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# *GREEN SOLUTION FOR EFFICIENT REMOVAL OF PER- AND POLY- FLUOROALKYL SUBSTANCES (PFAS) AND PHARMACEUTICAL COMPOUNDS (PCs) IN AQUEOUS SYSTEMS*

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*Deixa acontecer,*
*naturalmente*

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# Sommario (extended abstract)

L’esposizione alle sostanze chimiche avviene quotidianamente, sia per le matrici ambientali che per l’essere umano. Una delle vie di esposizione maggiormente impattante riguarda l’utilizzo di acqua contaminata o di acqua che non è stata correttamente trattata.

La storia del trattamento delle acque reflue non ha origini antiche: intorno al 1850 si comprese che la comparsa di alcune patologie umane era collegata all’utilizzo di acque contaminate e, contemporaneamente, vennero sviluppate le prime tecnologie per la depurazione delle stesse. Ad oggi, dopo quasi 150 anni, gli usi e i costumi della popolazione globale sono cambiati, così come vi è stato uno sviluppo importante della tecnologia e dell’industrializzazione. I primi trattamenti delle acque prevedevano dei trattamenti biologici per la rimozione di macroinquinanti organici, in quanto la necessità principale era l’abbattimento delle cariche batteriche. Oggigiorno, il crescente tasso di consumo di risorse e di prodotti ha impattato in modo significativo sulla contaminazione delle acque. I microinquinanti, come metalli pesanti (arsenico, cadmio, piombo), sostanze medicinali, stupefacenti, sostanze per- e poli- fluoro alchiliche, distruttori endocrini, pesticidi e altro ancora, sono stati individuati nei corpi idrici. È stato studiato che, tramite i soli trattamenti biologici, non si riesce a garantire la depurazione e l’abbattimento di tali inquinanti. Per questa ragione, si sono ricercate e sviluppate negli anni nuove e innovative tecniche di depurazione per rimediare al crescente tasso di inquinamento odierno. In questo contesto, è un assunto che la composizione delle sostanze chimiche ancora non è stata approfonditamente studiata, soprattutto a livello tossicologico. Esistono più di 100.000 sostanze chimiche nell’ambiente e solo una piccola percentuale di esse è stata studiata, anche considerando le eventuali conseguenze sull’uomo e sull’ambiente.

A valle di ciò, l’attenzione della pubblica opinione sui temi della tutela ambientale e dello sviluppo sostenibile sono aumentati negli ultimi anni. Il dibattito internazionale su tali tematiche ha mosso i primi passi tramite le commissioni delle Nazioni Unite negli anni ’80, che hanno innescato una serie di provvedimenti globali come il protocollo di Kyoto, le Conferenze delle Parti (COP), fino agli obiettivi dello sviluppo sostenibile. Lo sviluppo sostenibile è dato da una serie di azioni in grado di assicurare il soddisfacimento dei bisogni della generazione presente senza compromettere la possibilità delle generazioni future di realizzare i propri. Ed è in quest’ottica che l’acqua, come bene, interseca molti aspetti della vita quotidiana di ognuno. Ciò ha portato l’attenzione pubblica anche a considerare eventuali sprechi, come l'uso eccessivo d'acqua per i consumi urbani, industriali ed agricoli. In questo scenario, le normative a tutela dell'ambiente e, in particolare dell'acqua, sono divenute nel tempo sempre più restrittive. L'acqua, infatti, è una risorsa vulnerabile e con limitate capacità naturali di autodepurazione; quindi, la gestione delle risorse idriche non può che attuarsi secondo criteri di sostenibilità. L'ambiente è oggi oggetto di protezione diretta, come bene giuridicamente tutelato in sé e non solo oggetto di protezione indiretta.

Recentemente, nell’ottobre 2023, il Parlamento Europeo ha approvato la direttiva che aggiorna la disciplina sul trattamento delle acque reflue urbane. In particolare, la proposta, che modifica la

direttiva 91/271/CEE, prevede più rigorosi requisiti di monitoraggio di diversi inquinanti e microinquinanti persistenti nelle acque, come le sostanze per- e poli- fluoro alchiliche, nonché microplastiche, agenti patogeni e resistenza antimicrobica. Ciò implica che vi sia una estensione di responsabilità del produttore, ossia per le industrie farmaceutiche, chimiche, di cosmesi e altre, per la contribuzione nel coprire i costi di trattamento aggiuntivo dei microinquinanti nelle acque. In tal senso, le principali famiglie di microinquinanti prese in considerazione sono i composti farmaceutici (PCs) e le sostanze per- e poli- fluoro alchiliche (PFAS).

I composti farmaceutici sono presenti nelle acque in quanto emesse dal corpo umano dopo l'assunzione di farmaci o perché utilizzati per scopi agroalimentari come l'allevamento di bestiame. Questi esempi sono solo una delle vie di rilascio di tali sostanze nell'ambiente e, di conseguenza, nelle acque. I PCs sono stati classificati come microinquinanti in quanto presenti in concentrazione basse nelle matrici ambientali. Teoricamente, il loro utilizzo non presenta elementi negativi sulla salute umana, ma se tali sostanze vanno ad interagire con altre sostanze nelle acque, favorendo la sintesi di sostanze terze, non vi sono prove che siano innocue per l'ambiente. Molti farmaceutici sono composti organici aromatici e possono presentare rischi per la salute umana e animale date le loro proprietà persistenti, bioaccumulative, tossiche e di non biodegradabilità. Difatti, per un impianto di trattamento acque con tecniche convenzionali, si è visto che non è possibile rimuovere i composti farmaceutici, i quali vengono scaricati tal quali nel corpo idrico ricettore. Questo può, potenzialmente, portare all'insorgere di un problema terzo, che vede come protagonisti i microrganismi che interagiscono con tali composti farmaceutici: l'antibiotico-resistenza, considerato uno dei principali problemi di sanità pubblica a livello mondiale.

Le sostanze Per- e Poli- Fluoro Alchiliche (PFAS) entrano in un gruppo ampio di sostanze, le cui conseguenze sono ancora in studio, nonostante siano utilizzate nel settore industriale dagli anni '40. Questo perché sono sostanze di origine antropiche con proprietà eccellenti per molti impieghi industriali: i PFAS sono repellenti all'acqua e ai grassi, hanno una alta stabilità chimica quando in contatto con acidi, basi, agenti ossidanti ed agenti riducenti ed hanno un'alta stabilità termica. Per queste loro uniche proprietà, se dispersi nell'ambiente, i PFAS risultano persistenti e si possono immobilizzare nelle matrici ambientali, come suolo, acqua, aria e cibo. La loro presenza è rischiosa in quanto è stato dimostrato negli ultimi anni che hanno conseguenze tossiche e bioaccumulative sia sull'essere umano che sull'ambiente. È stato riconosciuto che i PFAS possono essere tossici e, difatti, molti studi riconoscono il loro danno potenziale alla salute umana. Le più comuni patologie a essi associati sono: cancro al fegato, ai testicoli, problemi alla tiroide, ipertensione durante la gravidanza, coliti ulcerose, aumento del colesterolo e molto altro. L'esposizione ai PFAS inizia con l'uso e successivo smaltimento di prodotti che contengono tali sostanze. Normalmente, si è notato che i siti contaminati da PFAS sono molto prossimi agli impianti industriali che utilizzano tali sostanze, come industrie di packaging, cosmetiche, di schiume antincendio, di pitture, di lubrificanti, cartaria, ecc.… Eppure, è stato dimostrato che le vie di esposizione di questi agenti chimici sono diffuse, non solo puntuali, in quanto sono state ritrovate concentrazioni significative di PFAS anche molto lontano dai siti industriali, nonché adese a differenti materiali e che, quindi, possono raggiungere qualsiasi luogo. È importante sottolineare che, per quanto riguarda i PFAS, il principale metodo di smaltimento di tali sostanze è mediante incenerimento, ma questo porta un problema su un altro piano: emissione di gas fluorurati (F-gases). Questi ultimi, essendo climalteranti, contribuiscono all'incremento dell'effetto serra.

Per la rimozione di PFAS e PCs sono stati sperimentati e studiati molte tipologie differenti di trattamenti: bioreattori a membrana, digestione anaerobica, osmosi inversa e nanofiltrazione, ossidazione avanzata, adsorbimento mediante carboni attivi, riduzione fotocatalitica, resine a scambio ionico. Uno dei più promettenti, risulta essere l'adsorbimento mediante carboni attivi: è un'operazione di trasferimento di massa dove una fase liquida contaminata entra in contatto con una fase solida, l'adsorbente; il contaminante da rimuovere dalla fase liquida viene detto adsorbato. In questo tipo di processo, sono molteplici le forze in gioco, come le interazioni di dipolo, la forza di Coulomb, le forze di Van der-Waals. Inoltre, vi è molta dipendenza dalla tipologia di adsorbente. Per questa ragione, vi è la necessità di caratterizzare il processo mediante test di laboratorio con lo specifico materiale adsorbente, fino a che non si raggiunge l'equilibrio termodinamico tra le fasi. Dopo la caratterizzazione, vi sono tutti i parametri per permettere lo scale-up del sistema di depurazione. L'efficienza di un processo di adsorbimento dipende molto dalla concentrazione e dalle caratteristiche (peso molecolare, struttura molecolare, polarità, solubilità) dell'adsorbato presente nella fase liquida, la quantità di adsorbente e dalla temperatura di processo. Il materiale adsorbente è il carbone attivo. Solitamente, è disponibile del carbone attivo a livello commerciale, ma può essere preparato in laboratorio da biomasse o da scarti, con l'intenzione di applicare i concetti di economia circolare.

Considerando quanto sopra, c'è un bisogno urgente di sviluppare una tecnologia efficiente e sostenibile per la rimozione dei PFAS e dei PCs, mediante lo sviluppo di strumenti e modelli dell'ingegneria ambientale e di processo.

Il presente lavoro è nato tramite una collaborazione tra "Alma Mater Studiorum – Università di Bologna" e "Universidade NOVA de Lisboa", nell'ambito del progetto europeo "MAR2PROTECT". L'obiettivo principale è di contribuire allo sviluppo ed alla ricerca di tecnologie nuove e sostenibili per la rimozione di microinquinanti. Ciò è avvenuto tramite un'attività di ricerca presso i laboratori della "Universidade NOVA de Lisboa" della durata di sei mesi. La ricerca è avvenuta, in primo luogo, mediante la sintesi di biomateriali da biomasse (Juncus Maritimus, Phragmites Australis e Coconut Shells) e caratterizzazione del biomateriale ottenuto; successivamente, tramite la sperimentazione in batch del processo di adsorbimento con tali biomateriali. Quest'ultima richiede la caratterizzazione del comportamento del materiale adsorbente in relazione alla rimozione dei microinquinanti presi in considerazione (Diclofenac, Valsartan, PFOA, PFBS, PFPeA). I risultati ottenuti risultano interessanti, in quanto il processo di adsorbimento tramite i biomateriali da biomassa risulta promettente in molti casi e quindi può essere ulteriormente approfondito e migliorato mediante successivi test in continuo, a scala di laboratorio o pilota, anche per valutarne la fattibilità per lo scale-up a livello ingegneristico.

# Abstract

Daily exposure to chemicals occurs through environmental matrices and human contact. One of the most significant pathways of exposure is through the use of contaminated or untreated water.

The link between human disease and the use of contaminated water was first identified in 1850. At the same time, the first water treatment technologies were developed. The initial water treatments focused on removing organic macro-pollutants through biological treatments to reduce bacterial loads. Micropollutants, such as heavy metals, medicinal substances, narcotics, per- and poly-alkyl fluorine substances, endocrine disruptors, and pesticides, have been detected in water bodies, leading to significant water contamination. Studies have shown that biological treatment alone cannot guarantee complete purification and removal of these pollutants. New purification techniques have been researched and developed to address the increasing pollution rate.

In recent years, there has been a growing public interest in environmental protection and sustainable development. Sustainable development involves taking actions that meet the needs of the present generation without compromising the ability of future generations to meet their own needs. Water is a commodity that intersects with many aspects of daily life. Regulations to protect the environment and water have become increasingly stringent over time. Water is a limited resource with a vulnerable natural capacity for self-purification. The management of water resources must therefore be based on sustainability criteria. Today, the environment is directly protected as a legally protected good in its own right, rather than just indirectly protected.

A directive updating the rules on urban wastewater treatment was adopted by the European Parliament in October. The proposal amends Directive 91/271/EEC and introduces more stringent monitoring requirements for persistent pollutants and micropollutants in water. This includes per- and poly-fluoroalkyl substances, microplastics, pathogens, and antimicrobial resistance, due to the release of pharmaceutical compounds in the environment.

Pharmaceutical compounds (PCs) are present in the environment and can be detected in the water. Due to their low concentrations in environmental matrices, PCs are considered micropollutants. Although the use of these substances is not harmful to human health, their interaction with other substances in the water, such as micro-organisms, can lead to antibiotic resistance, which is a major public health problem around the world.

Per- and poly-fluoroalkyl substances (PFAS) are a group of man-made chemicals that have been used in industry since the 1940s. These chemicals have unique properties such as water and grease repellence and high thermal stability. When dispersed in the environment, PFAS can persist and become immobilised in environmental matrices such as soil, water, air and food. Sites contaminated with PFAS are often found close to industrial facilities that use them, such as in packaging, cosmetics, firefighting foams, paints, lubricants and paper production. However, significant concentrations of PFAS have also been found far away from industrial sites and have been attached to a variety of materials, allowing them to travel to any location. PFASs are known to cause toxicity, with numerous studies identifying potential adverse human health effects, including liver and testicular cancers, thyroid problems and elevated cholesterol levels. Exposure to PFAS typically occurs through the use and disposal of products containing these substances.

Various treatments have been studied for the removal of PFAS and PCs from aqueous systems, including membrane bioreactors, anaerobic digestion, reverse osmosis, nanofiltration, advanced oxidation, adsorption using activated carbons, photocatalytic reduction, and ion exchange resins. Some of these treatments have shown promise, while others have not. One of the most promising technologies is the adsorption process with the activated carbon. A contaminated aqueous matrix is purified by placing a solid phase in contact with it, causing the contaminant to be adsorbed to the solid phase through molecular-level interactions.

The focus of research should now be on the development of cost-effective treatment strategies that can be implemented in real-world wastewater treatment plants, while at the same time ensuring the sustainability of the technology.

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# 1. Introduction and state of the art

Micropollutants (MPs) are substances such as chemicals, pesticides and pharmaceutical compounds that are present in water in very low concentrations (UFAM, 2023). The scientific community has only recently discovered this category of pollutants. Since the early 2000s, advancements in chemical-analytical techniques and studies on the toxicology of these new pollutants have made this a topic of global concern (Tartari et al., 2020). Therefore, the regulation of these substances is still under study and continuously in progress.

The MPs are originated mainly by anthropic action. For that reason, their presence in water is the result of a complex interaction between the human activity and the environment, as shown in Figure 1 (Chen et al., 2023). The stressors are external abiotic or biotic factors that arise from both natural and human disturbances (Sabater et al., 2019), including land use, pollution, hydrological regulation, climate change (Lemm et al., 2021). The interaction between these stressors can significantly alter the ecological status of rivers, resulting in biodiversity loss and functional alteration in many freshwater ecosystems (Morrison et al., 2020). The presence of micropollutants in aquatic environments has been linked to negative effects, such as endocrine disruption, antibiotic resistance in microorganisms, and short- and long-term toxicity (Kasprzyk-Hordern et al., 2008; Lenka et al., 2021; Ma et al., 2017). The interaction between various factors contributes to the occurrence of these micropollutants. Long-term exposure to micropollutants can pose risks to human health, as well as alter ecosystems and wildlife (Chen et al., 2023).

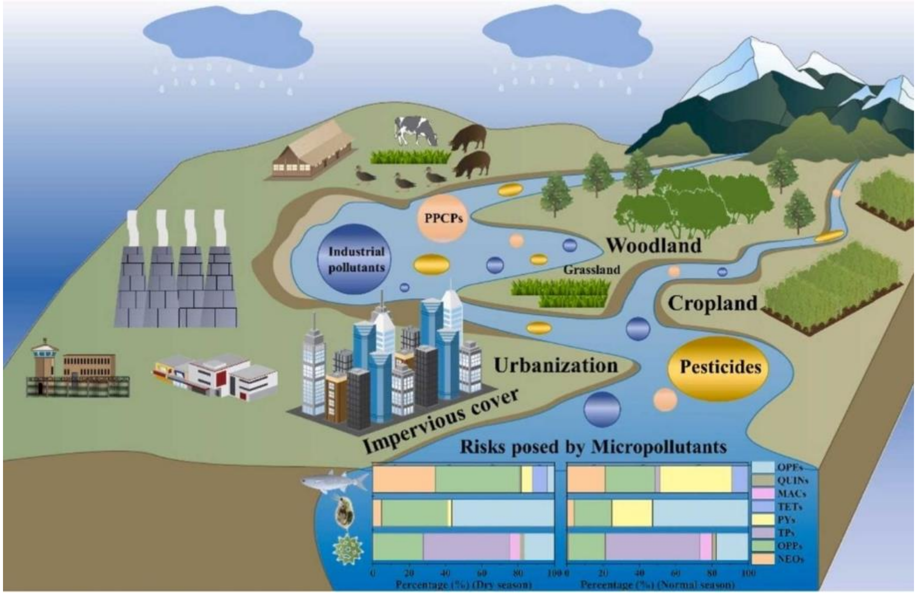


Figure 1. Schematic representation of the interaction between human activity and environment (Chen et al., 2023).

Currently, wastewater treatment plants aren't designed to treat the MPs (Lenka et al., 2021), as their discovery is recent. For this reason, MPs are directly involved in water cycle. Therefore, it is necessary to carefully analyse the operation of treatment plants for both wastewater and drinking water, which are essential for controlling pollution. Proper operation of treatment plants for POPs prevents their release into the environment, conserves natural resources and limits contamination of drinking water. Furthermore, treatments of drinking water are crucial in reducing risks to consumers (Tartari et al., 2020).

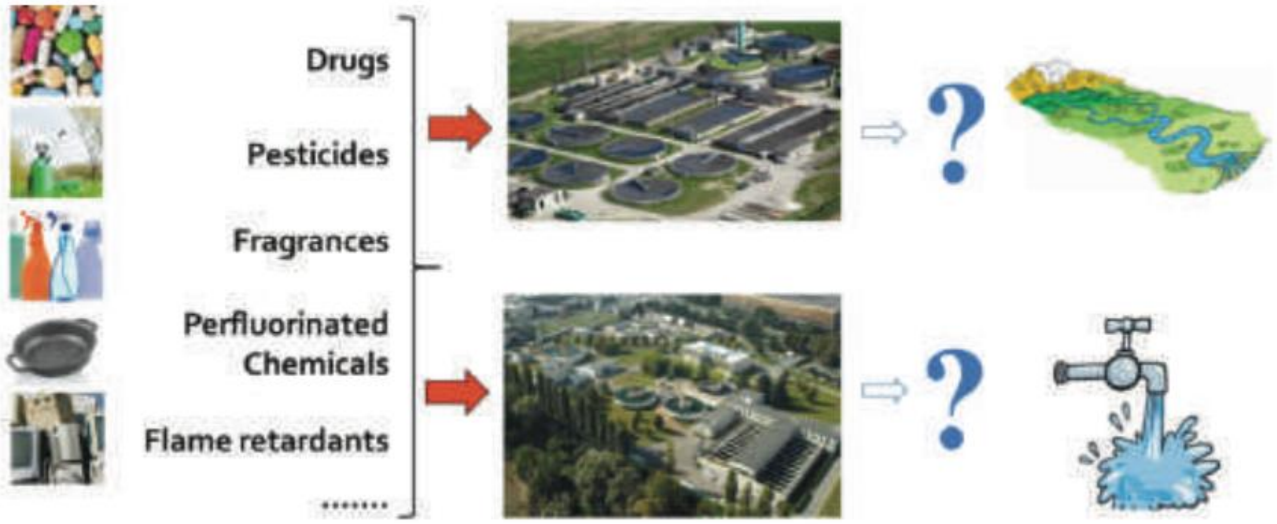


*Figure 2. Potential sources of risk for human and environment (Tartari et al., 2020).*

Starting with the main water pollutants, such as nutrients, inorganic pollutants, oil, and surfactants, the scientific community has been analysing micropollutants for the past twenty years. The sources of micropollutants are still being investigated, but it is known that they come mainly from the following sources (Tartari et al., 2020):

- Pesticides, their degradation and transport, transformation in the environment
- Drugs, pharmaceutical compounds, hormones, and cosmetics due to human use
- Endocrine disrupting chemicals, brominated flame retardant, perfluorinated compounds
- Nanomaterials and microplastics

The main scope of the scientific research is to find new biotechnologies for treating water contaminated by MPs. There are a several technologies tested in this field, such as membrane processes (Reverse Osmosis and Nanofiltration), adsorption with activated carbons, membrane bioreactors (MBR), advanced oxidating processes (AOP), and conventional activated sludge (CAS) (Gutkoski et al., 2024; Nguyen et al., 2019; Tartari et al., 2020). However, further studies are needed to clarify the most suitable techniques related to the behavior of specific micropollutants.

## 1.1 Per- and Poly- Fluoroalkyl Substances (PFAS)

Per- and Poly- Fluoroalkyl Substances (PFAS) are anthropogenic aliphatic chemicals that consist of perfluoroalkyl and polyfluoroalkyl substances. Perfluoroalkyl substances are fully fluorinated compounds, where each hydrogen atom attached to a carbon atom is replaced by fluorine atoms. Polyfluoroalkyl substances are partially fluorinated compounds, where at least one hydrogen atom attached to a carbon atom is replaced by fluorine atoms. (Buck et al., 2011; Manojkumar et al., 2023; Rahman et al., 2014). These substances have a strong resistance to thermal, biological and photolytic degradation; this is due to the high stability of their C-F covalent bonds (Gagliano, 2020; Lenka et al., 2021; Prevedouros et al., 2006). The PFAS are also known as “forever chemicals” because these substances are highly resistant to breakdown in the environment under natural condition. Furthermore, the PFAS family includes approximately 5,000 to 10,000 compounds (Manojkumar et al., 2023).

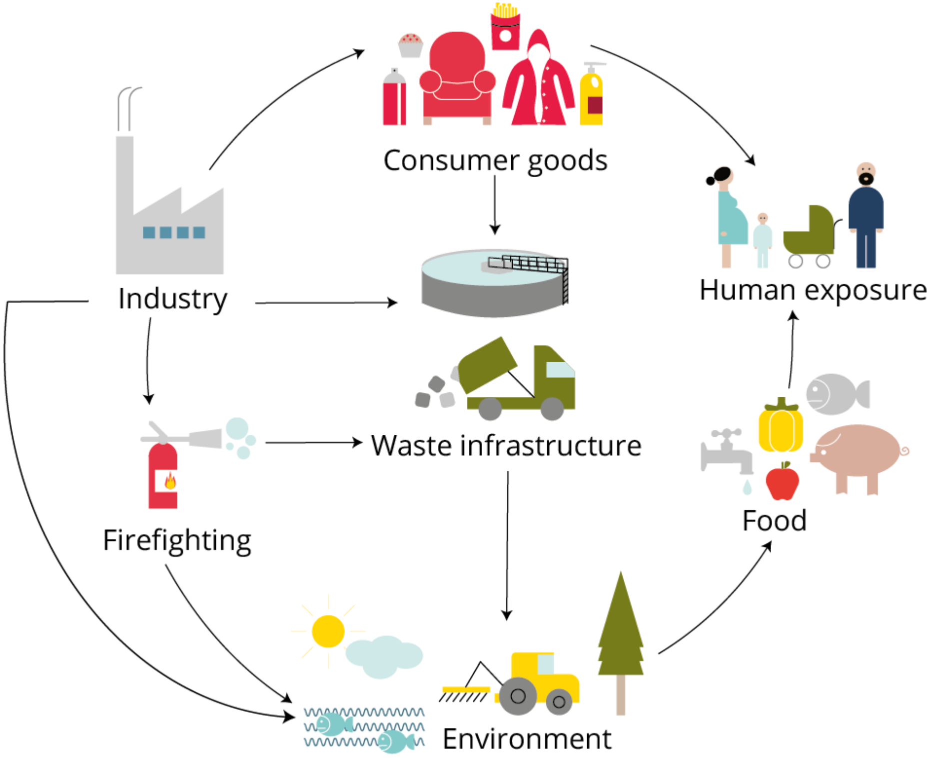


*Figure 3. Typical PFAS exposure pathway (European Environment Agency, 2023).*

PFAS have unique properties (e.g. thermal stability, stability against acid and base, oxidizing and reducing properties, hydrophobic and lipophobic behaviour) that make them extremely suitable as water and oil repellents (Fabregat-Palau et al., 2022; Manojkumar et al., 2023; Prevedouros et al., 2006). Due to their properties, PFAS are widely used in industrial and consumer applications, with consumer products being treated with PFAS to increase their lifespan and durability. However, this practice leads to the gradual exposure of humans, wildlife, and the environment to PFAS. (Herzke et al., 2012; Lenka et al., 2021).

Because of their versatility, PFAS are widely used in various industrial sectors such as paper manufacturing, metal painting, textiles, pesticides and pharmaceutical production, mining operations, cosmetics and personal care products, ink and paint production, food packaging, non-stick cooking utensils, firefighting foams, and waterproof products (European Environment Agency, 2023; Gagliano, 2020; Lenka et al., 2021; Wang et al., 2017).

Several studies have been conducted on the toxicology and eco-toxicology of PFAS. The results are varied, making it challenging to classify the response of humans and the environment to PFAS exposure. However, it is certain that PFAS are toxic and bio-accumulative in both humans and the environment. Epidemiological studies have investigated a broad range of health outcomes, including reproductive, developmental, behavioural, neurological, endocrine, immunological, metabolic, cardiovascular, and cancer outcomes. In December 2023, the International Agency for Research on Cancer (IARC), which is the cancer agency of the World Health Organization (WHO), released an update on the categorization of PFOA and PFOS, the two most studied and widespread PFAS. The new classification states that PFOA is carcinogenic to humans (Group 1), while PFOS is possibly carcinogenic to humans (Group 2B). (National Science and Technology Council (NSTC), 2023).

Figure 4 is a summary of all the potential adverse human health effects of PFAS exposure.

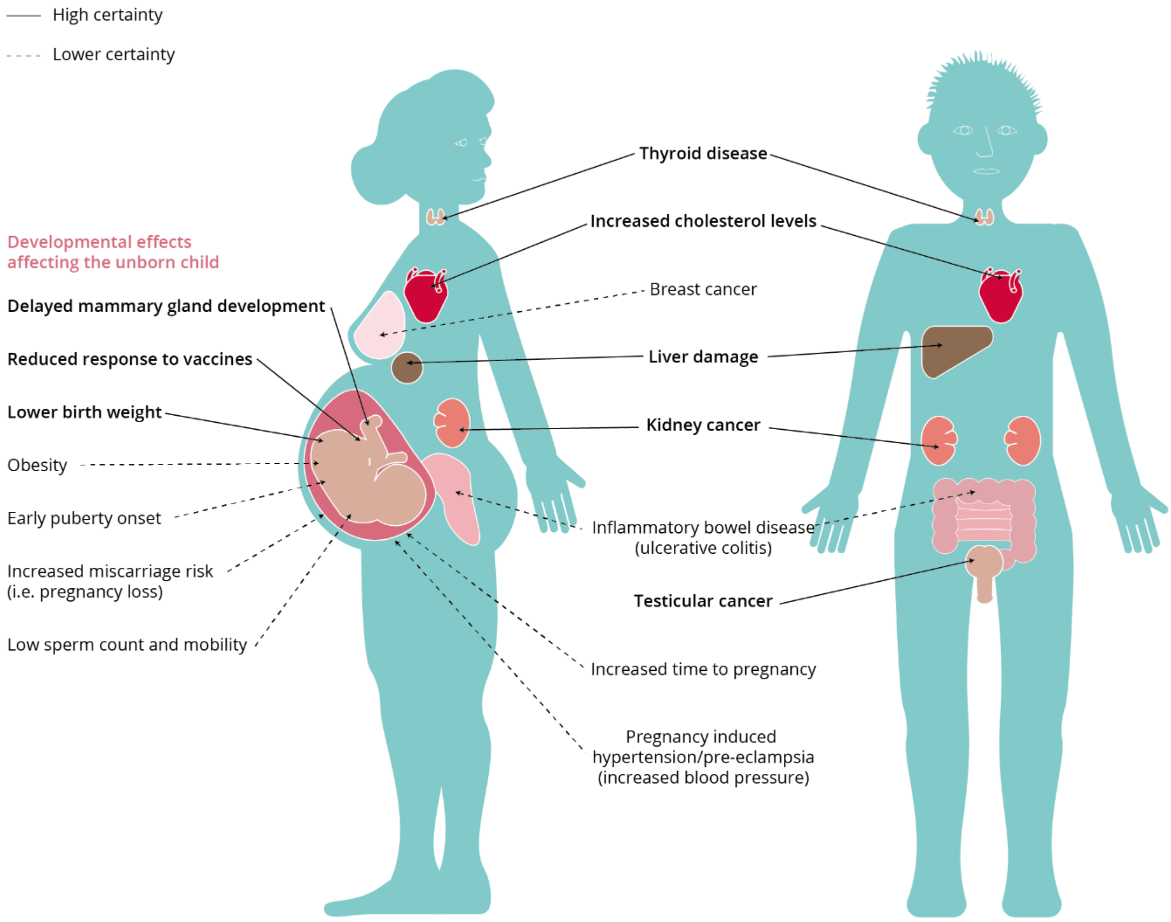


*Figure 4. Effects of PFAS on human health (European Environment Agency, 2023).*

Ecotoxicity data has increased significantly over the past several years, however, the depth and breadth of information for the wide range of aquatic and terrestrial species remains limited. Data currently available indicate that PFAS have the potential to cause both acute and chronic effects on marine vertebrates (e.g., fish, amphibians), invertebrates (e.g., insects, shellfish), and aquatic plants. The impacts of PFAS in the aquatic community include mortality, cellular membrane damage, impaired growth and development, reproductive failure, hormone disruption, nervous and immune system disruption, and liver and kidney damage. Similar effects have also been observed in terrestrial organisms.(National Science and Technology Council (NSTC), 2023).

Given the usefulness of these compounds in several sectors, PFAS contamination is now widespread, with studies finding PFAS in all types of environmental samples, including drinking water sources (Dai et al., 2015; Herzke et al., 2012; Santi, 2023; Shi et al., 2016). Also, rainstorms can exacerbate the issue by allowing PFAS to reach groundwater through soil run-off (Gagliano, 2020; Gellrich et al., 2012).

A recent maxi-inquiry, promoted by “Le Monde” and “The Guardian”, shows the map of the PFAS contaminated sites in Europe (Santi, 2023), reported in Figure 5:

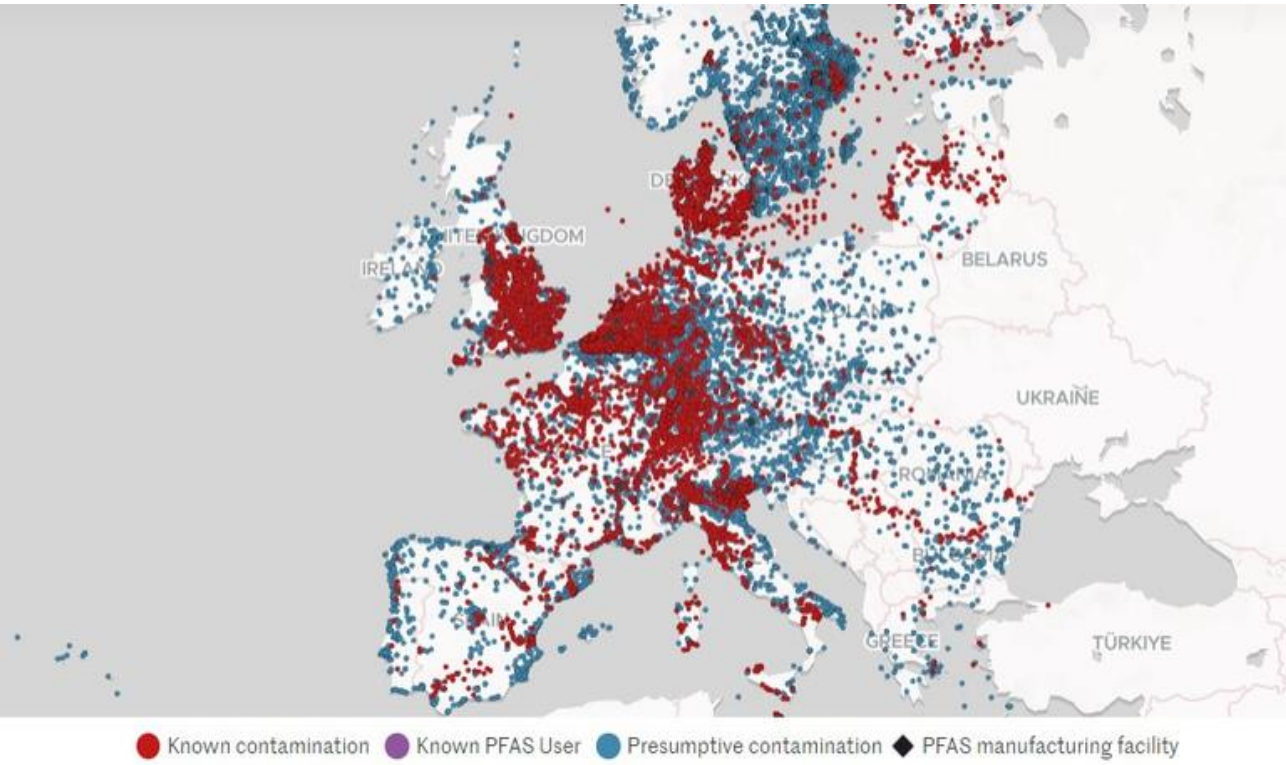


*Figure 5. European map on PFAS contaminated sites (Dagorn et al., 2023).*

The evidences from the map are several (Dagorn et al., 2023):

- About 20 producers of PFAS (chemical plants)
- Over 17,000 contaminated sites (soil, water, or biota) with more than 10 ng/L (studies from 2003 to 2023)

- About 232 industrial sites which use PFAS in their productive processes (plastics, pesticides, paintings, textile, and other chemicals)
- Over 21,000 presumed contamination sites. Presumed, because there are new or closed industrial activities or military bases where the contamination is expected because of the type of industry or the chemicals/substances involved (e.g. anti-firefighting foams, plastic, …) but no environmental sampling has been carried out to confirm this.

Over these evidences, identifying a suitable technology to treat this persistent chemical and developing new techniques to rapidly detect both PFAS and emerging PFAS are the primary objective of scientific researchers.

## 1.2 Pharmaceutical Compounds (PCs)

The presence of pharmaceutical compounds in the aquatic system is considered an emerging contaminant with potentially hazardous effects on biota and human health (Bernardo et al., 2016; Burkina et al., 2015; Vasquez et al., 2014). This category of compounds includes pharmaceuticals, personal care products, and illicit drugs. They can enter the environment through various sources, such as drug preparation and formulation, patient use and excretion, use in food production, agricultural runoff from livestock treatment, and improper disposal (Dai et al., 2015; Kasprzyk-Hordern et al., 2008; OECD, 2019). Pharmaceutical consumption is predicted to rise due to several factors, including longer life expectancy, intensified livestock and aquaculture practices, economic growth, and climate change, which can worsen diseases (Kolakovic et al., 2022; OECD, 2019; Vasquez et al., 2014; Wojcieszyńska et al., 2023).

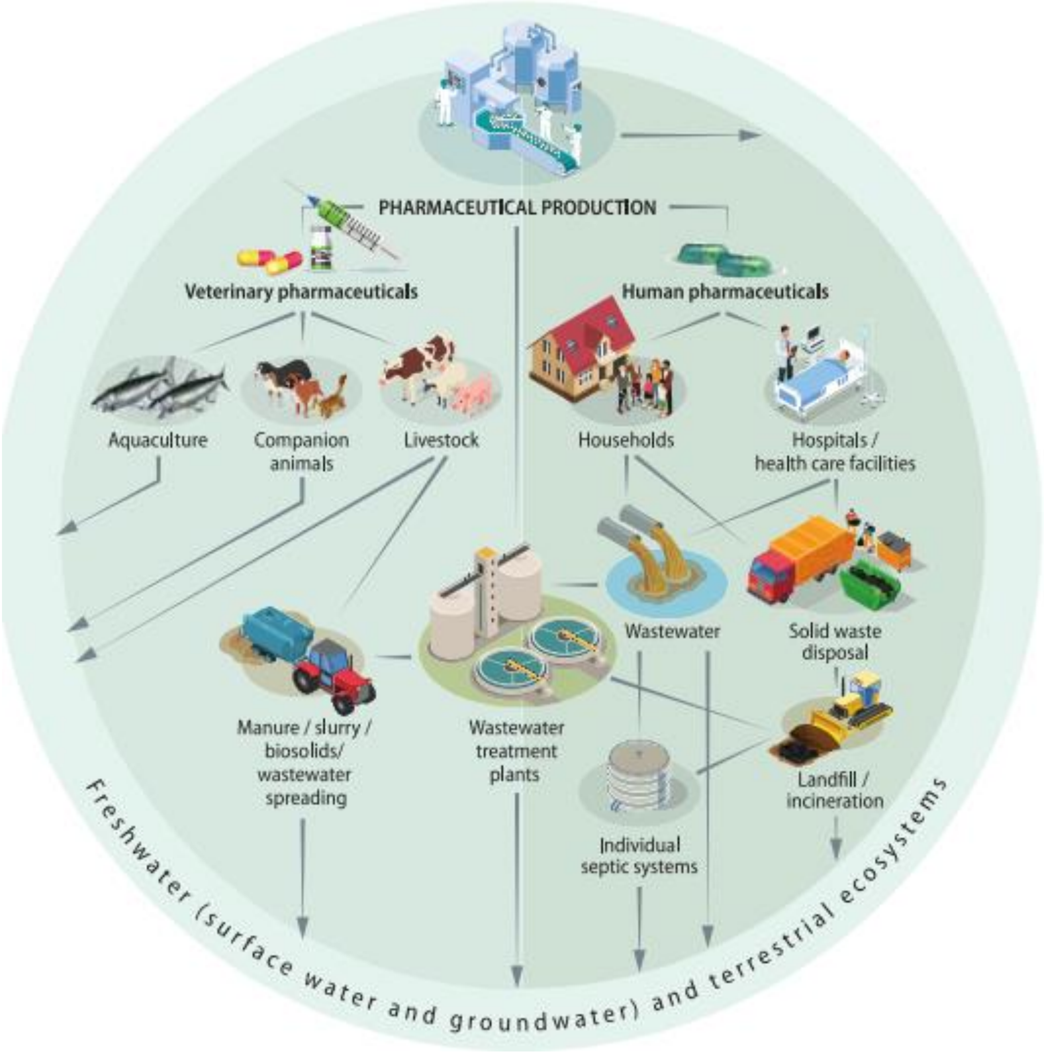
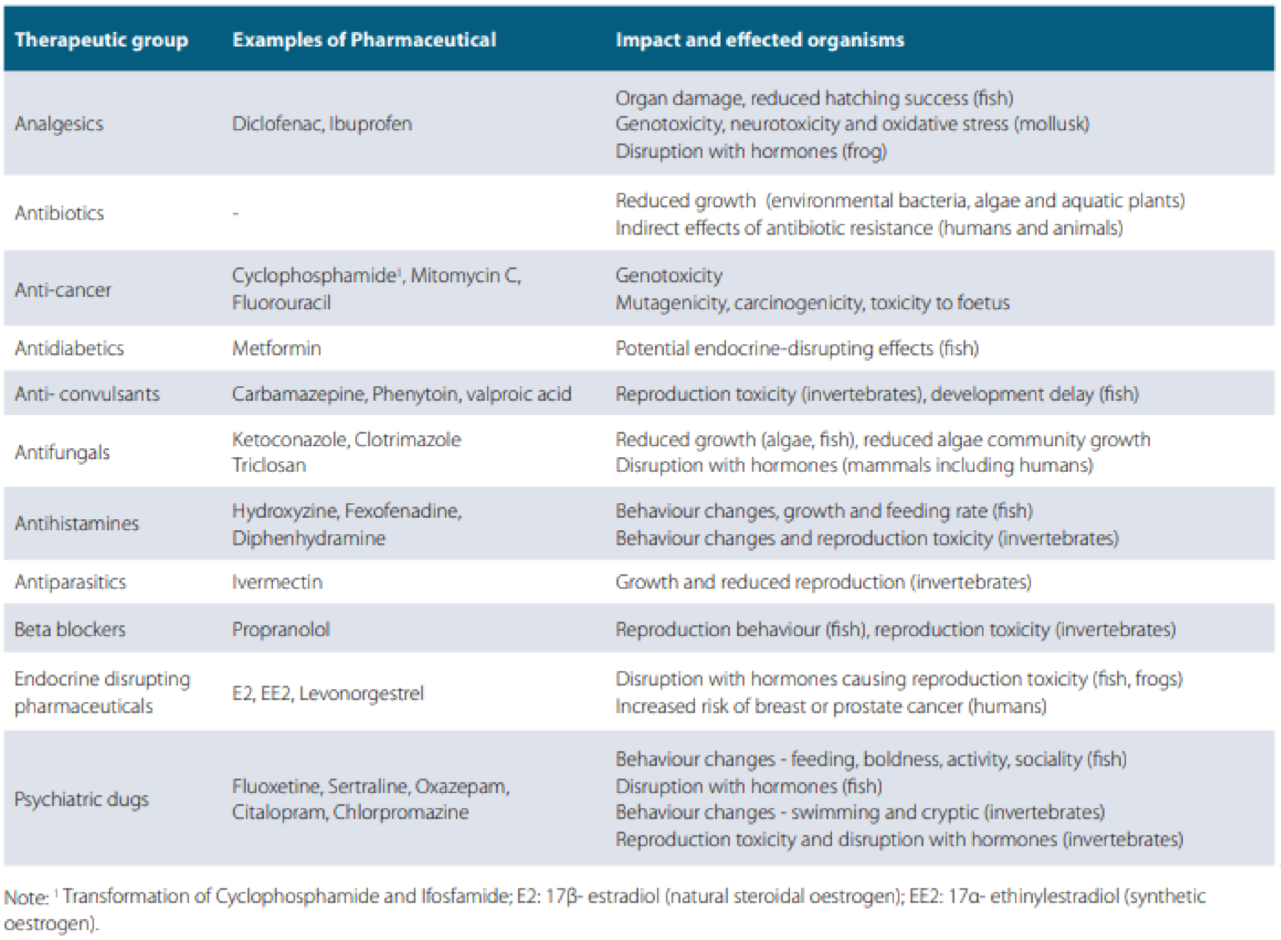


Figure 6. Major pathways of release of pharmaceuticals in the environment (OECD, 2019).

Pharmaceuticals, unlike other chemical, are unique in that they are specifically designed to interact with living systems and produce a pharmacological response at low doses (OECD, 2019; Vasquez et al., 2014). They are designed to be stable in order to reach and interact with target molecules (Carpenter et al., 2002; OECD, 2019) and this feature causes their degradation to occur slowly (Żur et al., 2020). Also, their continuous use leads to their release into the environment at rates that exceed degradation rates. As a result, even low concentrations of pharmaceuticals in the environment are of concern (Huerta-Fontela et al., 2011; Jones et al., 2001; OECD, 2019), and, additionally, conventional wastewater treatment methods are not very effective in degrading these compounds (Ebele et al., 2017; Snyder, 2008).

The most commonly detected pharmaceutical compounds include analgesics, antibiotics, diuretics, hormones, antidepressants, psychiatric drugs, and lipid regulators (Couto et al., 2019; Khalaf et al., 2009; Pomati et al., 2008, 2006). Figure 7 describes some pharmaceutical and their general effects and impacts on living organisms.



| Therapeutic group | Examples of Pharmaceutical | Impact and effected organisms |
|---|---|---|
| Analgesics | Diclofenac, Ibuprofen | Organ damage, reduced hatching success (fish)<br>Genotoxicity, neurotoxicity and oxidative stress (mollusk)<br>Disruption with hormones (frog) |
| Antibiotics | - | Reduced growth (environmental bacteria, algae and aquatic plants)<br>Indirect effects of antibiotic resistance (humans and animals) |
| Anti-cancer | Cyclophosphamide[1], Mitomycin C, Fluorouracil | Genotoxicity<br>Mutagenicity, carcinogenicity, toxicity to foetus |
| Antidiabetics | Metformin | Potential endocrine-disrupting effects (fish) |
| Anti- convulsants | Carbamazepine, Phenytoin, valproic acid | Reproduction toxicity (invertebrates), development delay (fish) |
| Antifungals | Ketoconazole, Clotrimazole<br>Triclosan | Reduced growth (algae, fish), reduced algae community growth<br>Disruption with hormones (mammals including humans) |
| Antihistamines | Hydroxyzine, Fexofenadine, Diphenhydramine | Behaviour changes, growth and feeding rate (fish)<br>Behaviour changes and reproduction toxicity (invertebrates) |
| Antiparasitics | Ivermectin | Growth and reduced reproduction (invertebrates) |
| Beta blockers | Propranolol | Reproduction behaviour (fish), reproduction toxicity (invertebrates) |
| Endocrine disrupting pharmaceuticals | E2, EE2, Levonorgestrel | Disruption with hormones causing reproduction toxicity (fish, frogs)<br>Increased risk of breast or prostate cancer (humans) |
| Psychiatric dugs | Fluoxetine, Sertraline, Oxazepam, Citalopram, Chlorpromazine | Behaviour changes - feeding, boldness, activity, sociality (fish)<br>Disruption with hormones (fish)<br>Behaviour changes - swimming and cryptic (invertebrates)<br>Reproduction toxicity and disruption with hormones (invertebrates) |

Note: [1] Transformation of Cyclophosphamide and Ifosfamide; E2: 17β- estradiol (natural steroidal oestrogen); EE2: 17α- ethinylestradiol (synthetic oestrogen).

*Figure 7. Examples of adverse effects of certain pharmaceuticals in the environment on aquatic organisms, and human and animal health (OECD, 2019).*

For the majority of wildlife, exposure to pharmaceuticals in the environment and its toxicological effects could be long-term (Burkina et al., 2015). The impact of this type of exposure is still being studied (Jones et al., 2001), but evidence suggests that oral contraceptives have caused feminisation in fish and amphibians (OECD, 2019). Additionally, antidepressants have altered fish behaviour, making them less risk-averse and more vulnerable to predators (OECD, 2019). Furthermore, the overuse and discharge of antibiotics into water bodies exacerbates the problem of antimicrobial resistance, which is the ability of a microbe to become insensitive to an antibiotic compound. In this last case, bacteria may exhibit intrinsic resistance to antibiotics or acquire resistance by obtaining new genetic material following exposure to antibiotics, resulting in increased tolerance (Itzhari and Ronen, 2023; OECD, 2019).

In this scenario, two significant strategies are relevant for scientific research. Firstly, there is a need for a better understanding of the long-term toxicology of PCs on the aquatic environment and subsequently on human health (Ebele et al., 2017; Evgenidou et al., 2015). Secondly, experimentation on contaminated water should improve depuration biotechnologies for water contaminated by PCs by testing new processes and optimizing the consolidated ones (Kolakovic et al., 2022; Vieno and Sillanpää, 2014; Wojcieszyńska et al., 2023).

## 1.3 UE Regulation

The regulation about the MPs is still under development. As discussed in the previous paragraph, the MPs are several and a detailed analysis, toxicological, sanitary, environmental, on every single pollutant is quite impossible to develop (Talluri, 2020). For this reason, the regulatory framework in Europe has been continuously developing and changing over the last twenty years.

The general principles of the environmental protection in the European Union have repercussions on the various aspect of the administrative apparatus (Facondini, 2019):

- Cooperation – the Nations and the Public Administration should share their information for improving the environmental protection.
- Prevention – improving a series of actions before a damage will happen.
- Precaution – adopting a series of environmental measures before the certainty on the toxic effect on the environment is known.
- Polluters pay – an action who translate the exploiting of the resources in an economic value, with the aim of avoiding environmentally harmful activities.
- High level of protection – theatrically, the environmental protection should be the main interest in comparison to others.

With this aim was promulgated the first European Directive about water resources and pollution: the Water Framework Directive (2000/60/CE), a document on the ecological quality of the water. With this directive, the approach for the monitoring and the chemical characterization of the pollutant has become a proper assessment of the ecological status through indicators of the biological state and the hydro-morphological disturbances of the water. Furthermore, the first class or group of substances of environmental concern has been identified and it should be updated every six years (Tartari et al., 2020). So, the scope of the Directive was protecting water resources, reaching high quality of the water, and the monitoring the quality of the ecosystems, not only though COD and BOD index, but also in respect of other pollutants (e.g. benzene, chlorinated substances, lead, …).

Member States, through the adoption of management plans and a program of measures at river basin district level, are responsible for:

- Preventing deterioration, improve and restore the condition of water bodies to good ecological and chemical conditions.
- Reduce pollution due to emissions of substances.

- Protect, improve, and restore groundwater conditions, with the aim of balancing extraction and refuelling.

- Preserve protected areas.

Additionally, the Decision 2001/2455/CE, Regulation 2004/850/CE, …, made possible the promulgation of the REACH regulation (2006/1907/CE) after a few years after the publication of the WFD. REACH is the main and the fundamental regulation on chemical substances in Europe, that include, for producer and importers, a series of steps for the trade of chemicals (Registration, Evaluation, Authorisation and Restriction of Chemicals) (Tartari et al., 2020).

After this period, the attention on micropollutants became increasingly, and other regulation on new topics were promulgated: Directive 2009/128/CE on the utilization of pesticides, Regulation 2009/1108/CE on the safe commercialization of pesticides, the Directive 2013/39/UE that modified the lists of pollutant of interest of the WFD (Tartari et al., 2020). The most recent regulations are from the Directive 2019/904/UE, that added the attention on microplastics, and from the Directive 2020/2184/UE, that include the limits on PFAS.

The last Directive establishes a new threshold limit value for the PFAS family of 0,5 µg/L, in addition to the limits of 0,1 µg/L of specific PFAS ("sum of PFAS"), that are (European Parliament, 2020; Talluri, 2020):

- Perfluorobutanoic acid (PFBA)
- Perfluoropentanoic acid (PFPA)
- Perfluorohexanoic acid (PFHxA)
- Perfluoroheptanoic acid (PFHpA)
- Perfluorooctanoic acid (PFOA)
- Perfluorononanoic acid (PFNA)
- Perfluorodecanoic acid (PFDA)
- Perfluoroundecanoic acid (PFUnDA)
- Perfluorododecanoic acid (PFDoDA)
- Perfluorotridecanoic acid (PFTrDA)
- Perfluorobutane sulfonic acid (PFBS)
- Perfluoropentane sulfonic acid (PFPS)
- Perfluorohexane sulfonic acid (PFHxS)
- Perfluoroheptane sulfonic acid (PFHpS)
- Perfluorooctane sulfonic acid (PFOS)
- Perfluorononane sulfonic acid (PFNS)
- Perfluorodecane sulfonic acid (PFDS)
- Perfluoroundecane sulfonic acid
- Perfluorododecane sulfonic acid
- Perfluorotridecane sulfonic acid

For these, the European Commission will establish the technical guidelines for the monitoring, that is the frequency of sampling, the detection limits, and the parametric values. This guidelines will be operating starting from January 2026 (Canas, 2023).

There are several strategies to mitigate the problem of PFAS pollution. One proposed solution is substitution, which involves using a less hazardous chemical than PFAS (Canas, 2023). This strategy is sometimes confused with using another substance from the PFAS family, such as the short-chain ones. However, this approach still poses a problem because these PFAS are also referred to as 'emerging PFAS' and have the same, or even worse, issues as the others (Manojkumar et al., 2023; Sinclair et al., 2020). Another strategy should be the transparency of the label: in this way, the consumers could choose product without PFAS, and the market strategies will change in favour of PFAS-free products.

The complete elimination of PFAS in the industrial sector is a utopic strategy, because the impact of this choice will be catastrophic for producer and importers of products; furthermore, a lot of products of daily life will be out from the markets. For this last aspect, a proper evaluation on pros and cons should be carried out (Canas, 2023).

Regarding the pharmaceutical compounds, the European Commission proposed a new directive and regulation to revise and replace the current pharmaceutical legislation. The main changes will influence the product lifecycles, from launch to decline (Dentons, 2023). This act is due to the identification of pharmaceutical and cosmetics residues as a source of micropollutants found in wastewater (Dentons, 2023; Euractiv, 2023). The main aspect of this regulation is the reinforcement of the Environmental Risk Assessment (ERA) of pharmaceutical compounds. The ERA consists in a document with the identification of potential risk of the substance, the measures for the risk mitigation to avoid emission in environmental matrixes and the evaluation of risk for antimicrobial resistance, which is considered one of the major public health problems worldwide (Dentons, 2023; Paknazer, 2023). The ERA should be promptly updated with new information from environmental monitoring, ecotoxicity studies, and updated risk assessments under other EU legislation, as well as environmental exposure data. This should be done without delay and reported to the relevant competent authorities (Dentons, 2023). Regarding wastewater contamination, the EU lawmakers adopted their position on the new rules for the collection, treatment, and discharge of urban wastewater on 5th October 2023. The objective of these rules is to protect the environment and human health (Euractiv, 2023). This means that producers in industries such as pharmaceuticals, chemicals, and cosmetics are responsible for contributing to the costs of treating micropollutants in water (Euractiv, 2023). In this sense, the main families of micropollutants considered are pharmaceutical compounds (PCs) and per- and polyfluoroalkyl substances (PFAS).

## 1.4 Technologies for MPs removal

Several biotechnologies have been investigated for the treatment of MPs. In Table 1**Errore. L'origine riferimento non è stata trovata.** there is a short overview of the processes tested in laboratory scale, pilot scale and industrial scale (Bhattacharya et al., 2018).

*Table 1. Overview of the treatment methods for MPs removal (adapted from Bhattacharya et al., 2018).*

| ***Physicochemical methods*** | ***Biological methods*** |
|---|---|
| Chlorination | Activated sludge process |
| Sorption | Biological activated carbon |
| Adsorption | Biosorption |
| Coagulation | Biological trickling filter and biofilm reactor |
| Immobilization | Biological nitrification and denitrification |
| Photolysis | Membrane bioreactor |
| Photo catalysis | Constructed wetlands (CWs) |
| Photo degradation | Subsurface flow CWs |
| Fenton process | Surface flow (SF) CWs |
| Electro-Fenton processes | Hybrid CW systems |
| Photo-Fenton process | Waste stabilization ponds (WSPs) |
| Sonochemical reaction | High-rate algal ponds (HRAPs) |
| Electrodialysis | Fungal reactors |
| Ultrafiltration | Daphnia reactors |
|  | Microalgae-/fungi-based treatment |
|  | Phytoremediation |

In this section the most investigated technologies will be discussed through their advantages and disadvantages.

### 1.4.1 Membrane separation processes

In the 1960s, the scientific community began to use membrane processes as a technology for water purification. The focus was on removing organic contaminants, suspended solids, and salt from aqueous solutions (Yadav et al., 2022). Nowadays, researchers have investigated the use of this pressure-driven processes for removing MPs and the most appropriate and effective membrane separation processes regarding this problematic are Reverse Osmosis (RO) and Nanofiltration (NF).

A membrane separation process involves a flux of contaminated water though a membrane, resulting in two separate fluxes: a more concentrated retentate containing the contaminant, and a depurated permeate. The removal of particles through membranes is mainly achieved by size exclusion, electrostatic repulsion, or adsorption (Georgieva et al., 2010).

It was observed that, at various feed concentrations of PFOS, the contaminant had a high retention rate: specifically, at concentrations up to 1500 $\frac{mg}{L}$, the retention rate was over 99% (Banks et al., 2020; Tang et al., 2006). A similar result was observed in the removal of PCs, e.g. diclofenac, primidone and phenacetine (Kimura et al., 2003). The mechanism that governed this high rate of removal was attributable to size exclusion (Tang et al., 2006; Yoon and Lueptow, 2005).

Another mechanism of removal observed in other studies is electrostatic repulsion (Fabregat-Palau et al., 2022; Taheran et al., 2016; Yadav et al., 2022). The surface material of membranes may have a charge, and if it is the same charge as the compound to be removed, this mechanism will enhance its retention. For negatively charged membranes, it has been reported that electrostatic repulsion significantly enhances the retention of negatively charged organic compounds (Banks et al., 2020; Yoon and Lueptow, 2005).

It is important to consider the quality of the inlet water, including its composition and the presence of suspended solids, and initial concentration of the contaminant to be removed (Tang et al., 2006), as these factors can significantly impact the performance of the process (Banks et al., 2020). This is due to the fact that these factors can lead to fouling, which it is the obstruction of the pores of the membrane (Taheran et al., 2016). In certain instances, initial fouling can create a gel layer on the surface of the membrane, which may improve removal performance (Nghiem et al., 2010; Taheran et al., 2016). However, more fouled the membrane becomes, a greater decrease in permeate flux is expected. There are several methods for cleaning a fouled membrane, but it has been observed that a membrane may only remain operational for up to 2 – 5 years (Yadav et al., 2022), in the most optimistic scenario.

For the reasons stated above, a membrane separation process is suitable for removing MPs. However, this process has some disadvantages, including high operational costs and the need for pre- and post-treatment of the fluxes (Yadav et al., 2022). The inlet water must be clear and free of turbidity, requiring pre-treatment. Additionally, the concentrate flux cannot be disposed, due to its high concentration of MPs, necessitating in post-treatment (Taheran et al., 2016; Yadav et al., 2022). In terms of costs, they are high for cleaning and replacing the modules due to their short lifespan and the energy required to reach the operating pressure (Taheran et al., 2016; Zhang et al., 2022). The required operating pressure varies between RO and NF. The former requires an operating pressure of 60 – 80 bars, while the latter requires 2 – 20 bars (Yadav et al., 2022). However, the choice between the two should not be taken lightly. RO and NF have different depuration capabilities. RO is more effective in depuration and the reuse of the permeate is a matter of fact (Flores et al., 2013; Kimura et al., 2003; Takagi et al., 2011). On the other hand, NF is more selective in removal and has better performance in removing short chain PFAS (Banks et al., 2020; Steinle-Darling and Reinhard, 2008). However, it has a more rapid decline of the permeate flux (Appleman et al., 2013; Kaya et al., 2011). Further studies are required to better understand the behaviour of these processes, the formation mechanism of fouling, and its influence on depuration performance (Simon et al., 2009; Taheran et al., 2016; Yüksel et al., 2013). These factors will enable better control of operating parameters and reduce costs on an industrial scale.

### 1.4.2 Destructive technology

Destructive technologies, as remediation processes, can break down contaminants into less toxic products in a large number of scenarios (Olatunde et al., 2020). Examples of destructive technologies, that have been successful in degrading MPs (in particular: PFOS and PFOA) include direct photolysis, photochemical oxidation, photocatalytic oxidation, sonodegradation, and electrochemical oxidation. These technologies have achieved removal efficiencies between 60% and 100% (Ahmed et al., 2020; Song et al., 2012; Yadav et al., 2022).

One of the most promising technologies is the photocatalytic oxidation. This process needs a light source, an oxidant and a catalyst (Banks et al., 2020; Olatunde et al., 2020). It has been shown that heterogeneous photocatalysts with nanoparticle modified $TiO_2$, e.g. UV/Fe-$TiO_2$ and UV/Cu-$TiO_2$, have a high potential to achieve PFOA removal, up to 90% (Banks et al., 2020; Olatunde et al., 2020). The UV wavelength tested was of 254 nm, in an aqueous solution with a pH of 5 (Olatunde et al., 2020). This, and several other studies, have shown the promise of this process. However, the design parameters, such as the characteristics of the aqueous stream (e.g. pH and dissolved oxygen concentration), the light source, and the type of catalyst used, still require further understanding (Gole et al., 2018; Hu et al., 2018; Lee et al., 2016).

Sonodegradation is another advanced method for removing MPs from aqueous systems (Im et al., 2015, 2014, 2013). This treatment uses ultrasound to produce cavitation, with sound waves ranging from 20 – 1000 kHz. However, this method requires high energy consumption (Chu et al., 2017; Joseph et al., 2009) and can result in an increase in temperature and pressure in the reactor (Yadav et al., 2022). The investigations of this process typically occur in lab-scale reactors using a synthetic polluted matrix. PFAS removal is high under various operating conditions, with removal values reaching up to 90-95% (Campbell et al., 2009; Vecitis et al., 2010). However, the results of the degradation are affected by the water quality conditions. For instance, the PFAS removal is significant higher under acidic conditions and, at the same time, if the pH level becomes neutral or basic, the removal process is slightly inhibited (Cheng et al., 2008; Lee et al., 2016). However, other studies focus on the degradation rate of PFAS, which is enhanced by a high concentration of salt and the contaminant itself (Meegoda et al., 2020). This evidence suggests that this technology is promising when combined with membrane processes. As previously discussed, the concentrate flux of a membrane process is rich in salt and contaminants, making its disposal difficult to handle. Sonodegradation could be applied to this type of flux to address the issue (Yadav et al., 2022). Nevertheless, the operating parameters of sonodegradation, such as power, frequency, chemistry of the solution, pH, and presence of organic matter, are still under investigation. These parameters can be combined in various ways to achieve a higher degree of depuration (Banks et al., 2020; Yadav et al., 2022).

Due to the specific operating environments required and associated capital, operating and maintenance costs, these technologies have not yet been widely adopted on a larger and industrial scale (Fang et al., 2021). However, with the right investment and support, these technologies have the potential to revolutionize the industry.

### 1.4.3 Adsorption process

The process of adsorption involves the transfer of one or more constituents from the liquid phase to another phase, typically solid. The substance that is removed from the liquid phase is known as the adsorbate, while the phase on which the adsorbate accumulates, whether solid, liquid or gas, is called the adsorbent (Metcalf & Eddy, Inc, 2006).

In wastewater purification, activated carbons (ACs) are commonly used as the adsorbent material in its solid phase. The process for the preparation of ACs involves producing a solid product called char or biochar from organic material or biomass through pyrolysis. In this process, the material is exposed to high temperatures in an oxygen-deficient atmosphere, typically not exceeding 700°C, to prevent combustion. In the second phase, the solid material is activated by being brought into contact with an oxidizing gas, typically nitrogen, water vapor or carbon dioxide, at temperatures ranging from 800-900°C (Liu et al., 2015). This process allows for the formation of a highly porous structure, resulting in carbons with a high specific surface area. The pores of the material are typically classified into three categories: macropores, which are larger than 25 nm, mesopores, which range from 1 to 25 nm, and micropores, which are smaller than 1 nm (Metcalf & Eddy, Inc, 2006). After analyzing the obtained material, two main categories are generally distinguished: powder activated carbon (PAC), with a size of no less than 0.074 mm, and granular activated carbon (GAC), with a size of more than 0.1 mm. The surface properties of activated carbon vary depending on the treatment conditions and the characteristics of the organic material used (Bhatnagar et al., 2013; Metcalf & Eddy, Inc, 2006).

ACs is commonly used in an adsorption process, but it can wear out over time as the pollutants saturate its pores, causing the process to become less efficient. However, there are techniques available to regenerate the saturated activated carbon and restore its adsorptive capacity. It is important to note that the activated carbon will lose its initial adsorptive capacity after undergoing these techniques.

The adsorption process with ACs takes place in four main steps (Dabrowski, 2001; Metcalf & Eddy, Inc, 2006):

1. transportation within the solution (external diffusion): the substances to be adsorbed, present in the liquid phase to be purified, move towards the stagnant liquid film surrounding the surface of the adsorbent material.

2. transport by diffusion within the liquid film (internal diffusion): the substances of interest diffuse through the stagnant liquid film until they reach the pores of the adsorbent material.

3. transport inside the pores (surface diffusion): the substances to be adsorbed are transported by diffusive mechanisms within the pores of the adsorbent material.

4. adsorption: the substances that need to be adsorbed bind to the adsorbent material at the active adsorption sites.

As this process occurs in a sequence of phases, the slowest kinetics determine the limiting phase. If the diffusion mechanism is the limiting factor, it is referred to as physical adsorption (Ateia et al.,

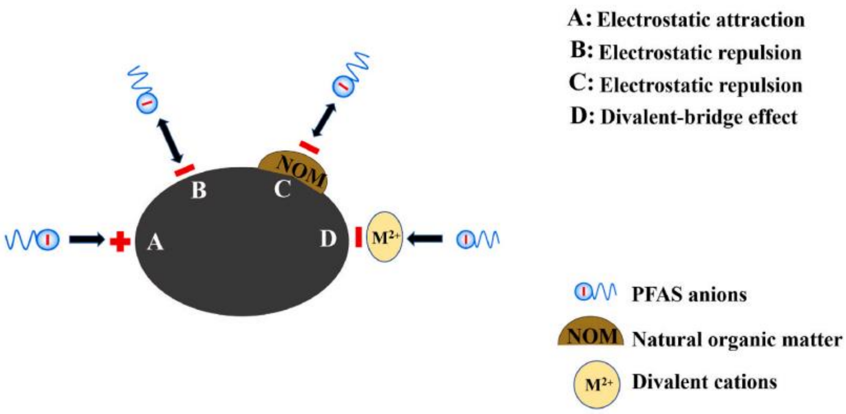


*Figure 8. PFAS adsorption: schematization of electrostatic attraction, repulsion and divalent-bridge effect (Lei et al., 2023).*

2019). In this case, the dominant forces are electrostatic and water-repellent interactions (Chandler, 2005; Lei et al., 2023). Alternatively, if the diffusive mechanisms have faster kinetics than the adsorption phase, it is referred to as chemical adsorption. In this case, the dominant forces may be ion exchange and ligand exchange (Wang et al., 2012, 2017). In each case, the forces at play in this sequence are various, e.g. Coulomb force, dipole-dipole interactions, Van der Waals forces, electrostatic attraction and repulsion, hydrogen bond formation (Lei et al., 2023). This evidence shows that it is difficult to distinguish between chemical and physical adsorption. The process is said to reach thermodynamic equilibrium when the adsorption rate equals the desorption rate. In this condition, the capacity of the activated carbon is exhausted.

The theoretical adsorption capacity of an activated carbon with respect to a given contaminant can be assessed by means of experimental tests consisting of the determination of adsorption isotherms and adsorption kinetics (Dabrowski, 2001). The influencing factors for obtaining the two experimental data are:

- concentration of the substance to be adsorbed.
- characteristics of the substance to be adsorbed, such as solubility, molecular weight, polarity, and molecular structure.
- the process temperature.

Isotherm tests involve placing a specific amount of activated carbon in contact with an aqueous matrix containing varying concentrations of the pollutant to be removed, at a fixed temperature and contact time.

On the other hand, adsorption kinetics testing follows a similar process, but with two key differences: the contact time varies, and the aqueous test matrix always contains the same concentration of contaminant to be adsorbed.

Several studies have been conducted on the application of this process to remove MPs (Gutkoski et al., 2024). Most of these, use synthetic wastewater to focus the research on the optimization of the process.

The adsorption process is highly effective in removing PCs and PFAS. Regarding PCs, the results indicate that removal values can often reach values between 70 – 95 % (Baccar et al., 2012; Husein et al., 2019; Jodeh et al., 2016; Mondal et al., 2020). It is important to note that the tested biomaterials exhibit a dependence on their characteristics, such as adsorption capacity and adsorption rate (Hasan et al., 2013; Mansouri et al., 2021).

In some studies, the use of biochar instead of commercial activated carbons resulted in increased removal of antibiotic substances (Peiris et al., 2017; Wang and Wang, 2019). In both cases, ACs or biochar are the most promising technologies for removing MPs since these substances are not significantly removed by conventional wastewater treatment.

Many studies have shown that the characteristics of wastewater, such as pH, temperature, and preparation conditions, can affect the adsorption of contaminants (Patel et al., 2019). However, it is important to note that real-world conditions may differ, as wastewater often contains other substances that can interact with the target substances and inhibit their removal.

For instance, in relation to PFAS, a high concentration of inorganic compounds, such as chloride, sulfate, calcium, and lead, can create competition for adsorption sites among the anionic species (Du et al., 2015, 2014; Vu and Wu, 2022). In this scenario, the pH of the solution is crucial. It has been observed that as the pH increases, the surface of the adsorbent becomes more negatively charged (Du et al., 2015, 2014). PFAS are mostly negatively charged, and this condition of equal charge inhibits their adsorption. Therefore, an acidic condition is preferred for PFAS treatment with adsorption (Deng et al., 2015; Gao et al., 2017).

The evidence presented in the Figure 10 pertains not only to adsorption with ACs but also with other adsorbent materials. Figure 10 displays the distribution of removal efficiencies of different sorbents, while the kernel density estimation represents the probability distribution for the removal efficiency of each sorbent. Long-chain PFAS distributions are shown in red, and short-chain PFAS in blue. The removal efficiency of long-chain per- and polyfluoroalkyl substances (PFAS) is higher than that of short-chain PFAS across all sorbents (Smaili and Ng, 2023).

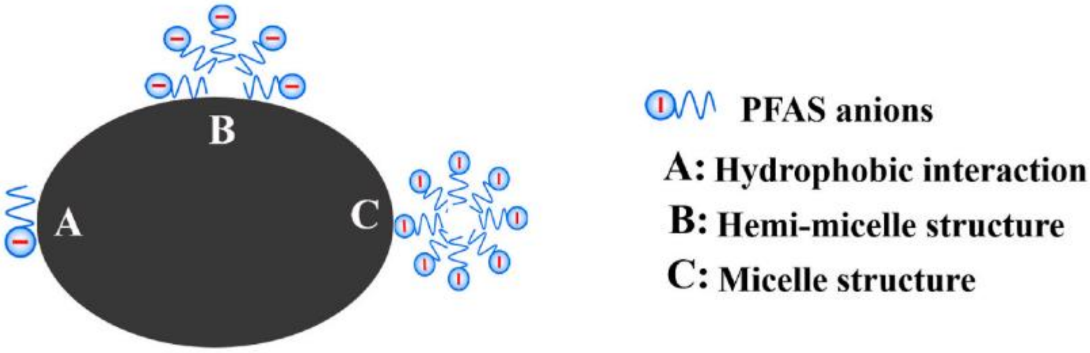


*Figure 9. PFAS adsorption: hydrophobic aggregation (Lei et al., 2023).*

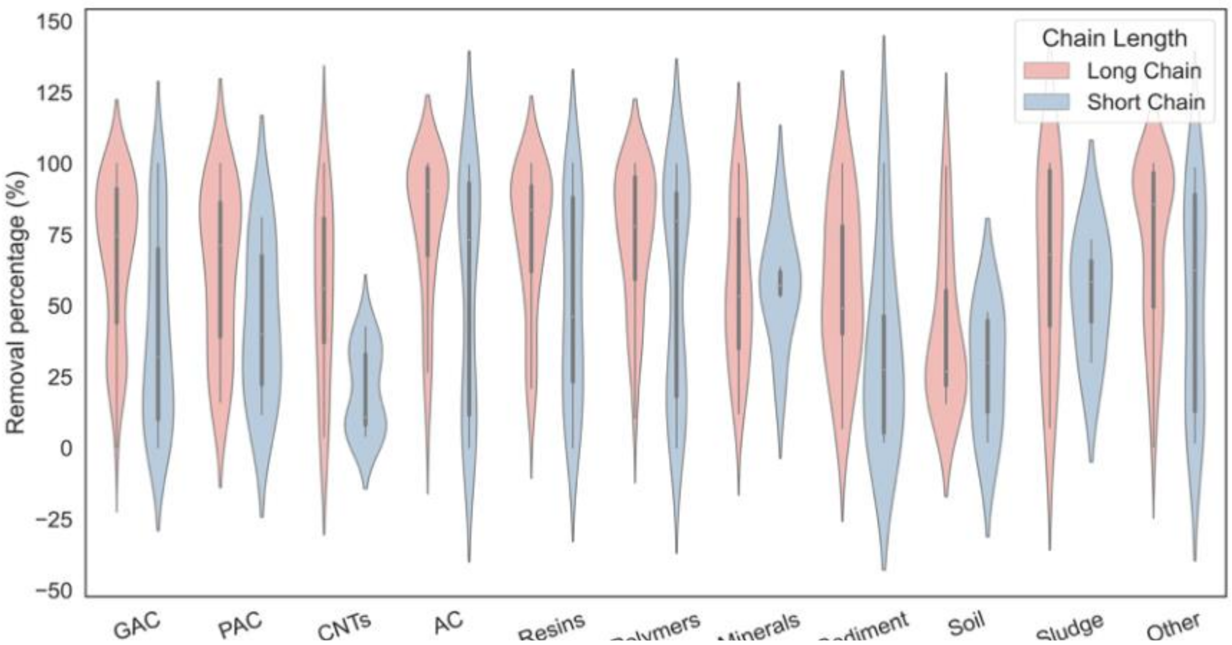


*Figure 10. Removal percentage of long-chain and short-chain PFAS across different sorbents (Smaili and Ng, 2023).*

In conclusion, there are several mechanisms to consider when removing MPs. Adsorption is considered the most effective technology due to its high efficiency, simple design, technological maturity, cost-effectiveness on an industrial scale, and versatility and adaptability in various cases. It can also be combined with other technologies (Gutkoski et al., 2024; Lei et al., 2023; Vecitis et al., 2009).

# 2. Goals of the project

This work is the outcome of a collaborative effort between “Alma Mater Studiorum - Università di Bologna” and “Universidade NOVA de Lisboa”, as part of the European project MAR2PROTECT. MAR2PROTECT will provide a holistic approach to prevent groundwater contamination resulting from the impacts of climate change and global change, using innovative technologies.

The main aim of this project is to develop an efficient and sustainable technology for the elimination of PFAS and PCs in the environment by means of advanced separation technologies, namely adsorption processes with carbon-based biomaterials. The use of carbon-based biomaterials is a potential solution for the removal of PFAS and PCs from aqueous systems due to their excellent properties, tunability and recyclability, an approach that is in line with the principles of the circular economy.

This was accomplished through a six-month research project at the laboratories of “Universidade NOVA de Lisboa”. The study began with the synthesis and characterisation of carbon-based biomaterials from *Juncus Maritimus*, *Phragmites Australis*, and *Coconut Shells*. The adsorbent material's behaviour was characterised concerning the removal of micropollutants, including:

- Diclofenac (Pharmaceutical Compound)
- Valsartan (Pharmaceutical Compound)
- PFOA, Perfluorooctanoic acid (PFAS family)
- PFBS, Perfluorobutanosulfonic acid (PFAS family)
- PFPeA, Perfluoro-n-pentanoic acid. (PFAS family)

# 3. Materials and methods

## 3.1 Preparation of Activated Carbons

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**Reagents**

Potassium carbonate, $K_2CO_3$ (purity > 98%, MERCK, made in Germany)
Zinc chloride, $ZnCl_2$ (purity > 98%, MERECK, made in Germany)
Deionized water (generation system of deionised water of FCT NOVA University of Lisbon)
Carbon dioxide, $CO_2$ (purity > 99.9%, liquid air, made in Portugal)
Nitrogen, $N_2$ (purity > 99.9%, liquid air, made in Portugal)
*Juncus Maritimus* (made in Portugal)
*Phragmites Australis* (made in Portugal)
*Coconut Shells* (made in Brazil)

**Equipment**

Microbalance, Ohaus Discoveys
Heating oven, Heraeus.

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Activated carbon, also known as biochar, is defined as a carbon-rich, porous solid. It is produced through the thermal decomposition of biomass in a reactor with limited gas flow, low oxygen supply, and moderate temperatures (usually between 350-700°C).

In this work, the preparation of the ACs follows a procedure in two different cases, since there are two types of activation:

- Chemical Activation
- Physical Activation

Both types of activation are part of a process called 'slow pyrolysis' (Liu et al., 2015). The methodology used to prepare the carbon involved heating the biomass without oxygen. This was necessary to avoid combustion, which would have burned the biomass and turned it into ash. Instead, the process was pyrolysis, which converted the biomass into activated carbon. The pyrolysis process in question is referred to as 'slow', due to the gradual increase in temperature at a rate of approximately 5-7°C per minute, with a maximum temperature of 800°C.

The two types of activation differ in terms of biomass preparation and gas flux during the pyrolysis process. Chemical activation involves a constant flux of nitrogen (N2) and the addition of a chemical, either $K_2CO_3$ for *Juncus Maritimus* and *Phragmites Australis* or $ZnCl_2$ for *Coconut Shells*. Physical activation, on the other hand, involves a change in gas flux during the phase of constant temperature, from nitrogen ($N_2$) to carbon dioxide ($CO_2$), and does not require any sample preparation.

The biomasses, used in this work to prepare ACs, were:

- *Juncus Maritimus* (JM)
- *Phragmites Australis* (PA)
- *Coconut Shells* (CS).

### 3.1.1 The biomasses

*Juncus Maritimus* is a rush species that grows on coastlines. It is widespread in Europe and Central Asia as it prefers sandy, wet, and salty soils. *Phragmites Australis* is a flowering plant species that appears to be native to Eurasia but has spread worldwide. It grows in dense reeds near swamps and humid areas, on the banks of lakes, ponds, ditches, and in wet uncultivated soils. It can tolerate a moderate level of salinity. As these plants are widely distributed worldwide, the aim is to collect pruning residues and use them to activate carbons, with the goal of waste-to-product conversion.

*Coconut shells* are a waste product of coconut commercialization. Due to their high consumption and robust properties, their disposal can be challenging using certain technologies. Regarding the other two types of biomasses, the researchers discovered that collecting and utilising these residuals could be significant in the production of biomaterials, in line with the principles of a circular economy.

*Figure 11. Juncus Maritimus (Google Images).*

*Figure 12. Phragmites Australis (Google Images).*

### 3.1.2 Physical activation

The equipment used for the physical activation, referring to the Figure 13, was:

1. Oven.
2. $N_2$ cylinder.
3. $CO_2$ cylinder.
4. Thermocouple.
5. Temperature controller.
6. Gas inlet.
7. Gas Outlet.
8. Reactor.
9. Flow controller.

*Figure 13. Equipment for the Physical Activation.*

The physical activation of this biomass followed the schematization of Figure 14. The biomass sample weighed 6 grams and underwent three main steps: first, slow pyrolysis was carried out by applying an increasing temperature from ambient to 800°C for 2 hours and 40 minutes under a constant nitrogen flux; second, activation was performed by maintaining the samples at 800°C for 2 hours while changing the gas flux from nitrogen to carbon dioxide; finally, the sample was cooled down under nitrogen flux, following a similar temperature decrease as in step one. The carbon was prepared using a three-step process and then passed through a sieve to obtain grains up to 150 µmeters. These activated carbons did not require any further treatment.

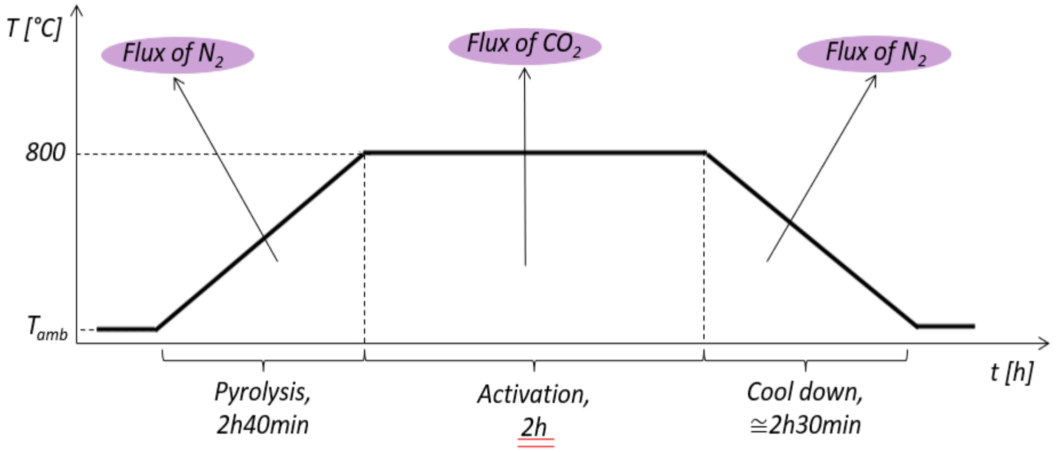

*Figure 14. Time versus Temperature graph for the physical activation of the biomaterials.*

The acronym for the carbon formulated from *Juncus Maritimus* biomass is “**JM-2h-$CO_2$**”.

### 3.1.3 Chemical Activation

The equipment used for the chemical activation, referring to the Figure 15, was:

1. Oven.
2. $N_2$ cylinder.
3. Flow controller.
4. Thermocouple.
5. Temperature controller.
6. Gas inlet.
7. Gas Outlet.
8. Reactor.

*Figure 15. Equipment for Chemical Activation.*

As mentioned above, chemical activation requires a chemical agent, in addition to the mentioned biomasses. In this work, the biomasses of *Juncus Maritimus* and *Phragmites Australis* were mixed, separately, with Potassium Carbonate ($K_2CO_3$) in a weight ratio of 1:3 (1 g of biomass and 3 g of $K_2CO_3$). Meanwhile, the *Coconut Shells* biomass was mixed with Zinc Chloride ($ZnCl_2$) in a weight ratio of 1:4 (1 g of biomass and 4 g of $ZnCl_2$). The biomass and chemicals were mixed in a mortar (see Figure 16) and then placed in the reactor.

Figure 16. The mortar used to mix the biomass and the chemical agent.

The chemical activation of this biomass follows the schematization of Figure 17. The process is similar to the physical activation process, but with some differences in the three steps. Firstly, slow pyrolysis in a nitrogen atmosphere was carried out, as in the physical activation process. Secondly, the activation process lasted for one hour instead of two, and there was no change in the gas flux. Finally, the sample was cooled down as in the first step. The ACs produced from the chemical activation process required further treatment due to the alkaline nature of the chemicals used. This was necessary to achieve a neutral pH condition.

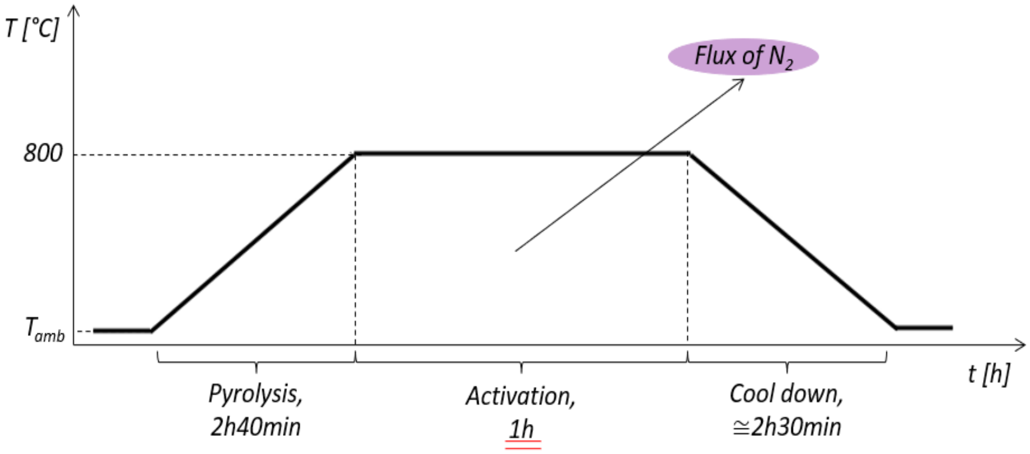

Figure 17. Time versus Temperature graph for the chemical activation of the biomaterials.

The equipment used, referring to the Figure 18, was:

1. Mixture of carbon and water
2. Vacuum flask
3. pH measurement
4. Deionized water

After several filtrations under vacuum, the carbons should have a pH similar to that of the deionized water used. As the ACs was wet, it needed to be dried in an oven. Following this, it was passed through a sieve to obtain grains up to 150 µmeters.

*Figure 18. Instrumentation for the treatment of the carbon obtained by chemical activation.*

The acronym for the carbon formulated from *Juncus Maritimus* biomass is "**JM-$K_2CO_3$**".

The acronym for the carbon formulated from *Phragmites Australis* biomass is "**PA-$K_2CO_3$**".

The acronym for the carbon formulated from *Coconut Shells* biomass is "**CS-$ZnCl_2$**".

## 3.2 Adsorption Equilibrium Assay

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**Reagents**

MilliQ water (generation system of MilliQ water of FCT NOVA University of Lisbon)
Perfluorooctanoic acid (PFOA), CAS: 335-67-1 (purity > 96%, ACROS ORGANICS, made in USA)
Perfluorobutanosulfonic acid (PFBS), CAS: 375-73-5 (purity > 98%, TCI, made in Japan)
Perfluoro-n-pentanoic acid (PFPeA), CAS: 2706-90-3 (Apollo Scientific, made in UK)
Perfluorooctane Sulphonic Acid (PFOS), CAS: 13973-14-3 (Apollo Scientific, made in UK)
Diclofenac Sodium Salt, CAS: 15307-79-6 (purity > 98%, TCI, made in Japan)
Valsartan, CAS: 137862-53-4 (purity > 98%, TCI, made in Japan)
Methanol grade LC/MS (Honeywell, made in France)
Acetonitrile grade LC/MS (Carlo Erba)
Formic Acid LC/MS (LiChropur$^{TM}$)
Ammonium format (Sigma-Aldrich)
Methanol (purity > 99.9%, Honeywell, made in France)
Activated Carbons discussed in the previous paragraph (FCT NOVA University of Lisbon)

**Equipment**

Microbalance, Ohaus Discoveys
pH-meter, Oakton, Series 2100
Centrifuge, VWR MEGA STAR 600R
Magnetic Stirrer, MULTISTIRRER, Velp Scientifica
Immersion Thermostat, Julabo
LC Agilent 1200 Series with binary bomb / MS Agilent 6130B Simple quadrupole with font ESI
Double beam spectrophotometer, VWR UV-6300PC
Digital Shaking Incubator 221 DS

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Since the PFAS family comprehend more than 5,000 substances, only three were selected PFAS: Perfluorooctanoic acid (PFOA), Perfluorobutanosulfonic acid (PFBS), and Perfluoro-n-pentanoic acid (PFPeA).

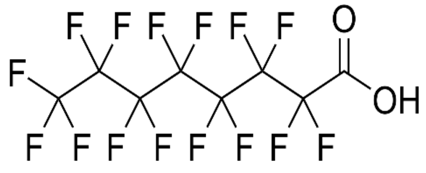

Figure 19. PFOA.

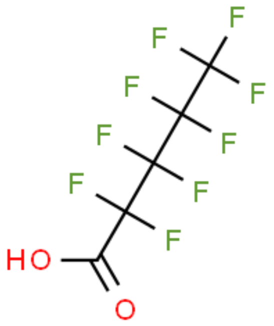

Figure 20. PFPeA.

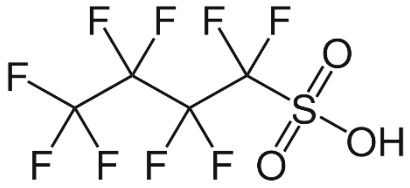

Figure 21. PFBS.

Pharmaceutical compounds, such as PFAS, comprise a large group of substances. The selected compounds for this study were diclofenac and valsartan, as they are commonly used in disease treatments.

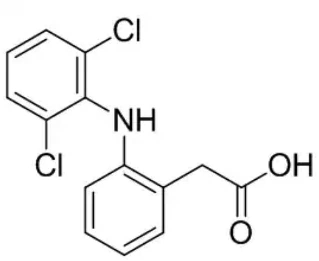

*Figure 22. Diclofenac.*

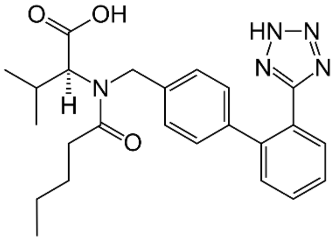

*Figure 23. Valsartan.*

The adsorption equilibrium study is carried out trough isothermal assays for the selected substances involving different combinations between MPs and ACs (see Table 2).

*Table 2. Combination between the Activated Carbons and the PCs selected.*

| MPs | | ACs | MPs | | ACs | MPs | | ACs |
|---|---|---|---|---|---|---|---|---|
| Diclofenac | x | CS-$ZnCl_2$ | Valsartan | x | JM-$K_2CO_3$ | PFOA | x | CS-$ZnCl_2$ |
| Diclofenac | x | JM-2h-$CO_2$ | Valsartan | x | PA-$K_2CO_3$ | PFPeA | x | CS-$ZnCl_2$ |
| Diclofenac | x | JM-$K_2CO_3$ | Valsartan | x | CS-$ZnCl_2$ | PFBS | x | CS-$ZnCl_2$ |
| Diclofenac | x | PA-$K_2CO_3$ | | | | | | |

The experimental test employed different materials for the equipment depending on the substance being assessed. This was necessary due to the varying behaviour and properties of the substances. To prevent PFAS from attaching to the equipment, which tends to happen with glass, all the falcons, syringes, and other equipment were made of polypropylene. The flasks used for the assay of PCs were made of glass and were dark to prevent any interaction between light and the PCs, as they are not affected by materials, but they can react with light.

The isothermal assay involves exposing ACs to varying concentrations of synthetic polluted matrix at specific contact times. For PCs, a contact time of 24 hours was used, with concentrations ranging from 25 to 300 $\frac{mg}{L}$ for diclofenac and 25 to 100 $\frac{mg}{L}$ for valsartan. For PFAS, the contact time was 48 hours and the concentration tested ranged from 25 to 1000 $\frac{mg}{L}$ for each compound. The amount of ACs was 0,005 g for the tests on PCs and was 0,010 g for the tests on PFAS.

Beyond these differences, the quantity of synthetic polluted matrix in contact with ACs were 25 mL for each combination (see Table 2). The synthetic aqueous matrix was agitated with ACs for the required contact time at ambient pressure and temperature ($P = 1\ atm$; $T = 25 \pm 2\ °C$ ).

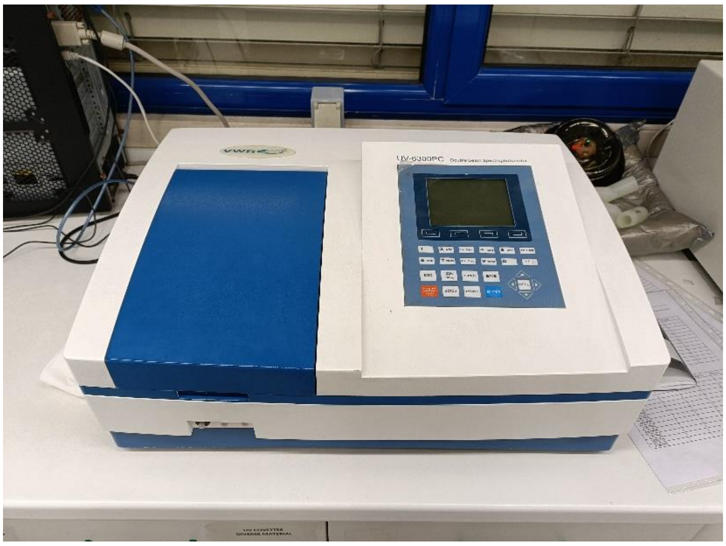

Figure 24. UV/VS equipment.

After the contact time, the liquid had to be free of any suspended solids. To achieve this, each sample was filtered using the appropriate material for the substance being assessed.

Once the samples were ready, they were analysed using the appropriate equipment. The final concentrations for PCs were measured using spectrometry techniques with double beam spectrophotometer UV/VS equipment (see Figure 24). The equipment measures the wavelength of the sample. Observing a specific value of wavelength is important to quantify the concentration of the PCs:

- for diclofenac was 275 nm
- for valsartan was 250 nm

The final concentrations of PFAS were measured using liquid chromatography – mass spectrometry technique (LC/MS). Prior to instrumental analysis, the samples needed to be diluted and an internal standard of PFOS was added. Once this step was completed, the samples were analysed.

The pH of each sample was measured before and after the contact time using appropriate equipment (see Figure 25). The aim of this measurement was to measure the pH variation before and after the adsorption process and its correlation with the percentage of micropollutant removal.

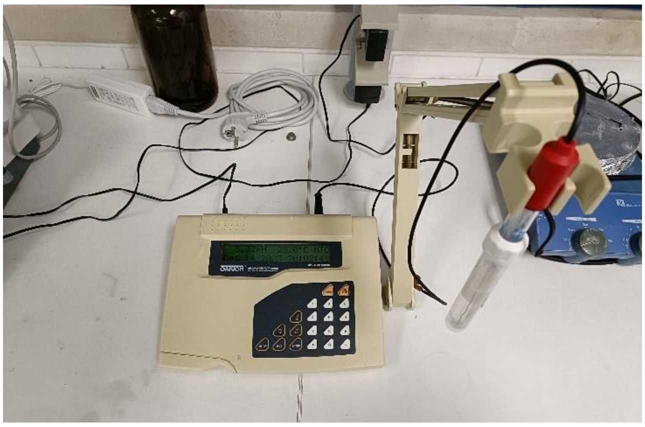

Figure 25. pH-meter.

# 4. Results and discussion

## 4.1 Biomaterials

The biomaterial analysis involves elementary analysis, thermogravimetric analysis (TGA), and textural parameter analysis.

The elementary analysis is used for describing the content of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) of the biomaterial prepared in this work. The results are shown in Table 3.

The results indicate that *Coconut Shell* biomass has a higher carbon content compared to the other biomasses. This could be due to the fact that *Juncus Maritimus* and *Phragmites Australis* are primarily composed of cellulose and hemicellulose, while the other biomass is composed of fibres and carbohydrates. Additional evidence can be found in the nitrogen content of *Juncus Maritimus* activated through physical means. This type of activation appears to increase the nitrogen content compared to chemical activation. Furthermore, biomaterials made from *Coconut Shells* and *Phragmites Australis* do not contain sulphur, while *Juncus Maritimus* does.

The Thermogravimetric Analysis (TGA) enables the determination of the weight loss of biomaterial as the temperature increases. This analysis is crucial in understanding the behaviour of the biomaterial with respect to decomposition and stability. Additionally, it can aid in the regeneration of saturated carbon. Through thermal destruction, the adsorbate will volatilise, and the adsorbent can regenerate its adsorption capacity.

The test for this work were conducted over a temperature range of 30°C to 905°C, with a temperature increase of 5°C per minute. The curves for the prepared biomaterials are displayed in Figure 36 in Annex I. All four carbons experienced a weight loss of approximately 15 – 20 %, except for the one prepared with Coconut Shell, which exhibited better (around 10 – 15 % of weight loss).

*Table 3. Elementary analysis of the activated carbons prepared in this work.*

| Biomaterial | Activation | C [%] | H [%] | N [%] | S [%] |
|---|---|---|---|---|---|
| CS-$ZnCl_2$ | Chemical | 80,62 | 1,22 | 0,85 | <L.Q |
| JM-$K_2CO_3$ | Chemical | 55,38 | 1,98 | 0,70 | 0,09 |
| JM-2h-$CO_2$ | Physical | 56,92 | 1,64 | 2,33 | 0,39 |
| PA-$K_2CO_3$ | Chemical | 44,73 | 1,75 | 0,48 | <L.Q |

The structural characterization is useful for determining the surface area and porosity of biomaterials. This allows for the characterization of ACs as microporous, mesoporous, or macroporous. The results for the biomaterials prepared in this study are shown in Table 4.

*Table 4. Textural characterization of the activated carbons prepared in this work.*

| **Biomaterial** | **Activation** | **$S_{BET}$ [m$^2$/g]** | **$V_{total}$ [cm$^3$/g]** | **$V_{micro}$ [cm$^3$/g]** | **$V_{meso}$ [cm$^3$gg]** |
|---|---|---|---|---|---|
| CS-$ZnCl_2$ | Chemical | 1391,000 | 0,859 | 0,240 | 0,619 |
| JM-$K_2CO_3$ | Chemical | 1635,000 | 0,732 | 0,568 | 0,164 |
| JM-2h-$CO_2$ | Physical | 631,020 | 0,330 | 0,252 | 0,078 |
| PA-$K_2CO_3$ | Chemcal | 1422,000 | 0,692 | 0,503 | 0,189 |

The parameters are: (I) the apparent specific area, $S_{BET}$, (II) the total volume of the pores $V_{total}$, and (III) the volume of micropores and mesopores, respectively $V_{micro}$ and $V_{macro}$. As shown in the Table 4, the chemical activation results in a higher $S_{BET}$ compared to physical activation. The microporous activated carbon is obtained from *Juncus Maritimus* and *Phragmites Australis* biomasses, while the *Coconut Shell* biomaterials are classified as mesoporous. This difference in porosity can be attributed to the distinct structure of the biomasses, as previously mentioned.

## 4.2 Adsorption Equilibrium Studies

In this study, the adsorption equilibrium was evaluated using adsorption isotherms. The experimental data were modelled with both Langmuir and Freundlich models through the minimum of the least-squares method, and the best-fitting model was chosen through the highest determination coefficient, $R^2$.

The most commonly used isothermal model is the Freundlich, which is described by an analytical relationship (adapted from Metcalf & Eddy, Inc, 2006):

$$\frac{x}{m} = K_F \cdot C_e^{\frac{1}{n}}$$

where:

$\frac{x}{m} = q_e = \ mass\ of\ adsorbate\ per\ unit\ mass\ of\ adsorbent\ material, \frac{mass\ of\ adsorbate}{mass\ of\ adsorbent}\left[\frac{mg}{g}\right]$

$K_F = Freundlich\ capacity\ coefficient,\ \left[\left(\frac{mg/_g}{mg/_L}\right)^n\right]$

$C_e = concentration\ of\ the\ species\ of\ interest\ in\ solution\ at\ equilibrium,\ \left[\frac{mg}{L}\right]$

$\frac{1}{n} = Freundlich\ intensity\ coefficient, [-]$

This relationship can be rewritten in logarithmic form, as follows (Metcalf & Eddy, Inc, 2006):

$$log\left(\frac{x}{m}\right) = log(K_f) + \frac{1}{n} \cdot log(C_e)$$

For some toxic organic compounds, characteristic parameter values are tabulated by the main environmental protection agencies.

Alternatively, the Langmuir isotherm can be used. This model is based on the ideal monolayer adsorbed model (Dabrowski, 2001), which depends on the underlying assumptions (Metcalf & Eddy, Inc, 2006):

1. there is a fixed number of accessible adsorption sites on the surface of the adsorbent material, each with the same energy value.
2. the adsorption process is reversible.

Under these assumptions, the analytical relation describing the process is (adapted from Metcalf & Eddy, Inc, 2006):

$$\frac{x}{m} = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$$

where:

$$\frac{x}{m} = q_e = \text{ } mass\ of\ adsorbate\ per\ unit\ mass\ of\ adsorbent\ material, \frac{mass\ of\ adsorbate}{mass\ of\ adsorbent}\left[\frac{mg}{g}\right]$$

$$K_L = Languimuir\ constant, \left[\frac{L}{mg}\right]$$

$$q_{max} = adsorption\ capacity\ in\ the\ monolayer, \left[\frac{mg}{g}\right]$$

$$C_e = concentration\ of\ the\ species\ of\ interest\ in\ solution\ at\ equilibrium, \left[\frac{mg}{L}\right]$$

The fact that an experimental data set fits this law does not necessarily mean that the assumptions underlying the relationship are verified. The relationship can also be rewritten as (Metcalf & Eddy, Inc, 2006):

$$\frac{C_e}{({}^{x}/_{m})} = \frac{1}{q_{max} \cdot K_L} + \frac{1}{K_L} \cdot C_e$$

Both models were used to fit the data for PCs and PFAS: Table 5 provides the estimated parameters of Langmuir model, whereas Table 16 of Annex IV provides the Langmuir ones. This section will focus more on the Langmuir model as it was found to best fit the data of both MPs.

*Table 5. Estimated parameters of Langmuir isotherm model adjusted to the experimental data of MPs adsorption.*

| LANGMUIR MODEL PARAMETERS | | |
|---|---|---|
| **$q_{max}$ [mg/g]** | **$K_L$ [L/mg]** | **$R^2$** |
| | DICLOFENAC x CS-ZnCl2 | |
| 253,914 | 0,700 | 0,808 |
| | DICLOFENAC x JM-2h-CO2 | |
| 238,282 | 1,456 | 0,521 |
| | DICLOFENAC x JM-K2CO3 | |
| 268,793 | 2,520 | 0,694 |
| | DICLOFENAC x PA-K2CO3 | |
| 234,566 | 0,537 | 0,788 |
| | VALSARTAN x JM-K2CO3 | |
| 282,918 | 1,247 | 0,732 |
| | VALSARTAN x PA-K2CO3 | |
| 232,811 | 0,254 | 0,855 |

| | | |
|---|---|---|
| | VALSARTAN x CS-ZnCl2 | |
| 370,242 | 2,579 | 0,788 |
| | PFOA x CS-ZnCl2 | |
| 374,435 | 0,060 | 0,723 |
| | PFPeA x CS-ZnCl2 | |
| 183,964 | 0,009 | 0,987 |
| | PFBS x CS-ZnCl2 | |
| 292,271 | 0,008 | 0,895 |

The Langmuir model was found to provide a better representation of PFAS adsorption for several reasons. At low initial concentrations, the contaminant forms a monolayer on the homogeneous surface of the ACs (Wan et al., 2022; Yu et al., 2009), as evidenced by the isotherm graphs in Table 6. These graphs show a focus on another aspect: for PFOA and PFBS, there is a curvature for low concentrations that changes behavior at higher concentrations. However, for PFPeA, this evidence does not occur. For accuracy, changes in curvature occur at concentrations ($C_e$) higher than 300 $\frac{mg}{L}$ for PFOA and 600 $\frac{mg}{L}$ for PFBS. The evidence is explicit when the model is linearized (see Annex III).

Other researchers have also noted the occurrence of this phenomenon, which is linked to the structure of PFAS molecules. It is important to note that PFAS can have either long or short chains, with PFOA and PFBS having long chains and PFPeA having a shorter chain (Gagliano, 2020). During the sorption process, long-chain PFAS accumulates in a thin film near the AC surface due to both electrostatic and hydrophobic effects. A rapid coagulation of PFAS occurs with the positively charged surface of ACs, resulting in the formation of hemi-micelles. As the concentration of PFAS increases, the ACs surface becomes gradually coated by hemi-micelles. Once the monolayer on the ACs surface is saturated, a second layer of PFAS forms (Chen et al., 2011; Gagliano, 2020). The bilayer's presence enhances the hydrophobic interaction of PFAS, resulting in a change in the curvature of the isotherm graphs.

Table 6. Langmuir isotherm model graphs: PFAS adsorption.

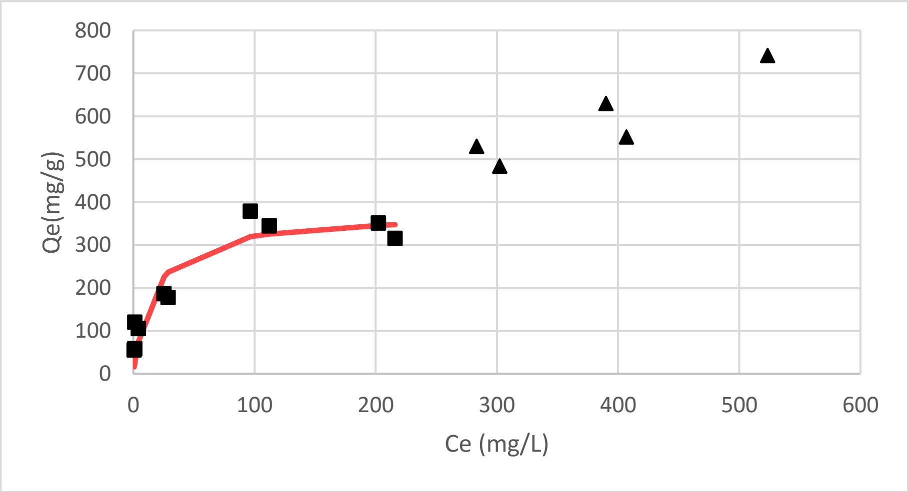

Figure 26. Adsorption equilibrium curve of PFOA x CS-ZnCl$_2$; contact time = 48 h; solution volume = 25mL (Langmuir).

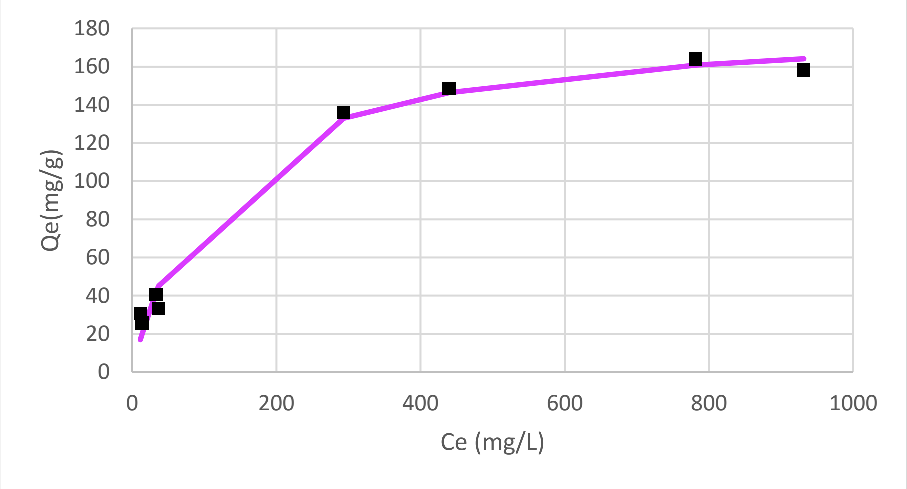

*Figure 27. Adsorption equilibrium curve of PFPeA x CS-ZnCl$_2$; contact time = 48 h; solution volume = 25mL (Langmuir)*

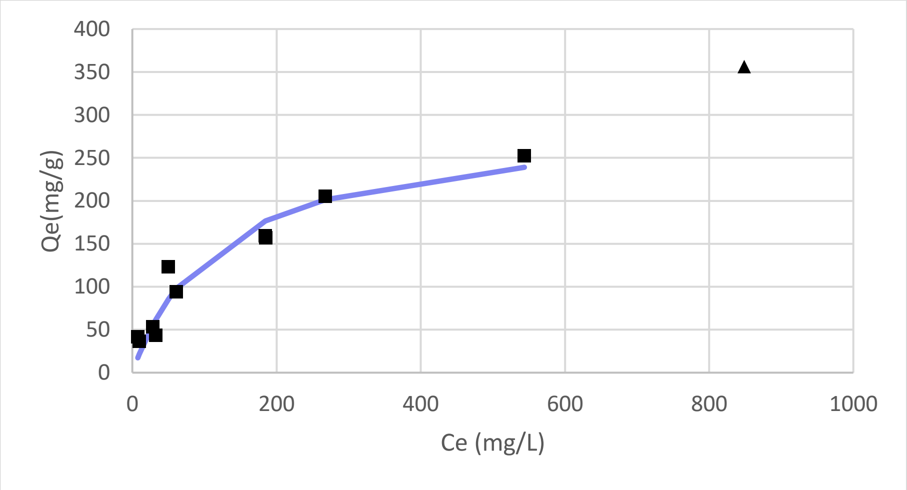

*Figure 28. Adsorption equilibrium curve of PFBS x CS-ZnCl$_2$; contact time = 48 h; solution volume = 25mL (Langmuir).*

This change leads to an enhanced adsorption capacity value (Park et al., 2020), albeit distorted, because is due to the contaminant over the biomaterial.

This occurrence is commonly referred to as the 'surfactant effect'. The experimental data shows a high adsorption capacity for high initial concentrations of PFOA and PFBS. The disparity in adsorption capacity between low and high concentrations, coupled with the data fitting, indicates that the adsorption capacity at high concentrations is distorted due to the more pronounced surfactant effect. PFPeA does not exhibit a surfactant effect, noticeable both in curve and linearized Langmuir isotherm.

Freundlich isotherm tends to undercompensate the isotherm curvature, assuming an exponential distribution. This assumption means that the model considers infinite the number of available sites of adsorption, that could be true for systems with low adsorbate concentrations (Kumar et al., 2019; Mokhati et al., 2022). If the initial concentration of the contaminant is high, this model could provide a good data fitting. This assumption is noticed by Park et al., 2020: observation suggests that the monolayer adsorption occurs, but when the initial concentration of PFAS increase, the hydrophobic interaction creates the surfactant effect. The experimental data shown that the adsorbent / adsorbate system reached saturation. For that reason, the Langmuir model best-fit the experimental data, since in its hypothesis there is the fixed number of adsorption sites (Ateia et al., 2019; Du et al., 2015; Gagliano, 2020; Zhang et al., 2023).

*Table 7. Removal efficiency for adsorption batch experiment on PFAS.*

| | PFAS | |
|---|---|---|
| **$C_0$ [mg/L]** | **$C_e$ [mg/L]** | **removal [%]** |
| | PFOA x CS-ZnCl2 | |
| 913,52 | 523,46 | 42,70 |
| 569,26 | 406,97 | 28,51 |
| 730,74 | 390,23 | 46,60 |
| 524,98 | 302,46 | 42,39 |
| 475,02 | 283,5 | 40,32 |
| 382,93 | 215,98 | 43,60 |
| 317,07 | 202,43 | 36,16 |
| 232,56 | 112,19 | 51,76 |
| 267,44 | 96,68 | 63,85 |
| 98,39 | 28,79 | 70,74 |
| 101,61 | 25,32 | 75,08 |
| 50,09 | 4,18 | 91,66 |
| 49,91 | 1,28 | 97,44 |
| 25,61 | 1,22 | 95,24 |
| 24,39 | 0,75 | 96,92 |
| | PFPeA x CS-ZnCl2 | |
| 837,75 | 931,61 | -11,20 |
| 766,40 | 781,25 | -1,94 |
| 519,64 | 439,43 | 15,44 |
| 328,25 | 293,44 | 10,60 |
| 54,78 | 36,70 | 33,01 |
| 45,22 | 33,27 | 26,43 |
| 27,31 | 13,62 | 50,12 |
| 22,69 | 11,44 | 49,59 |
| | PFBS x CS-ZnCl2 | |
| 989,74 | 848,85 | 14,23 |
| 575,11 | 543,76 | 5,45 |
| 325,41 | 267,85 | 17,69 |
| 269,94 | 185,20 | 31,39 |
| 230,06 | 184,24 | 19,92 |
| 110,45 | 61,31 | 44,49 |

| | | |
|---|---|---|
| 89,55 | 50,17 | 43,98 |
| 50,02 | 32,64 | 34,74 |
| 49,98 | 28,66 | 42,66 |
| 25,09 | 9,72 | 61,25 |
| 24,91 | 7,62 | 69,41 |

Although the molecular structure of PFAS could potentially affect the accuracy of the adsorption capacity measurement, the experimental data presented in Table 7 demonstrates significant removal of both PFOA and PFBS. The results show that for PFOA, removal rates can exceed 90%, while for PFBS, removal rates can reach up to 70%. These values are observed when the initial PFAS concentration is up to 50 $\frac{mg}{L}$. For more concentrated solutions, the removal rate is lower. The saturation of AC particles may be due to the quantity of ACs used in the batch systems, which means that they are no longer able to adsorb additional substances. In contrast, PFPeA exhibits unstable adsorption, with a low adsorption capacity and a removal rate of no more than 50%, even at low initial concentrations. These results are consistent with other studies that have focused on the removal of PFAS and have linked the adsorption to the type of activated carbon used. It has been observed that the efficiency of removal is affected by the molecular structure of the pollutant. For larger molecules, mesoporous or macroporous carbons are preferred over microporous carbons. On the other hand, microporous carbons are preferred for smaller molecules as mesoporous carbons allow for competitive adsorption mechanisms between small molecules, larger molecules, and organic matter (Appleman et al., 2013; Du et al., 2014; McCleaf et al., 2017). The reason why PFOA and PFBS have better results than PFPeA could be explained by the mesoporous structure of the *Coconut Shells* carbon (see Table 4).

The experimental data includes information on the pH of the solution before and after the adsorption process. As PFAS are acidic, the initial pH ranged from 2 to 4 depending on the pollutant concentration. The ACs prepared did not significantly modify the pH value after treatment. Therefore, the pH values are not reported in this work.

*Table 8. Langmuir isotherm model graphs: diclofenac adsorption.*

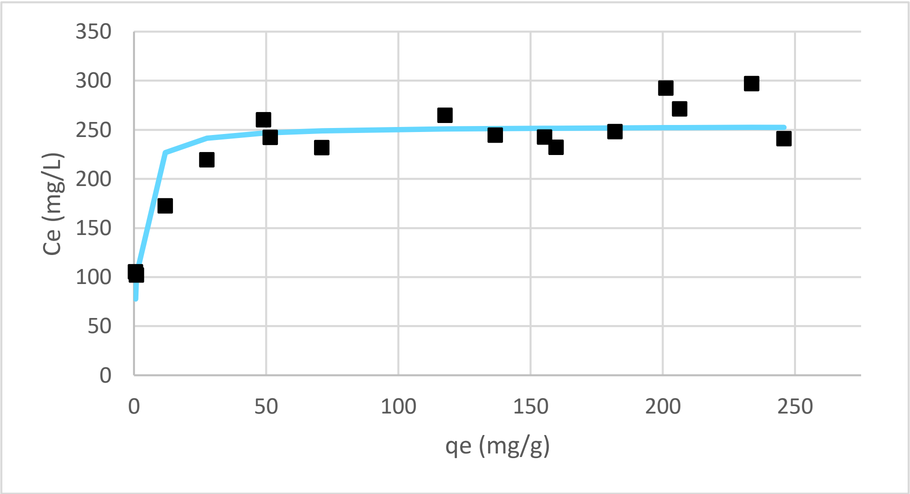

*Figure 29. Adsorption equilibrium curve of DCF x CS-ZnCl$_2$; contact time = 24 h; solution volume = 25mL (Langmuir).*

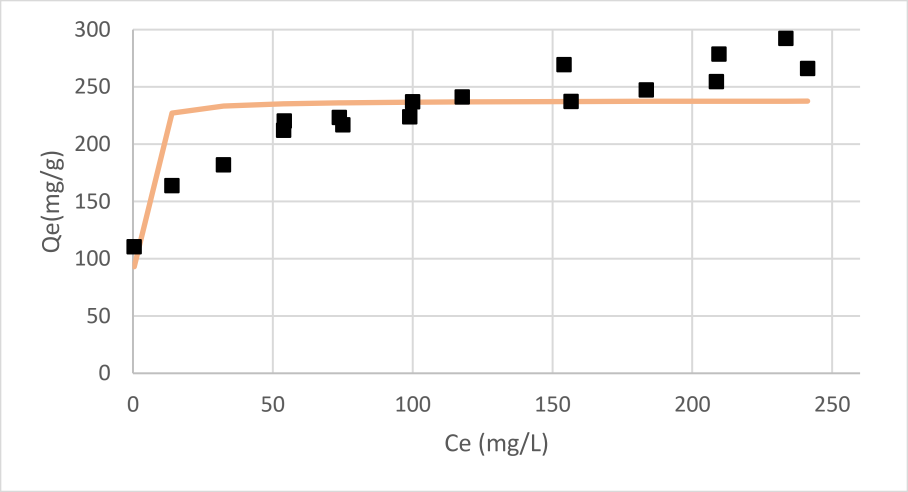

*Figure 30.Adsorption equilibrium curve of DCF JM-2h-$CO_2$; contact time = 24 h; solution volume = 25mL (Langmuir).*

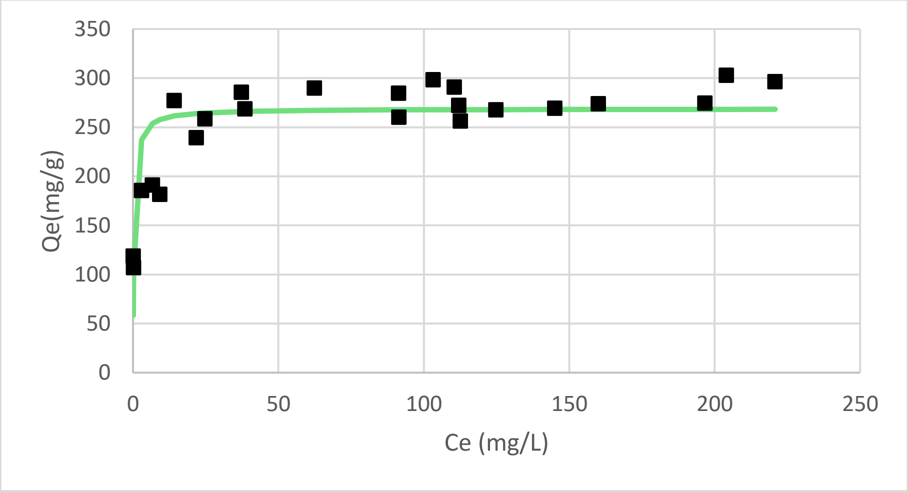

*Figure 31. Adsorption equilibrium curve of DCF x JM-$K_2CO_3$; contact time = 24 h; solution volume = 25mL (Langmuir).*

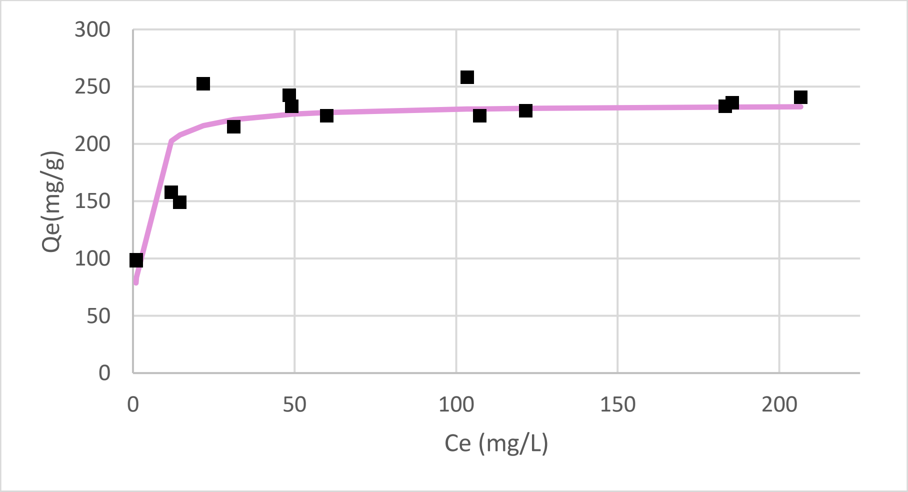

*Figure 32. Adsorption equilibrium curve of DCF x PA-$K_2CO_3$; contact time = 24 h; solution volume = 25mL (Langmuir).*

The experimental data in Table 8 and Table 12 of Annex II and the graphs in Table 9 and Table 13 of Annex II of adsorption of diclofenac and valsartan, respectively, show a monolayer adsorption, according with the hypothesis of the Langmuir model. The curvature observed in the graphs (see Table 8 and Table 9 indicates that the behavior aligns with the theoretical model, with a clear plateau visible after a certain value. This observation is further supported by the linearization of the model, which suggests that the adsorption process is limited to a specific number of active adsorption sites.

Upon observation of the data for diclofenac, it was found that all four carbons tested exhibited a good adsorption capacity. Notably, the JM-$K_2CO_3$ carbon demonstrated a higher adsorption capacity compared to the other carbons tested. This result may be attributed to the textural characteristics of the carbon, which has a higher $S_{BET}$ and $V_{micro}$ compared to the others. However, the differences in experimental data for the four carbons were not significant. Although the JM-2h-$CO_2$ has a lower $S_{BET}$ than the other carbons, its efficiency is still comparable to those with higher $S_{BET}$.

*Table 9. Langmuir isotherm model graphs: valsartan adsorption.*

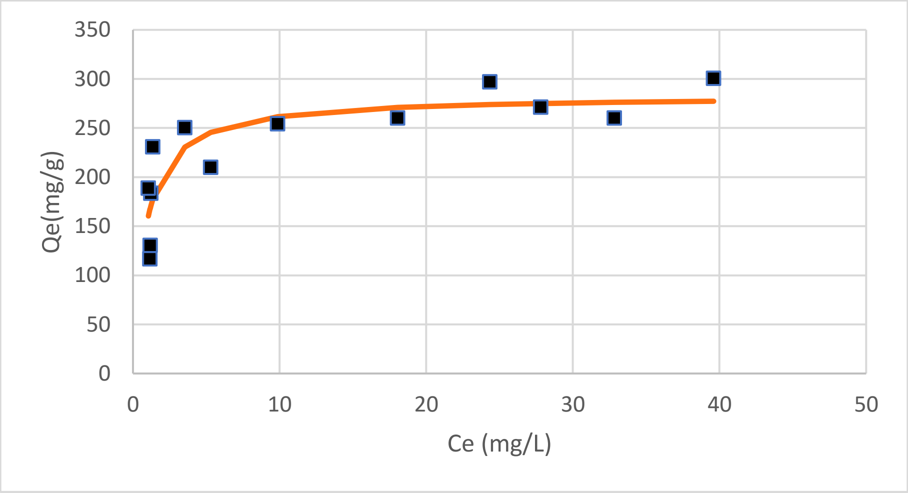

*Figure 33. Adsorption equilibrium curve of VLT x JM-$K_2CO_3$; contact time = 24 h; solution volume = 25mL (Langmuir).*

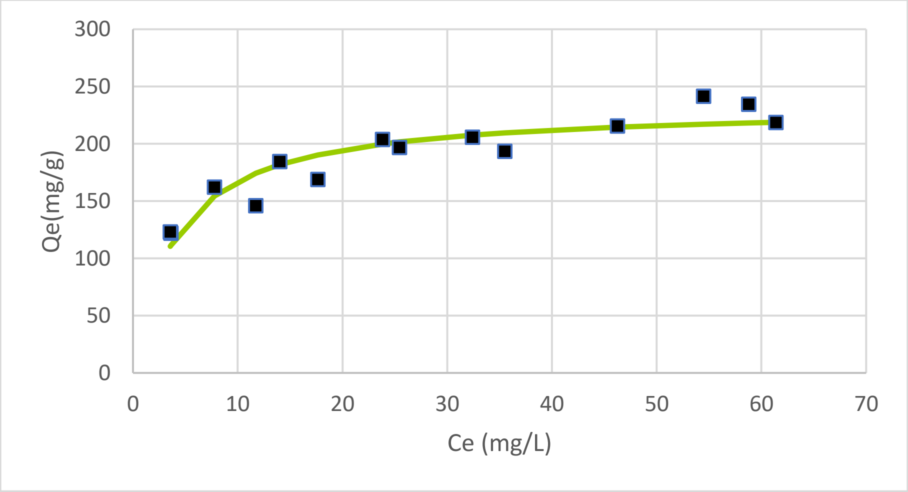

*Figure 34. Adsorption equilibrium curve of VLT x PA-$K_2CO_3$; contact time = 24 h; solution volume = 25mL (Langmuir).*

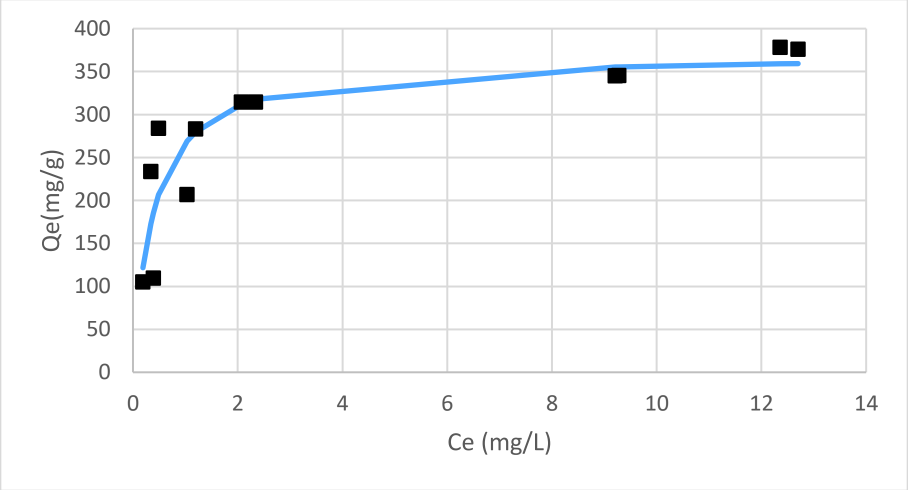

*Figure 35. Adsorption equilibrium curve of VLT x CS-ZnCl$_2$; contact time = 24 h; solution volume = 25mL (Langmuir).*

However, the experimental data for valsartan presents a different scenario. The CS-ZnCl$_2$ exhibits a significantly higher adsorption capacity compared to the other tested carbons. The variation between the three carbons tested for valsartan is in the $V_{meso}$, which is higher for the carbon that demonstrated better results. This suggests that the molecular structure of valsartan is more compatible with mesoporous carbons.

The removal efficiency of both PCs is high (see Table 10 and Table 11): both microporous carbons by chemical activation, PA-K$_2$CO$_3$ and JM-K$_2$CO$_3$, exhibit high removal efficiency for diclofenac, while mesoporous carbons such as CS-ZnCl$_2$ are better suited for removing valsartan. The results show that diclofenac can be easily removed with an efficiency higher than 75% when the initial concentration is under 50 $\frac{mg}{L}$. This means that diclofenac could be easily removed from low concentrated synthetic matrix by microporous carbon. Similarly, CS-ZnCl$_2$ can remove more than 85% of valsartan, even at high initial concentrations, confirming its affinity for mesoporous carbons.

*Table 10. Removal efficiency for adsorption batch experiment on diclofenac.*

| Pharmaceutical Compounds: Diclofenac | | |
|---|---|---|
| **$C_0$ [mg/L]** | **$C_e$ [mg/L]** | **removal [%]** |
| | DICLOFENAC x CS-ZnCl2 | |
| 294,52 | 245,83 | 16,53 |
| 294,52 | 233,66 | 20,66 |
| 266,15 | 206,40 | 22,45 |
| 266,15 | 201,18 | 24,41 |
| 235,50 | 181,94 | 22,74 |
| 208,19 | 159,68 | 23,30 |
| 208,19 | 155,35 | 25,38 |
| 190,10 | 136,67 | 28,11 |
| 171,03 | 117,64 | 31,22 |
| 120,92 | 71,02 | 41,27 |

| | | |
|---|---|---|
| 102,03 | 51,61 | 49,42 |
| 102,03 | 49,00 | 51,97 |
| 73,20 | 27,54 | 62,37 |
| 49,04 | 11,88 | 75,77 |
| 23,29 | 0,97 | 95,83 |
| 23,29 | 0,63 | 97,29 |
| | DICLOFENAC x JM-2h-CO2 | |
| 294,52 | 241,23 | 18,09 |
| 294,52 | 233,51 | 20,71 |
| 266,15 | 209,53 | 21,27 |
| 266,15 | 208,65 | 21,60 |
| 235,50 | 183,56 | 22,05 |
| 208,19 | 156,65 | 24,75 |
| 208,19 | 154,20 | 25,93 |
| 171,03 | 117,80 | 31,12 |
| 148,91 | 100,03 | 32,82 |
| 148,91 | 99,05 | 33,48 |
| 120,92 | 75,12 | 37,88 |
| 120,92 | 73,80 | 38,97 |
| 102,03 | 54,15 | 46,93 |
| 102,03 | 53,92 | 47,15 |
| 73,20 | 32,33 | 55,83 |
| 49,04 | 13,98 | 71,49 |
| 23,29 | 0,44 | 98,11 |
| | DICLOFENAC x JM-K2CO3 | |
| 284,86 | 220,80 | 22,49 |
| 265,78 | 204,00 | 23,25 |
| 258,16 | 196,65 | 23,83 |
| 219,13 | 159,98 | 26,99 |
| 201,92 | 145,01 | 28,18 |
| 186,08 | 124,81 | 32,93 |
| 168,90 | 112,53 | 33,38 |
| 172,40 | 112,07 | 34,99 |
| 172,40 | 110,49 | 35,91 |
| 168,90 | 103,22 | 38,89 |
| 145,61 | 91,43 | 37,21 |
| 155,68 | 91,35 | 41,32 |
| 121,52 | 62,36 | 48,68 |
| 100,38 | 38,54 | 61,61 |
| 100,38 | 37,30 | 62,84 |

| | | |
|---|---|---|
| 78,08 | 24,77 | 68,28 |
| 69,67 | 21,79 | 68,72 |
| 69,67 | 14,23 | 79,57 |
| 45,64 | 9,27 | 79,69 |
| 45,64 | 6,67 | 85,39 |
| 45,30 | 2,97 | 93,44 |
| 22,11 | 0,25 | 98,87 |
| 24,32 | 0,11 | 99,55 |
| DICLOFENAC x PA-K2CO3 | | |
| 258,16 | 206,63 | 19,96 |
| 235,55 | 185,45 | 21,27 |
| 235,55 | 183,26 | 22,20 |
| 172,40 | 121,52 | 29,51 |
| 155,68 | 107,39 | 31,02 |
| 155,68 | 103,41 | 33,58 |
| 110,07 | 60,00 | 45,49 |
| 100,38 | 49,23 | 50,96 |
| 100,38 | 48,37 | 51,82 |
| 78,08 | 31,23 | 60,00 |
| 78,08 | 21,79 | 72,09 |
| 45,30 | 14,52 | 67,95 |
| 45,30 | 11,85 | 73,84 |
| 22,11 | 1,03 | 95,34 |
| 22,11 | 0,94 | 95,75 |
| 44,73 | 1,03 | 97,70 |
| 62,40 | 0,49 | 99,21 |
| 23,65 | 0,39 | 98,35 |
| 53,72 | 0,34 | 99,37 |
| 23,65 | 0,19 | 99,20 |

*Table 11. Removal efficiency for adsorption batch experiment on valsartan.*

| Pharmaceutical Compounds: Valsartan | | |
|---|---|---|
| **$C_0$ [mg/L]** | **$C_e$ [mg/L]** | **removal [%]** |
| VALSARTAN x JM-K2CO3 | | |
| 100,60 | 39,60 | 60,64 |
| 89,96 | 32,84 | 63,50 |
| 82,31 | 27,81 | 66,21 |
| 89,96 | 24,33 | 72,95 |

| | | |
|---|---|---|
| 70,73 | 18,05 | 74,48 |
| 61,14 | 9,86 | 83,87 |
| 50,65 | 5,30 | 89,54 |
| 61,14 | 3,54 | 94,21 |
| 50,65 | 1,35 | 97,33 |
| 40,68 | 1,22 | 97,00 |
| 30,78 | 1,17 | 96,20 |
| 25,67 | 1,16 | 95,48 |
| 40,68 | 1,05 | 97,42 |
| VALSARTAN x PA-K2CO3 | | |
| 109,80 | 61,38 | 44,10 |
| 109,80 | 58,79 | 46,46 |
| 103,04 | 54,49 | 47,12 |
| 91,36 | 46,27 | 49,35 |
| 78,01 | 35,50 | 54,49 |
| 78,01 | 32,42 | 58,44 |
| 66,35 | 25,45 | 61,65 |
| 66,35 | 23,84 | 64,07 |
| 54,71 | 17,66 | 67,72 |
| 54,71 | 14,03 | 74,35 |
| 43,56 | 11,73 | 73,07 |
| 43,56 | 7,78 | 82,14 |
| 28,43 | 3,62 | 87,27 |
| 28,43 | 3,56 | 87,48 |
| VALSARTAN x CS-ZnCl2 | | |
| 91,02 | 12,70 | 86,05 |
| 91,02 | 12,36 | 86,42 |
| 82,37 | 9,28 | 88,73 |
| 82,37 | 9,21 | 88,82 |
| 72,10 | 2,34 | 96,75 |
| 72,10 | 2,07 | 97,13 |
| 62,40 | 1,20 | 98,08 |
| 44,73 | 1,03 | 97,70 |
| 62,40 | 0,49 | 99,21 |
| 23,65 | 0,39 | 98,35 |
| 53,72 | 0,34 | 99,37 |
| 23,65 | 0,19 | 99,20 |

# 5. Conclusions and future perspective

The experimental project was executed to understand the potential of biomaterials in wastewater treatment from a circular economy perspective. Additionally, these biomaterials underwent testing in an adsorption process to remove micropollutants.

Biomaterials offer a potential eco-friendly solution for capturing micropollutants such as PFOA, PFPeA, PFBS, diclofenac, and valsartan. These micropollutants are present in varying concentrations in both civil and industrial wastewater. Additionally, the presence of PFAS has been documented, and their contamination is a significant concern.

To achieve this objective, four ACs were prepared using different techniques. The characterization of these biomaterials showed that chemical activation yields higher $S_{BET}$ values than physical activation. This textural parameter is directly proportional to the total pore volume of these materials.

It should be noted that the characterization of biomaterials does not always accurately predict their behaviour during an adsorption process. Although JM-2h-$CO_2$ exhibited a lower $S_{BET}$, it still demonstrated a good adsorption capacity.

The batch experiments were conducted to improve the understanding of the operating conditions of an adsorption process. The results indicate that the tested PCs are more stable in the adsorption process than PFAS. However, PFAS have unique properties that make them more difficult to treat than PCs. These findings suggest the need for further studies on PFAS, while also highlighting the importance of investigating adsorption on PCs. In future studies, the adsorption of a mixture of pharmaceuticals on a lab-scale column with the tested ACs could yield promising results.

Another task should investigate the PFAS removal with activated carbon. This would allow for further investigation of the removal process and the removal efficiency. As previously mentioned, the surfactant effect of PFAS can lead to distorted values of the adsorption capacity. This phenomenon requires further study, particularly in the concentration range where it occurs, to gain a better understanding of the adsorption process of PFAS with activated carbons, in addition to the relation of their molecular structure. Such an approach could reveal additional aspects of PFAS adsorption.

Furthermore, it is recommended that the regeneration of activated carbons be investigated for both future works on PFAS and PCs. This regeneration was preliminarily assessed by TGA.

# 6. Annex and notes

## Annex I: Thermogravimetric Analysis (TGA) for the Activated Carbons

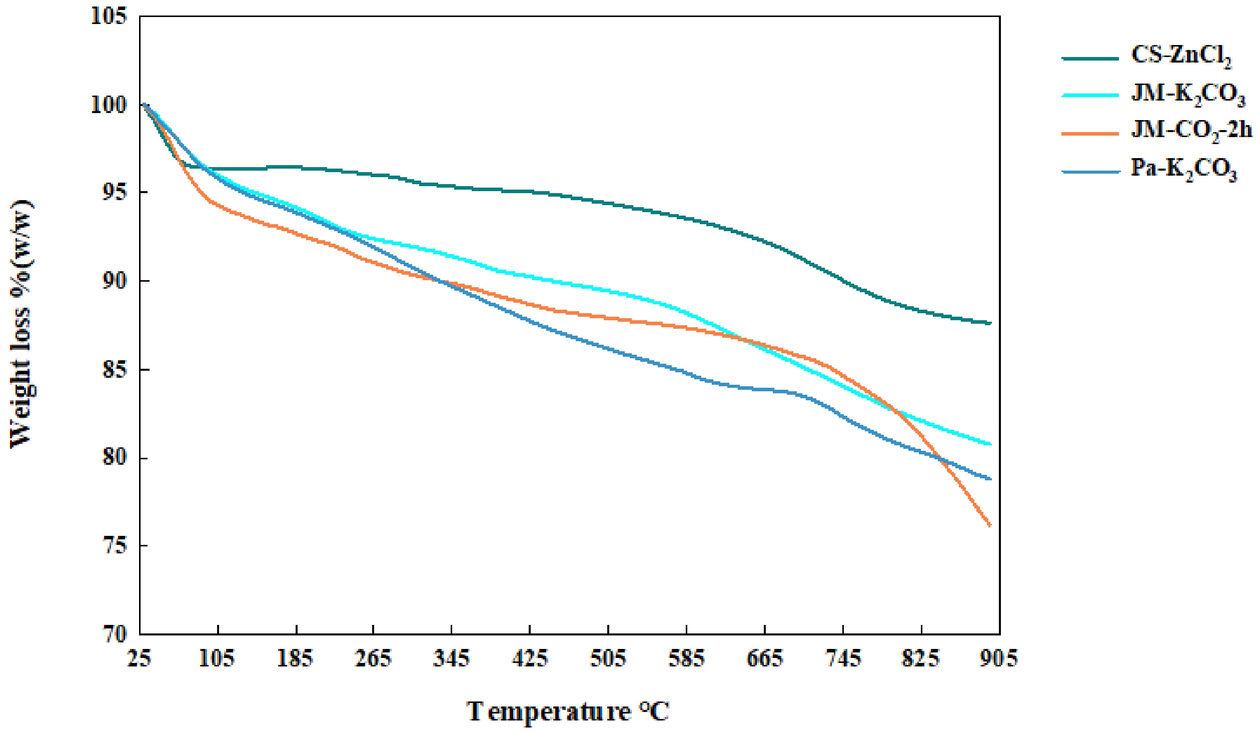

*Figure 36. TGA for the biomaterials prepared in this work.*

# Annex II: Langmuir model: correlation for the isotherm graphs

*Table 12. Parameters of Langmuir isotherm model adjusted to the experimental data of diclofenac adsorption.*

| Pharmaceutical Compounds: Diclofenac | | |
|---|---|---|
| LANGMUIR MODEL | | |
| **$C_e$ [mg/L]** | **$q_e$ [mg/g]** | **$q_{eth}$[mg/g]** |
| DICLOFENAC x CS-ZnCl2 | | |
| 245,83 | 241,00 | 252,45 |
| 233,66 | 297,14 | 252,37 |
| 206,40 | 271,59 | 252,17 |
| 201,18 | 292,65 | 252,12 |
| 181,94 | 248,40 | 251,93 |
| 159,68 | 232,29 | 251,66 |
| 155,35 | 242,80 | 251,60 |
| 136,67 | 244,64 | 251,29 |
| 117,64 | 264,85 | 250,87 |
| 71,02 | 231,91 | 248,90 |
| 51,61 | 242,40 | 247,07 |
| 49,00 | 260,45 | 246,72 |
| 27,54 | 219,52 | 241,39 |
| 11,88 | 172,65 | 226,65 |
| 0,97 | 102,35 | 102,65 |
| 0,63 | 105,49 | 77,68 |
| DICLOFENAC x JM-2h-CO2 | | |
| 241,23 | 265,90 | 237,61 |
| 233,51 | 292,19 | 237,58 |
| 209,53 | 278,61 | 237,50 |
| 208,65 | 254,40 | 237,50 |
| 183,56 | 247,30 | 237,39 |
| 156,65 | 237,28 | 237,24 |
| 154,20 | 269,41 | 237,22 |
| 117,80 | 241,10 | 236,90 |
| 100,03 | 236,79 | 236,66 |
| 99,05 | 223,78 | 236,64 |
| 75,12 | 216,89 | 236,12 |
| 73,80 | 223,11 | 236,08 |
| 54,15 | 220,03 | 235,30 |
| 53,92 | 212,12 | 235,28 |
| 32,33 | 181,77 | 233,32 |

| | | |
|---|---|---|
| 13,98 | 163,81 | 227,12 |
| 0,44 | 110,26 | 93,04 |
| DICLOFENAC x JM-K2CO3 | | |
| 220,80 | 296,60 | 268,31 |
| 204,00 | 302,85 | 268,27 |
| 196,65 | 274,61 | 268,25 |
| 159,98 | 273,84 | 268,13 |
| 145,01 | 269,47 | 268,06 |
| 124,81 | 267,79 | 267,94 |
| 112,53 | 256,25 | 267,85 |
| 112,07 | 272,24 | 267,84 |
| 110,49 | 290,90 | 267,83 |
| 103,22 | 298,56 | 267,76 |
| 91,43 | 260,45 | 267,63 |
| 91,35 | 284,67 | 267,63 |
| 62,36 | 290,04 | 267,09 |
| 38,54 | 268,87 | 266,05 |
| 37,30 | 285,73 | 265,96 |
| 24,77 | 258,79 | 264,55 |
| 21,79 | 239,40 | 263,99 |
| 14,23 | 277,19 | 261,50 |
| 9,27 | 181,87 | 257,76 |
| 6,67 | 191,05 | 253,70 |
| 2,97 | 185,65 | 237,11 |
| 0,25 | 107,13 | 103,88 |
| 0,11 | 118,67 | 58,33 |
| DICLOFENAC x PA-K2CO3 | | |
| 206,63 | 240,79 | 232,47 |
| 185,45 | 235,90 | 232,23 |
| 183,26 | 233,02 | 232,21 |
| 121,52 | 229,16 | 231,02 |
| 107,39 | 224,41 | 230,57 |
| 103,41 | 258,26 | 230,41 |
| 60,00 | 224,69 | 227,50 |
| 49,23 | 232,92 | 226,01 |
| 48,37 | 242,60 | 225,87 |
| 31,23 | 214,90 | 221,36 |
| 21,79 | 252,20 | 216,09 |
| 14,52 | 148,85 | 207,89 |
| 11,85 | 157,78 | 202,70 |

| | | |
|---|---|---|
| 1,03 | 98,52 | 83,51 |
| 0,94 | 97,84 | 78,66 |

*Table 13. Parameters of Langmuir isotherm model adjusted to the experimental data of valsartan adsorption.*

| Pharmaceutical Compounds: Valsartan | | |
|---|---|---|
| LANGMUIR MODEL | | |
| **$C_e$ [mg/L]** | **$q_e$ [mg/g]** | **$q_{eth}$[mg/g]** |
| VALSARTAN x JM-K2CO3 | | |
| 39,60 | 300,79 | 277,30 |
| 32,84 | 260,12 | 276,18 |
| 27,81 | 271,44 | 274,99 |
| 24,33 | 297,22 | 273,89 |
| 18,05 | 260,24 | 270,89 |
| 9,86 | 254,36 | 261,64 |
| 5,30 | 209,98 | 245,74 |
| 3,54 | 250,45 | 230,68 |
| 1,35 | 230,83 | 177,50 |
| 1,22 | 183,71 | 170,73 |
| 1,17 | 130,55 | 167,88 |
| 1,16 | 116,92 | 167,30 |
| 1,05 | 188,72 | 160,43 |
| VALSARTAN x PA-K2CO3 | | |
| 61,38 | 218,51 | 218,77 |
| 58,79 | 234,43 | 218,19 |
| 54,49 | 241,33 | 217,11 |
| 46,27 | 215,53 | 214,54 |
| 35,50 | 193,21 | 209,55 |
| 32,42 | 205,74 | 207,58 |
| 25,45 | 196,64 | 201,60 |
| 23,84 | 203,61 | 199,79 |
| 17,66 | 168,68 | 190,34 |
| 14,03 | 184,53 | 181,77 |
| 11,73 | 145,72 | 174,27 |
| 7,78 | 162,04 | 154,55 |
| 3,62 | 121,89 | 111,48 |
| 3,56 | 122,88 | 110,51 |

| | | |
|---|---|---|
| VALSARTAN x CS-ZnCl2 | | |
| 12,70 | 375,81 | 359,27 |
| 12,36 | 378,17 | 358,98 |
| 9,28 | 345,43 | 355,39 |
| 9,21 | 345,11 | 355,28 |
| 2,34 | 314,23 | 317,61 |
| 2,07 | 314,31 | 311,83 |
| 1,20 | 283,30 | 279,82 |
| 1,03 | 206,90 | 268,98 |
| 0,49 | 283,95 | 206,68 |
| 0,39 | 109,70 | 185,65 |
| 0,34 | 233,73 | 172,97 |
| 0,19 | 105,08 | 121,75 |

*Table 14. Parameters of Langmuir isotherm model adjusted to the experimental data of PFAS adsorption.*

| PFAS | | |
|---|---|---|
| LANGMUIR MODEL | | |
| **$C_e$ [mg/L]** | **$q_e$ [mg/g]** | **$q_{eth[}$mg/g]** |
| PFOA x CS-ZnCl2 | | |
| 523,46 | 742,14 | -- |
| 406,97 | 552,35 | -- |
| 390,23 | 630,52 | -- |
| 302,46 | 484,18 | -- |
| 283,5 | 530,63 | -- |
| 215,98 | 316,08 | 347,51 |
| 202,43 | 351,37 | 345,85 |
| 112,19 | 344,52 | 325,84 |
| 96,68 | 379,50 | 319,19 |
| 28,79 | 178,03 | 236,81 |
| 25,32 | 186,71 | 225,45 |
| 4,18 | 106,06 | 74,84 |
| 1,28 | 120,61 | 26,61 |
| 1,22 | 58,85 | 25,45 |
| 0,75 | 56,13 | 16,06 |
| PFPeA x CS-ZnCl2 | | |
| 931,61 | 158,30 | 164,08 |

| | | |
|---|---|---|
| 781,25 | 163,70 | 160,74 |
| 439,43 | 148,46 | 146,37 |
| 293,44 | 135,95 | 132,86 |
| 36,70 | 33,24 | 45,14 |
| 33,27 | 40,61 | 41,88 |
| 13,62 | 25,64 | 19,81 |
| 11,44 | 30,55 | 16,93 |
| | PFBS x CS-ZnCl2 | |
| 848,85 | 356,49 | -- |
| 543,76 | 252,96 | 284,17 |
| 267,85 | 205,37 | 214,73 |
| 185,20 | 157,29 | 176,74 |
| 184,24 | 159,62 | 176,22 |
| 61,31 | 93,90 | 81,88 |
| 50,17 | 123,35 | 69,50 |
| 32,64 | 43,40 | 48,03 |
| 28,66 | 53,36 | 42,78 |
| 9,72 | 36,74 | 15,57 |
| 7,62 | 41,78 | 12,31 |

# Annex III: Langmuir model: isotherms linearization for PFAS adsorption

*Table 15. Freundlich isotherm model graphs: PFAS adsorption.*

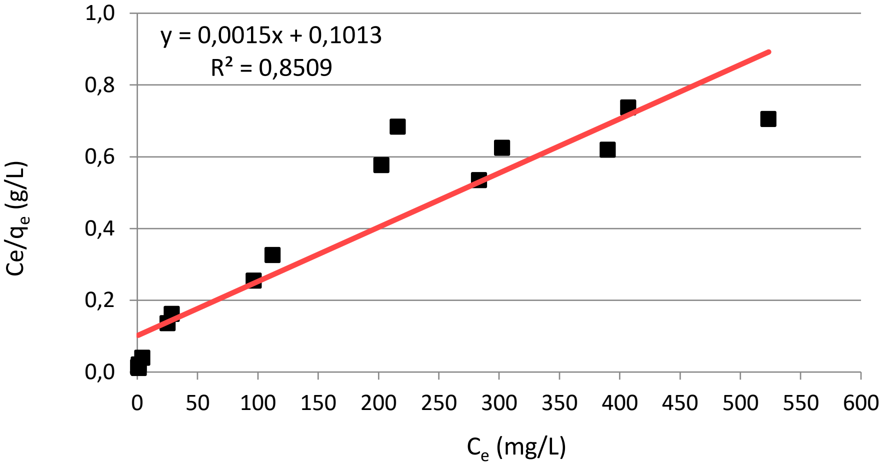

*Figure 37. Isotherm linearization of PFOA x CS-ZnCl2; contact time = 24 h; solution volume = 25mL (Langmuir).*

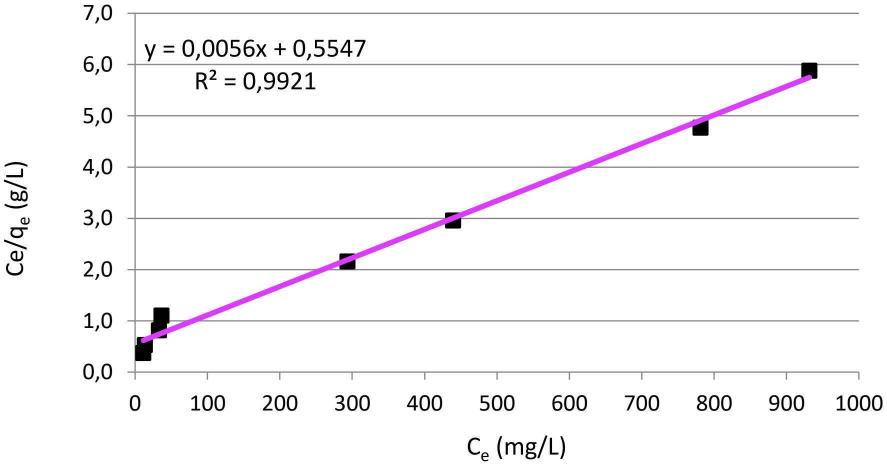

*Figure 38. Isotherm linearization of PFPeA x CS-ZnCl2; contact time = 24 h; solution volume = 25mL (Langmuir).*

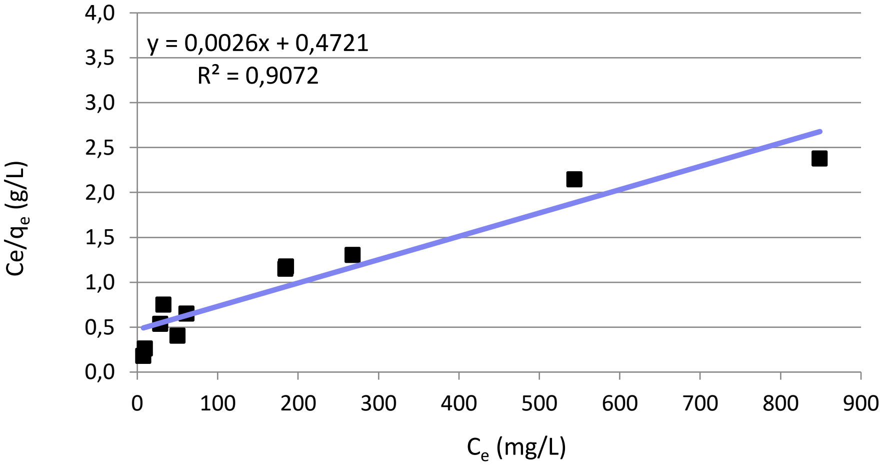

*Figure 39. Isotherm linearization of PFBS x CS-ZnCl2; contact time = 24 h; solution volume = 25mL (Langmuir).*

# Annex IV: Freundlich model: parameters of the equation

*Table 16. Estimated parameters of Freundlich isotherm model adjusted to the experimental data of MPs adsorption.*

| FREUNDLICH MODEL | | |
|---|---|---|
| **$K_F$** | **1/n** | **$R^2$** |
| | DICLOFENAC x CS-ZnCl2 | |
| 124,849 | 0,145 | 0,854 |
| | DICLOFENAC x JM-2h-CO2 | |
| 110,006 | 0,164 | 0,933 |
| | DICLOFENAC x JM-K2CO3 | |
| 165,403 | 0,112 | 0,828 |
| | DICLOFENAC x PA-K2CO3 | |
| 121,646 | 0,142 | 0,751 |
| | VALSARTAN x JM-K2CO3 | |
| 172,376 | 0,147 | 0,708 |
| | VALSARTAN x PA-K2CO3 | |
| 96,173 | 0,215 | 0,912 |
| | VALSARTAN x CS-ZnCl2 | |
| 238,248 | 0,187 | 0,730 |
| | PFOA x CS-ZnCl2 | |
| 42,315 | 0,438 | 0,931 |
| | PFPeA x CS-ZnCl2 | |
| 11,822 | 0,396 | 0,947 |
| | PFBS x CS-ZnCl2 | |
| 12,325 | 0,494 | 0,970 |

# Annex V: Freundlich model: correlation for the isotherm graphs

*Table 17. Parameters of Freundlich isotherm model adjusted to the experimental data of diclofenac adsorption.*

| Pharmaceutical Compounds: Diclofenac | | |
|---|---|---|
| FREUNDLICH MODEL | | |
| $C_e$ [mg/L] | $q_e$ [mg/g] | $q_{e,th}$ [mg/g] |
| DICLOFENAC x CS-ZnCl2 | | |
| 245,83 | 241,00 | 277,26 |
| 233,66 | 297,14 | 275,23 |
| 206,40 | 271,59 | 270,32 |
| 201,18 | 292,65 | 269,32 |
| 181,94 | 248,40 | 265,43 |
| 159,68 | 232,29 | 260,45 |
| 155,35 | 242,80 | 259,42 |
| 136,67 | 244,64 | 254,64 |
| 117,64 | 264,85 | 249,17 |
| 71,02 | 231,91 | 231,59 |
| 51,61 | 242,40 | 221,12 |
| 49,00 | 260,45 | 219,47 |
| 27,54 | 219,52 | 201,88 |
| 11,88 | 172,65 | 178,72 |
| 0,97 | 102,35 | 124,30 |
| 0,63 | 105,49 | 116,76 |
| DICLOFENAC x JM-2h-CO2 | | |
| 241,23 | 265,90 | 270,82 |
| 233,51 | 292,19 | 269,37 |
| 209,53 | 278,61 | 264,62 |
| 208,65 | 254,40 | 264,44 |
| 183,56 | 247,30 | 258,93 |
| 156,65 | 237,28 | 252,28 |
| 154,20 | 269,41 | 251,63 |
| 117,80 | 241,10 | 240,74 |
| 100,03 | 236,79 | 234,36 |
| 99,05 | 223,78 | 233,99 |
| 75,12 | 216,89 | 223,60 |
| 73,80 | 223,11 | 222,95 |
| 54,15 | 220,03 | 211,89 |
| 53,92 | 212,12 | 211,75 |
| 32,33 | 181,77 | 194,69 |

| | | |
|---|---|---|
| 13,98 | 163,81 | 169,64 |
| 0,44 | 110,26 | 96,13 |
| DICLOFENAC x JM-K2CO3 | | |
| 220,80 | 296,60 | 302,55 |
| 204,00 | 302,85 | 299,88 |
| 196,65 | 274,61 | 298,65 |
| 159,98 | 273,84 | 291,83 |
| 145,01 | 269,47 | 288,64 |
| 124,81 | 267,79 | 283,84 |
| 112,53 | 256,25 | 280,57 |
| 112,07 | 272,24 | 280,44 |
| 110,49 | 290,90 | 280,00 |
| 103,22 | 298,56 | 277,87 |
| 91,43 | 260,45 | 274,13 |
| 91,35 | 284,67 | 274,10 |
| 62,36 | 290,04 | 262,64 |
| 38,54 | 268,87 | 248,87 |
| 37,30 | 285,73 | 247,96 |
| 24,77 | 258,79 | 236,86 |
| 21,79 | 239,40 | 233,49 |
| 14,23 | 277,19 | 222,62 |
| 9,27 | 181,87 | 212,20 |
| 6,67 | 191,05 | 204,53 |
| 2,97 | 185,65 | 186,83 |
| 0,25 | 107,13 | 141,64 |
| 0,11 | 118,67 | 129,21 |
| DICLOFENAC x PA-K2CO3 | | |
| 206,63 | 240,79 | 258,93 |
| 185,45 | 235,90 | 254,99 |
| 183,26 | 233,02 | 254,56 |
| 121,52 | 229,16 | 240,17 |
| 107,39 | 224,41 | 236,00 |
| 103,41 | 258,26 | 234,74 |
| 60,00 | 224,69 | 217,31 |
| 49,23 | 232,92 | 211,30 |
| 48,37 | 242,60 | 210,78 |
| 31,23 | 214,90 | 198,10 |
| 21,79 | 252,20 | 188,25 |
| 14,52 | 148,85 | 177,73 |
| 11,85 | 157,78 | 172,69 |

| | | |
|---|---|---|
| 1,03 | 98,52 | 122,16 |

*Table 18. Parameters of Freundlich isotherm model adjusted to the experimental data of valsartan adsorption.*

| Pharmaceutical Compounds: Valsartan | | |
|---|---|---|
| FREUNDLICH MODEL | | |
| **$C_e$ [mg/L]** | **$q_e$ [mg/g]** | **$q_{e,th}$ [mg/g]** |
| VALSARTAN x JM-K2CO3 | | |
| 39,60 | 300,79 | 295,92 |
| 32,84 | 260,12 | 287,89 |
| 27,81 | 271,44 | 280,95 |
| 24,33 | 297,22 | 275,48 |
| 18,05 | 260,24 | 263,66 |
| 9,86 | 254,36 | 241,25 |
| 5,30 | 209,98 | 220,23 |
| 3,54 | 250,45 | 207,55 |
| 1,35 | 230,83 | 180,14 |
| 1,22 | 183,71 | 177,49 |
| 1,17 | 130,55 | 176,40 |
| 1,16 | 116,92 | 176,18 |
| 1,05 | 188,72 | 173,62 |
| VALSARTAN x PA-K2CO3 | | |
| 61,38 | 218,51 | 232,75 |
| 58,79 | 234,43 | 230,61 |
| 54,49 | 241,33 | 226,88 |
| 46,27 | 215,53 | 219,05 |
| 35,50 | 193,21 | 206,94 |
| 32,42 | 205,74 | 202,95 |
| 25,45 | 196,64 | 192,67 |
| 23,84 | 203,61 | 189,99 |
| 17,66 | 168,68 | 178,13 |
| 14,03 | 184,53 | 169,55 |
| 11,73 | 145,72 | 163,16 |
| 7,78 | 162,04 | 149,39 |
| 3,62 | 121,89 | 126,76 |
| 3,56 | 122,88 | 126,31 |
| VALSARTAN x CS-ZnCl2 | | |

| | | |
|---|---|---|
| 12,70 | 375,81 | 383,21 |
| 12,36 | 378,17 | 381,27 |
| 9,28 | 345,43 | 361,37 |
| 9,21 | 345,11 | 360,86 |
| 2,34 | 314,23 | 279,30 |
| 2,07 | 314,31 | 272,97 |
| 1,20 | 283,30 | 246,51 |
| 1,03 | 206,90 | 239,57 |
| 0,49 | 283,95 | 208,50 |
| 0,39 | 109,70 | 199,78 |
| 0,34 | 233,73 | 194,72 |
| 0,19 | 105,08 | 174,65 |

*Table 19. Parameters of Freundlich isotherm model adjusted to the experimental data of PFAS adsorption.*

| | PFAS | |
|---|---|---|
| | FREUNDLICH MODEL | |
| **$C_e$ [mg/L]** | **$q_e$ [mg/g]** | **$q_{e,th}$ [mg/g]** |
| | PFOA x CS-ZnCl2 | |
| 523,46 | 742,14 | 657,40 |
| 406,97 | 552,35 | 588,75 |
| 390,23 | 630,52 | 578,01 |
| 302,46 | 484,18 | 516,96 |
| 283,5 | 530,63 | 502,50 |
| 215,98 | 316,08 | 446,03 |
| 202,43 | 351,37 | 433,55 |
| 112,19 | 344,52 | 334,75 |
| 96,68 | 379,50 | 313,63 |
| 28,79 | 178,03 | 184,46 |
| 25,32 | 186,71 | 174,36 |
| 4,18 | 106,06 | 79,19 |
| 1,28 | 120,61 | 47,15 |
| 1,22 | 58,85 | 46,17 |
| 0,75 | 56,13 | 37,30 |
| | PFPeA x CS-ZnCl2 | |
| 931,61 | 158,30 | 177,01 |
| 781,25 | 163,70 | 165,09 |

| | | |
|---|---|---|
| 439,43 | 148,46 | 131,47 |
| 293,44 | 135,95 | 112,05 |
| 36,70 | 33,24 | 49,21 |
| 33,27 | 40,61 | 47,33 |
| 13,62 | 25,64 | 33,24 |
| 11,44 | 30,55 | 31,02 |
| PFBS x CS-ZnCl2 | | |
| 848,85 | 356,49 | 343,78 |
| 543,76 | 252,96 | 275,94 |
| 267,85 | 205,37 | 194,56 |
| 185,20 | 157,29 | 162,17 |
| 184,24 | 159,62 | 161,75 |
| 61,31 | 93,90 | 93,97 |
| 50,17 | 123,35 | 85,12 |
| 32,64 | 43,40 | 68,85 |
| 28,66 | 53,36 | 64,57 |
| 9,72 | 36,74 | 37,87 |
| 7,62 | 41,78 | 33,58 |

# Annex VI: Freundlich model: isotherm graphs for MPs adsorption

*Table 20. Freundlich isotherm model graphs: diclofenac adsorption.*

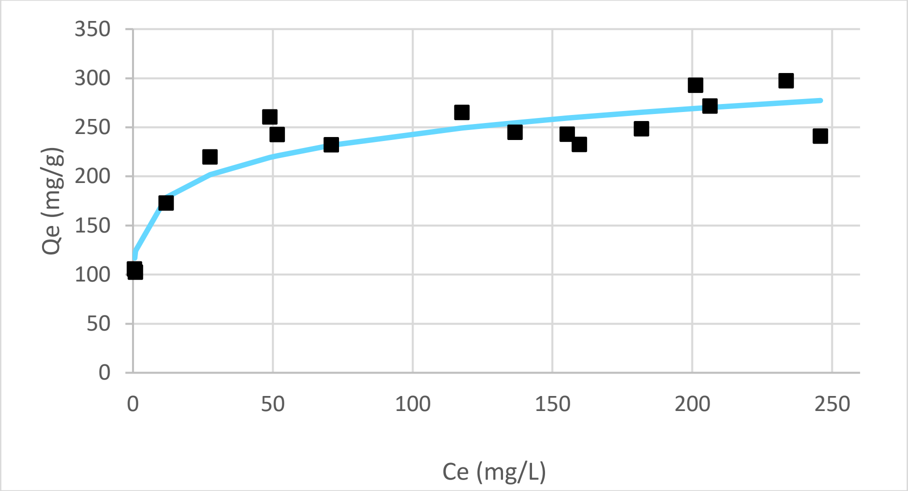

*Figure 40. Adsorption equilibrium curve of DCF x CS-$ZnCl_2$; contact time = 24 h; solution volume = 25mL (Freundlich).*

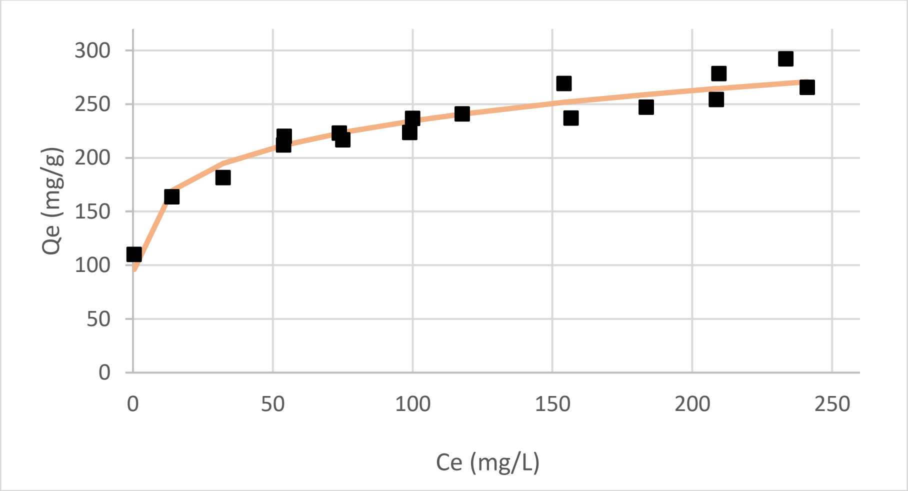

*Figure 41. Adsorption equilibrium curve of DCF x JM-2h-$CO_2$; contact time = 24 h; solution volume = 25mL (Freundlich).*

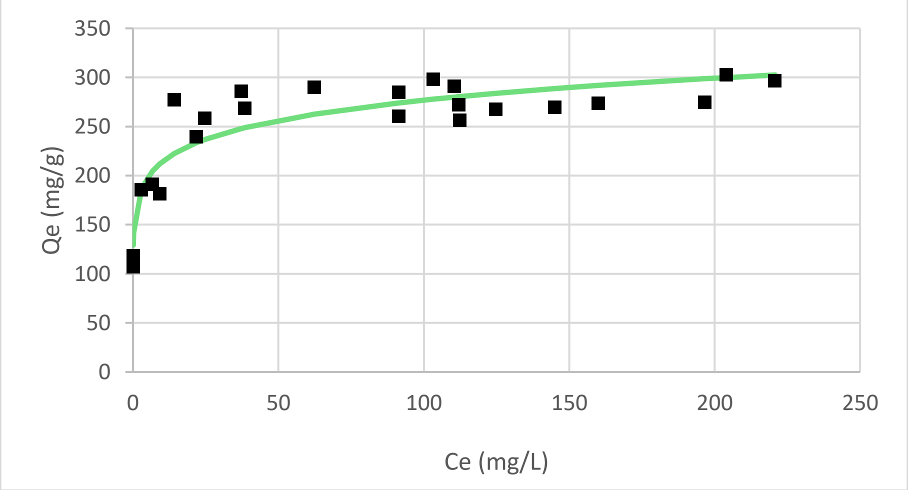

*Figure 42. Adsorption equilibrium curve of DCF x JM-$K_2CO_3$; contact time = 24 h; solution volume = 25mL (Freundlich).*

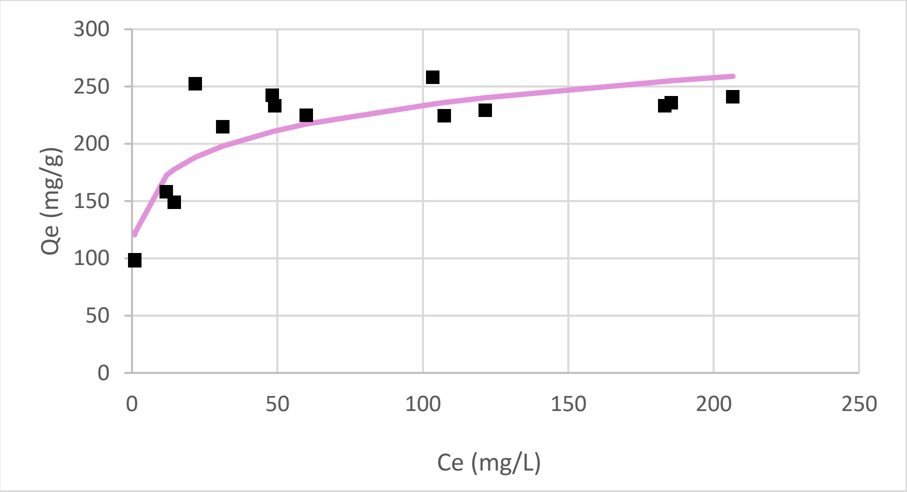

*Figure 43. Adsorption equilibrium curve of DCF x PA-$K_2CO_3$; contact time = 24 h; solution volume = 25mL (Freundlich).*

*Table 21. Freundlich isotherm model graphs: valsartan adsorption.*

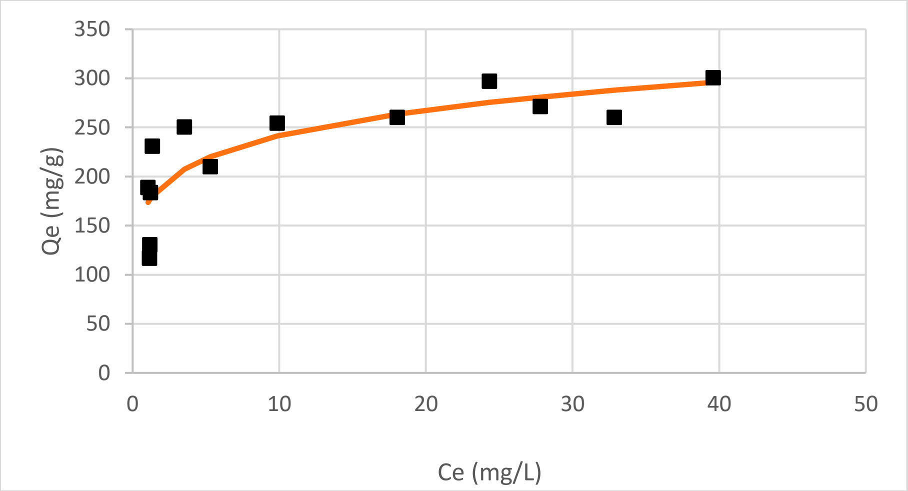

*Figure 44. Adsorption equilibrium curve of VLT x JM-$K_2CO_3$; contact time = 24 h; solution volume = 25mL (Freundlich).*

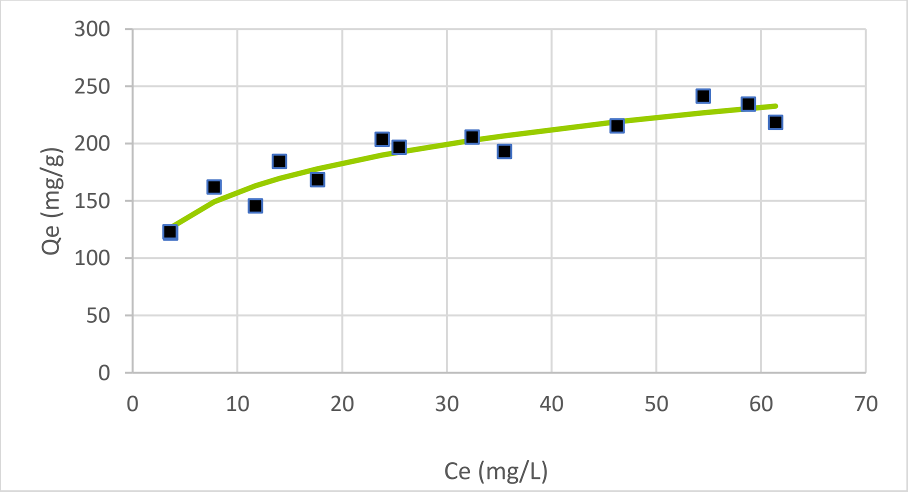

*Figure 45. Adsorption equilibrium curve of VLT x PA-$K_2CO_3$; contact time = 24 h; solution volume = 25mL (Freundlich).*

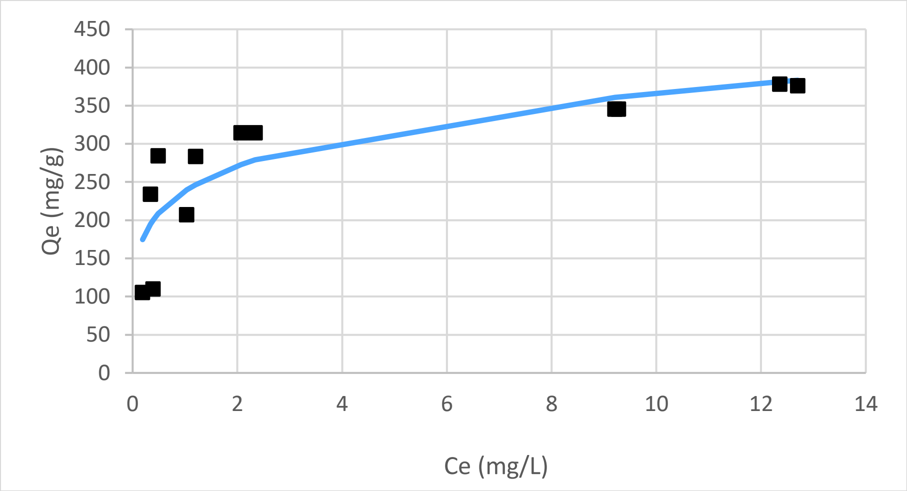

*Figure 46. Adsorption equilibrium curve of VLT x CS-ZnCl$_2$; contact time = 24 h; solution volume = 25mL (Freundlich).*

*Table 22. Freundlich isotherm model graphs: PFAS adsorption.*

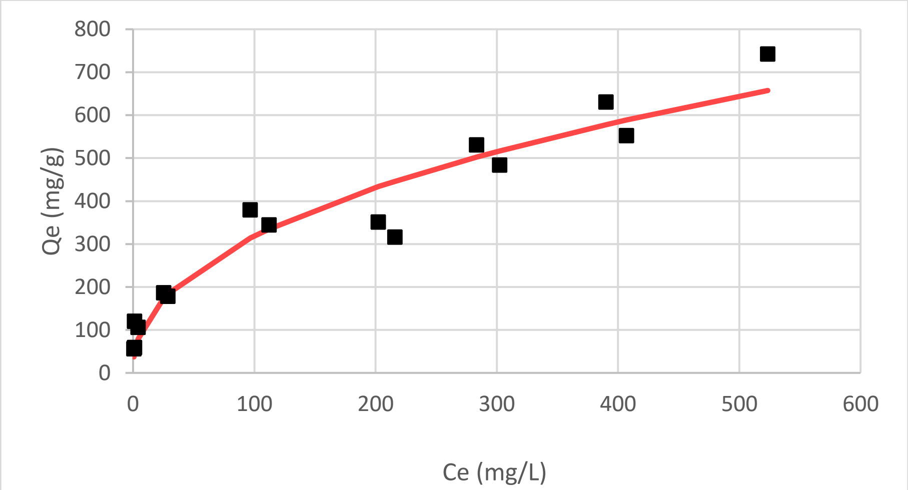

*Figure 47. Adsorption equilibrium curve of PFOA x CS-ZnCl$_2$; contact time = 48 h; solution volume = 25mL (Freundlich).*

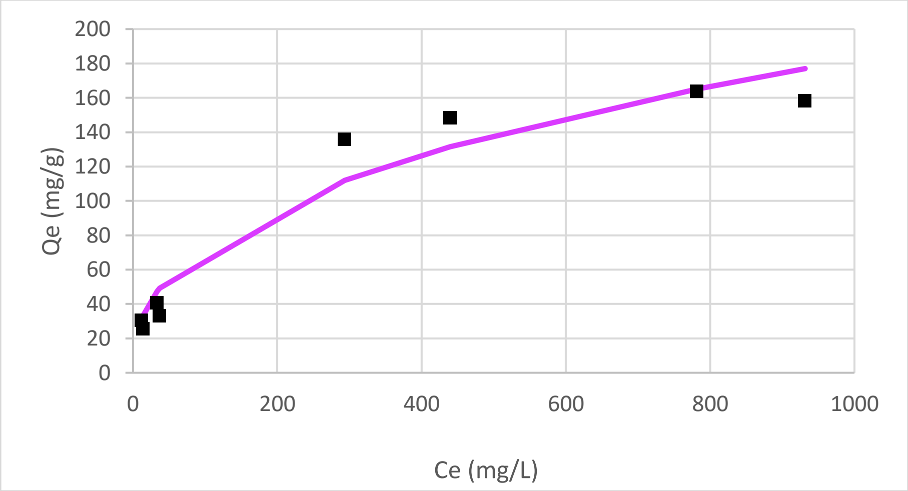

*Figure 48. Adsorption equilibrium curve of PFPeA x CS-ZnCl$_2$; contact time = 48 h; solution volume = 25mL (Freundlich).*

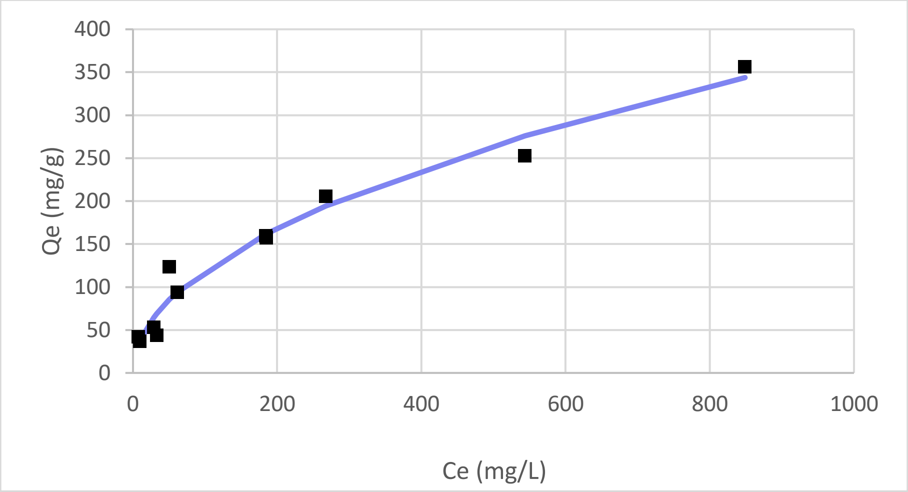

*Figure 49. Adsorption equilibrium curve of PFBS x CS-ZnCl$_2$; contact time = 48 h; solution volume = 25mL (Freundlich).*

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