indicate that all samples are stable up to 250 °C. The degradation proceeds in one single step for the samples prepared by precipitation and in two steps for the bulk one. The perfect overlap of two materials prepared with the precipitation method showed that increasing the reaction time did not affect material stability.

Adsorption kinetic tests were also conducted on the samples. The results demonstrate that the bulk material had the highest adsorption capacity, exceeding 80% after only 20 mins of static incubation (without stirring). However, the results indicated that increasing the reaction time gives lower adsorption capacity in the precipitation synthesis.

MIP composition evaluation

Considering the aforementioned results, the bulk polymerisation strategy was selected to prepare the other MIPs. For each pharmaceutical chosen (DCF, IBU and CBZ), ten materials were prepared combining the two cross-linkers and the five monomers. Ten reference polymers were also prepared combining only the cross-linkers and the monomers without any pharmaceutical imprinting. FTIR analysis confirmed that in all polymers the double bonds had reacted.

The thermal stability was maintained up to 250 °C for all materials. In the case of MIPs prepared with the trifunctional cross-linker, they exhibited higher thermal stability. A general trend of degradation in a double step was noted, which is related to a more cross-linked structure. Adsorption capacities, indicating the most valuable materials synthesized, are reported in Deliverable 2.3. For the most promising materials, the compression strength was measured. Results showed that all synthesised materials were quite comparable to the reference resin.

MIP washing techniques

For Carbamazepine, the minimum time required to remove the maximum amount of CBZ in the extraction solution was evaluated by assessing the concentration of the pharmaceutical in a preliminary extracting step using both incubation and sonication techniques at different time intervals. Subsequently, several washing steps were conducted until CBZ was no longer detected in the extraction solution. For both techniques, it was assumed that four washing steps were enough.

Adsorption capacity tests were then conducted on two polymer samples each washed with a different technique and the same residence time and number of washing steps. Results showed that the materials washed with the incubation and sonication techniques exhibited better adsorption compared to the ones washed with the Büchner technique. Additionally, the incubation method appears to adsorb slightly more than the sonication method at higher concentrations. The incubation method had a lower release of CBZ, which can be attributed to a better removal of the template during the washing step. After this study, the three CBZ-MIPs with the highest adsorption capacity were resynthesized and washed using the incubation method.

A Soxhlet extraction and a 4-step incubation method were applied. In this case, a different solvent, suitable for further biodegradation treatment, was used and results indicated that the 4-step incubation is the most preferable one. Tests were performed on MIP_DCF_T_2, being the most promising sample for DCF removal from wastewater treatment plant (WWTP) as reported in Deliverable 2.3

The adsorption capacities of the materials analyzed are reported in Deliverable 2.3.

MIP synthesis for Clarithromycin

Six materials for clarithromycin were prepared by combining three monomers consisting of two pyridine derivatives and an acrylic monomer, with the two cross-linkers. The success of the reactions was confirmed by FTIR analysis. The thermal stability was evaluated by TGA and all the samples are stable up to 270 °C.

MIP for carbamazepine using bio-based monomers

Materials prepared with the trifunctional crosslinker have shown higher adsorption. Therefore, it was assumed that a more rigid structure promotes better immobilisation

of pharmaceuticals inside the polymers. Then five new materials were prepared, using bulk polymerisation to study how innovative bio-based monomers impact the adsorption of CBZ, aiming to produce a completely bio-based material, in which pi-pi interactions or hydron bonding interactions with the target pharmaceutical might be involved. As revealed by FTIR analyses the material spectra were quite similar due to the same main reagent (the cross-linker). In all the spectra, the double bond (1638 cm^{-1}) relative to T disappeared or decreased significantly, indicating that the reaction had occurred. From the thermogravimetric, all materials presented a double degradation step, exhibiting higher thermal stability and degrading mainly in the second step.

2.5.3 Conclusions

Bulk polymerisation is better for obtaining MIPs with good adsorptive capacities. All the materials were stable up to $250\text{ }^{\circ}\text{C}$. The best washing technique Bulk polymerisation proved to be better for obtaining MIPs with good adsorptive capacities. All the materials obtained were found to be stable up to $250\text{ }^{\circ}\text{C}$. The best washing technique in all cases, independent of the solvent used, was found to be the 4-step incubation. The most promising material compositions in terms of adsorption capacities are reported in Deliverable 2.3.

2.6 Biochar composite preparation from different biomass sources (ISSBAT)

2.6.1 Introduction

Pharmaceutical products are among the most found environmental contaminants, due to their persistency. The most effective described treatment for the removal of pharmaceuticals is adsorption, using several materials. Biochar has been shown to be a promising solution due to its low cost, and high adsorption efficiency (Fernandes et al., 2019; Bencheikh et al., 2020; Puga et al., 2022). In order to remove the target micropollutants (diclofenac-DCF, bisphenol A-BPA and ofloxacin-OFX), we tried several biomaterials from different available agriculture wastes from which we prepared biochar. This choice was based on the abundance of these agriculture wastes and the main chemical and physical properties of biochars towards their application as adsorbent material (relatively high porosity and specific surface area, high surface charge and high-water holding capacity) (Akintola et al., 2023). Biochar production is eco-friendly and less expensive than the typical activated carbons that require costly and energy-consuming activation processes. To improve the ability of biochar to immobilize the selected micropollutants, a functionalized biochar/clay composite was prepared. Clay minerals have been widely used to develop cost-effective adsorbents for pollutant removal from water, but preparation methods and the clay nature and origin are different (Han et al., 2019).

2.6.2 Results and Discussion

In the framework of Task 2.1, the ISSBAT team worked on the development of novel cost-effective (bio)materials from several agricultural waste materials for the monitoring and selective removal of diclofenac, ofloxacin and bisphenol A. A first set of experiments was performed to determine the most effective adsorbent. Then, several materials were selected for preliminary adsorption tests. The different materials were washed with boiling distilled water, to remove residual oils and phenolic compounds and then dried in ambient air.

An initial assessment allowed to retain 2 biomaterials based on the availability of materials and higher recovery rates after pyrolysis. These biomaterials were tested as raw material and biochar. Ten different adsorbents were tested. The different biomass wastes were pyrolyzed in a muffle furnace. The pyrolysis was made without any gas supply. Prior to use, the obtained biochars were grounded and sieved to obtain a material of uniform particle size. The collected clay was ground into a fine powder and sieved through a 0.5 mm size to remove all the debris and further rinsed with water and oven-dried. The recovered clay suspension is first dried in an oven and then grinded.

Chemical surface functionalization was carried out to improve biochar adsorption performance. This step will allow the formation of the biochar-clay composite. The purified clay is dissolved in a low volume of water and progressively added drop by drop. The obtained suspension is centrifuged and washed with distilled water. The biochar-clay composite is dried in an oven to be characterized and used in adsorption batch tests. The characterization of biochars was performed for the selected adsorbents, based on their removal capacity. The surface morphology of the biochars was studied using Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectrometry (EDS). The specific surface area (BET) and pore size distribution were determined. The Fourier Transform Infrared (FTIR) analysis was performed using a spectrometer Elmer/Frontier IR/FIR. Finally, the structural characterization was determined by X-ray diffraction analysis (XRD) using a powder diffractometer.

Preliminary adsorption tests were performed using different biochars. An amount of the adsorbent was added to a solution containing diclofenac (DCF), ofloxacin (OFX) or bisphenol A (BPA) at room temperature and without pH adjustment. The samples were stirred for predetermined time intervals ranging from 15 to 300 min. Samples are collected continuously and immediately centrifuged, which ensures that all solid is separated from the supernatant (Fernandes et al., 2019). The supernatant was analysed by a UV-visible spectrophotometer. Then, the percentage of pharmaceutical removal was calculated. Following these preliminary tests, only the adsorbents which gave the best results will be characterized. The variation of adsorption onto biochar was investigated in the pH range 2–12. The effect of temperature on adsorption onto tested biochar was investigated in the range of 25 to 60 °C. Finally, the adsorbent capacity to remove micropollutants was investigated for DCF and BPA initial concentrations between 10 mg/L - 1 g/L.

For the kinetic experiments, biochar in a solution containing DCF, BPA and OFX were used and stirred at room temperature. An aliquot was collected every 15 minutes, centrifuged, and analysed. Adsorption isotherms are crucial to understand how the micropollutant molecules interact with the surface sites of the selected optimised biochars. Isotherm models of Freundlich and Langmuir were fitted on the adsorption experimental data to study adsorption capacity and mechanism. The clay material used for the functionalization of biochar was collected and characterized to identify which clay family it belongs to.

Preliminary adsorption tests were performed on the 10 biomaterials. The best results were obtained with the biochar-clay composite for DCF, BPA and OFX. The variation of adsorption onto biochar was investigated in the pH range 2–12. The optimal pH for the adsorption of diclofenac and bisphenol A was 2. These results indicated that when pH is lower than the pKa of these micropollutants (pKa = 4.20 for DCF and 9.2 for BPA),

the van der Waal interaction between DCF/BPA and the adsorbent surface increased by physical adsorption process. However, the pH of 6 will be used for the next steps because it is more appropriate for a larger scale use, and it is more suitable for microbiological assays.

The effect of temperature on adsorption onto biochar was investigated in the range of 25 to 60 °C. Results show that DCF adsorption decreased with increasing temperature. The highest percentage of adsorption performance was at 25 °C. Increasing temperature will cause an increase in solubility of water which will decrease the adsorption process and decrease the attraction forces between DCF and the adsorbent. Indeed, the BPA adsorption is slightly increased at 45 °C and then decreased (at 60 °C). Varying the dose of the micropollutant adsorbent from 10 mg/L to 1 g/L allowed the selection of the dose of 20 mg/L as the optimal dose for maximum adsorption. Beyond this value, all sites will be saturated and can no longer adsorb these micropollutants. The effect of contact time on adsorption was determined to characterise the equilibrium adsorption time for the 4 selected biochars for each micropollutant (DCF and BPA). This assay gives information about the rate at which the retention takes place and the minimum contact time required to reach the equilibrium. Based on these results, the best adsorbent was selected. It gives the highest adsorption rate for diclofenac removal. This adsorbent will serve for the next assays on real treated wastewater.

The application of Langmuir and Freundlich equations were applied to the experimental measurements. According to the obtained results, the Langmuir model is more suitable for the adsorption of DCF. Langmuir's model assumes monolayer adsorption over an energetically homogeneous adsorbent surface. Concerning BPA, the Freundlich model is the most suitable. It assumes the existence of heterogeneous adsorption sites on the surface of the adsorbent.

2.6.3 Conclusions

The functionalisation of biochar allowed to obtain a low-cost functionalised adsorbent which, after optimisation of the operating conditions, permits the removal of 91 % and 83 % of DCF and BPA, respectively. The adsorption was performed on mono layers for the DCF since it obeys the Langmuir model. However, BPA follows the Freundlich model. This optimised adsorbent will be tested in the real environment to assess its adsorption capacity, especially with low micropollutant concentrations.

3 Conclusions

This document describes the preparation and characterisation of functionalised biomaterials developed in the scope of the MAR2PROTECT project. These materials were further applied in the technologies for the emerging contaminants removal, GHG removal and application as sensing layers for the real-time monitoring sensors as further described in Deliverable 2.3 “Preliminary assessment of WP2 technology performances” and Deliverable 3.1 “Bio and chemical optical-based sensors”.

NOVA prepared 6 Fluorinated Ionic Liquids (FILs) of the family of phosphoniums, described in section 2.1, that proved no significant toxic effect on cellular viability at lower concentrations. FILs were synthesised and characterised for the absorption of PFAS. Section 2.2 describes the preparation and characterisation of 16 activated carbons prepared by NOVA using physical and chemical activation from corn cobs, coconut shells and biomass from the Lima River estuary (CIIMAR) in Portugal. These materials were prepared for the adsorption of PFAS and selected pharmaceuticals in demo site 3 Frielas, Portugal. Furthermore, 36 Deep Eutectic Solvents (DES) were prepared for sorption materials and sensing layers are described in Section 2.3. 48 “eutectogels” soft ionic materials with 5 biocompatible acrylate polymer networks were formulated using these DES. Only 6 homogeneous membranes contained the best properties for their application as sensing layers in real-time monitoring. The best membrane was selected and proved to be highly sensitive to fluorescence and PFAS. Different Molecular Imprinted Polymers (MIPs) were prepared by NOVA for selective sorption of PFAS (section 2.4), and although MIPs prepared for diclofenac presented poor performance, UNIBO further developed MIPs targeting diclofenac, carbamazepine, ibuprofen, and clarithromycin described in section 2.5. Finally, ISSBAT prepared biochars from locally available agricultural waste to remove diclofenac and bisphenol A (Section 2.6).

More than 60 different materials were prepared in total and tested for the selective removal of target pollutants from three demo sites: Demo Site 2 Oued Souhil in Tunisia, Demo Site 3 Frielas in Portugal and Demo Site 4 Emilia Romagna in Italy. The Innovative MIPs and low-cost (bio)materials prepared from different biomass waste available in the local environments of each demo site, demonstrated promising results for the selective adsorption of two important groups of emerging contaminants: pharmaceuticals and PFAS. Furthermore, Deep Eutectic Solvents (DES) were prepared and proved to be highly sensitive to fluorescence and PFAS, as well as MIPs developed for selective sorption of PFAS. Then, they will be applied for the selective sensing layers of novel sensors, that will significantly facilitate the real-time water quality monitoring.

4 Bibliography

Akintola, A.T., Ayankunle, A.Y. (2023). Improving Pharmaceuticals Removal at Wastewater Treatment Plants Using Biochar: A Review. *Waste Biomass Valor* 14, 2433–2458 <https://doi.org/10.1007/s12649-023-02070-2>

Azizi, A. a. (2020). A critical review of molecularly imprinted polymers for the analysis of organic pollutants in environmental water samples. *Journal of Chromatography A* 1614, 460603.

Bencheikh, I., Azoulay, K., Mabrouki, J., El Hajjaji, S., Dahchour, A., Moufti, A., Dhiba, D. (2020), The adsorptive removal of MB using chemically treated artichoke leaves: Parametric, kinetic, isotherm and thermodynamic study, *Scientific African*, Volume 9, <https://doi.org/10.1016/j.sciaf.2020.e00509>.

Cantarella, M. e. (2019). Molecularly imprinted polymer for selective adsorption of diclofenac from contaminated water. *Chemical engineering journal* 367, 180-188.

Cennamo, N., D'Agostino, G., Porto, G., Biasiolo, A., Perri, C., Arcadio, F., Zeni, L. (2018), A Molecularly Imprinted Polymer on a Plasmonic Plastic Optical Fiber to Detect Perfluorinated Compounds in Water. *Sensors* 18, <https://doi.org/10.3390/s18061836>.

Criado-Gonzalez, M., Alegret, N., Fracaroli, A., M., Mantione, D., Guzmán-González, G., Del Olmo, R., Tashiro, K., Tomé, L., C., Picchio, M., L., Mecerreyes, D. (2023), Mixed Conductive, Injectable, and Fluorescent Supramolecular Eutectogel Composites. <https://doi.org/10.1002/anie.202301489>.

Czerwinska, N., Giosuè, C., Matos, I., Sabbatini, S., Ruello, M., L., Bernardo, M. (2024), Development of activated carbons derived from wastes: coffee grounds and olive stones as potential porous materials for air depollution. *Science of The Total Environment* 914, <https://doi.org/10.1016/j.scitotenv.2024.169898>.

Dias, D., Bernardo, M., Matos, I., Fonseca, I., Pinto, F., Lapa, N. (2020), Activation of co-pyrolysis chars from rice wastes to improve the removal of Cr³⁺ from simulated and real industrial wastewaters. *Journal of Cleaner Production* 267, <https://doi.org/10.1016/j.jclepro.2020.121993>.

Fernandes, M. J., Moreira, M. M., Paíga, P., Dias, D., Bernardo, M., Carvalho, M., Lapa, N., Fonseca, I., Morais, S., Figueiredo, S., Delerue-Matos, C. (2019). Evaluation of the adsorption potential of biochars prepared from forest and agri-food wastes for the removal of fluoxetine, *Bioresource Technology*, Volume 292, <https://doi.org/10.1016/j.biortech.2019.121973>.

Gong, J., Fang, T., Peng, D., Li, A., Zhang, L. (2015), A highly sensitive photoelectrochemical detection of perfluorooctanic acid with molecularly imprinted polymer-functionalized nanoarchitected hybrid of AgI–BiOI composite. *Biosensors and Bioelectronics* 73, <https://doi.org/10.1016/j.bios.2015.06.008>.

Han, H., Khalid Rafiq, M., Zhou, T., Xu, R., Mašek, O., Li, X. (2019). A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants, *Journal of Hazardous Materials*, Volume 369, Pages 780-796, <https://doi.org/10.1016/j.jhazmat.2019.02.003>.

Louati, S. Baklouti, S. Samet, B. (2016). Geopolymers Based on Phosphoric Acid and Illito-Kaolinitic Clay, *Advances in Materials Science and Engineering*, vol. 2016, Article ID 2359759, 7 pages, <https://doi.org/10.1155/2016/2359759>

Mahmoudi, S. H. (2018). "A Molecularly Imprinted Polymer (MIP)-based Biomimetic Potentiometric sensing device for the analysis of Clarithromycin. 1654-1667.

Medri, V. e. (2022). Ammonium removal and recovery from municipal wastewater by ion exchange using a metakaolin K-based geopolymer. *Water Research* 225, 119203.

Mohiuddin, I. A. (2020). Efficient recognition and determination of carbamazepine and oxcabazepine in aqueous and biological samples by molecularly imprinted polymers. *Journal of analytical chemistry* 75, 7.

Naranjo, M. C.; Redondo, A. E.; Acuña, J. C.; Vieira, N. S. M.; Araújo, J. M. M.; Pereiro, A. B. (2022). Synthesis and Characterization of Fluorinated Phosphonium Ionic Liquids to Use as New Engineering Solvents. *ChemEngineering*, 6, 38. <https://doi.org/10.3390/chemengineering6030038>.

Nwosu, F.O., Ajala, O.J., Owoyemi, R.M. (2018). Preparation and characterization of adsorbents derived from bentonite and kaolin clays. *Appl Water Sci* 8, 195 <https://doi.org/10.1007/s13201-018-0827-2>

Olcer, Y. A. (2017). Development of molecularly imprinted polymers (MIPs) as a solid phase extraction (SPE) sorbent for the determination of ibuprofen in water. *RSC advances* 7.50, 31441-31447.

Pereiro, A., Araújo J., M., M., Martinho, S., Alves, F., Nunes, S., Matias, A., Duarte, C., M., M., Rebelo, L., P., N., Marrucho, I., M. (2013), Fluorinated Ionic Liquids: Properties and Applications. *ACS Sustainable Chem. Eng.* 2013, 1, 4, 427–439, <https://doi.org/10.1021/sc300163n>.

Puga, A., Moreira, M. M., Pazos, M., Figueiredo, S. A., Sanromán M. A., Delerue-Matos, C., Rosales, E. (2022), Continuous adsorption studies of pharmaceuticals in multicomponent mixtures by agroforestry biochar, *Journal of Environmental Chemical Engineering*, Volume 10, Issue 1, <https://doi.org/10.1016/j.jece.2021.106977>.

Sarpong, K. A. (2019). The development of molecularly imprinted polymers in the clean-up of water pollutants: a review. *American Journal of Analytical Chemistry* 10.5, 206-226.

Sosa, J., E., Santiago, R., Redondo, A., E., Avila, J., Lepre, L., F., Costa Gomes, M., Araújo, J., M., M., Palomar, J., Pereiro, A. (2022), Design of Ionic Liquids for Fluorinated Gas Absorption: COSMO-RS Selection and Solubility Experiments, *Environ. Sci. Technol.* 2022, 56, 9, 5898–5909, <https://doi.org/10.1021/acs.est.2c00051>.

Tomé L., C., Mecerreyes, D. (2020), Emerging Ionic Soft Materials Based on Deep Eutectic Solvents. *J. Phys. Chem. B* 124, <https://pubs.acs.org/doi/10.1021/acs.jpccb.0c04769>.