

Influence of Wastewater DOM Fractions on the Adsorption of Pharmaceuticals onto Activated Carbon

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Preface

This thesis is a part of the Master's programme in Water Resources Engineering. As this research concludes my education, firstly, I am grateful for an opportunity to study at Department of Chemical Engineering, Lund University along with The J. Gust. Richert Foundation for financial support under KARAT project. This work has enabled me to gain deeper insights into the wastewater treatment for micropollutant removal. With this knowledge, the biggest achievement in my life that I can think of is to receive a Nobel prize. Too farfetched perhaps. But who knows what is planned in one's future! Maybe I might change career and end up working as a chef. But before that, I would like to acknowledge the people who helped get to this point in life. Hence, starting with a quote in my mother tongue, Marathi,

‘स्वामी तिन्ही जगाचा आईविना भिकारी’

which translates to *‘Master of the three worlds (earth, heaven and hell), without mother, is a beggar’*. Therefore, I humbly dedicate this thesis to my mother, Snehal and her twin sister, Soumya Tirodkar (whom I consider as my second mother). I am here because of their love and nourishment. They have given me everything I asked even when they had to sacrifice something they might have hold dear. I ask nothing but their blessings because I will not be able to pay the debt they levied on me. Furthermore, I thank my father, Ravindra and uncle, Keshav Tirodkar for their endless support in my endeavours and my brother, Kaivalya and his wife, Netra, for their constant encouragement. To my all of my cousins, I appreciate our long talks almost every weekend. You are a big part of my life and I love you all very much.

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Lund, June 8th, 2022

Summary

Micropollutants in our sources of freshwater is an issue which requires immediate attention. The presence of pharmaceuticals, endocrine disrupting agents, pesticides and other harmful compounds have proven to have impact on the aquatic as well as on human life. Treated wastewater being a major source of ingress of micropollutants into the aquatic environment, the current standards do not stipulate any significant restriction on discharge but focuses on the monitoring. This is majorly due to two reasons, lack of understanding about the different compounds and available treatment options are not fully investigated.

Dissolved organic matter (DOM) in the wastewater has proven to have significant impact on the treatment processes designed to remove micropollutants. Even the DOM are less toxic, they often enable transport for various toxic substances such as pharmaceuticals if not treated. In case of activated carbon, DOMs compete with micropollutants for sorption on active sites. Micropollutants have different characteristics and therefore, to optimize these processes, a deeper understanding about the influent along with the treatment process itself is important.

This research focus on the elimination of dissolved organic carbon (DOC) based on size exclusion and hydrophobic/hydrophilic fraction and its effect on the removal of pharmaceuticals using activated carbon. In this research, membrane filtration was used to eliminate DOC and based on elimination of different size fractions, the performance of removal of pharmaceuticals using powdered activated carbon was evaluated. It was observed that the effect of DOC on the treatment is not only a function of molecular weight distribution but the presence of hydrophobicity/hydrophilicity in the wastewater. To study this, the wastewater was fractionated to remove hydrophilic and hydrophobic fractions using a rapid fractionation method and the effect of removal of one fraction on the competition for removal of pharmaceuticals was studied.

The study affirms the finding by various researchers that the presence of high molecular weight compounds (>25 kDa) does not considerably affects the performance of activated carbon for removal of pharmaceuticals but a significant impact was observed due to the competition by low molecular weight compounds. Another important part of the study was to comprehend the effect of hydrophobicity and hydrophilicity and the study indicates that the presence of hydrophobic compounds contributes to most of the competition with pharmaceuticals for sorption on activated carbon. Furthermore, the study also suggests that the use of DOC concentrations of wastewater to evaluate the dosing requirements of activated carbon for efficient removal of pharmaceuticals may not be a good practice.

Popular Science Summary

Do we really understand the wastewater enough to remove micropollutants?

Water is an important aspect of our lives. Up to 60% of our body is made up of water. Therefore, to take care of our body we need to supply it with quality products. We often take the quality of water for granted and trust on our municipalities to provide us with good quality water. The treatment of water is a complex process but if something goes wrong, consumers can easily identify it such as bad smell, taste or often colour. But there are more things present in the water that we should be worried about than just these.

A micropollutant is a manmade compound which has several impacts on the environment including aquatic ecosystem and human being. Even though these compounds are not found to cause acute conditions, consumption at low concentrations for a very long time may induce chronic diseases. We drink water on daily basis and these compounds accumulate in our body, a process called biomagnification. The sources of the micropollutants are anthropogenic i.e. we use them as pesticides, domestic cleaning agents, chemicals used in industries, etc. Especially, medicines which are anti-inflammatory, antibiotics, etc. contain certain active substances such as diclofenac and sulfamethoxazole which after consumption end up in our faeces or urine which ultimately reach the wastewater treatment plants. These compounds are very stable and require specialized removal methods. But once released in the environment, they are diluted. Water being a circular system, these micropollutants end up in the drinking water treatment plants. Due to extreme low concentrations, it is hard and costly to treat water for these compounds. Therefore, it is more beneficial to remove the micropollutants from the wastewater than from drinking water. But it is a hard task to undertake. Wastewater treatment plants have complex treatment systems than water treatment plants. Treatment of micropollutants is a part of the problem. It is often recognised that we haven't established all of the micropollutants present in the wastewater because it is impossible given the compounds have multiple sources and could undergo various transformations to form new compounds. Various researchers focus on the development of treatment options whereas, some focus on understanding the characteristics of the wastewater and micropollutants itself. In this research, the focus is on the both sides as it is important to understand the features of the wastewater and use it to optimize the performance of the treatment selected for the removal of micropollutants.

The wastewater is composed of various organic material including human faeces. These are referred to as total organic matter. Total organic matter is further divided into two parts which are particulate and dissolved organic matter. Most of the particulate and some dissolved organic matter is removed in primary treatment steps. The rest of the dissolved organic matter along with micropollutant requires additional treatment. There are various methods used but this research was focused on the membrane filtration and activated carbon. Membrane filtration is a filtration method which removes some compounds based on their size. Each membrane has pores and allows smaller compounds to pass through but retains bigger compounds. Activated carbon works as a sticky surface which allows micropollutants to attach (adsorb). Activated carbon does not selectively allow the micropollutants to adsorb but all of the compounds including the organic matter can adsorb onto the surface. The removal by activated carbon depends upon the competition between the compounds. Therefore, the understanding about the affinity of these compounds towards the activated carbon is an important aspect investigated in this study.

Wastewater contains different compounds with different properties. In this research, they are divided as hydrophobic and hydrophilic compounds. Hydrophilic compounds are in completely dissolved state whereas hydrophobic are partially separate from dissolved state. On activated carbon, the hydrophobic compounds quickly adsorb onto the surface and reduces the surface available for micropollutants. This is a major problem in the use of activated carbon for removal of micropollutants. Most of the researchers estimate the requirement of activated carbon based on the concentration of dissolved organic matter. But it may not represent the various compounds with different properties present in the wastewater. Therefore, this research seeks to understand the effect of hydrophobic/hydrophilic compounds present in the wastewater and probes the current practices used to maximize removal of micropollutants.

Abbreviations

| | |
|-----------------------|----------------------------------|
| ¹⁴C | Radiocarbon or Carbon-14 isotope |
| AC | Activated carbon |
| BV | Bed volume |
| CHA | Charged hydrophilic acids |
| CPM | Counts per minute |
| DBP | Disinfection byproduct |
| DI | Deionized (water) |
| DOC | Dissolved organic carbon |
| GAC | Granular activated carbon |
| HMW | High molecular weight |
| LMW | Low molecular weight |
| MF | Microfiltration |
| MP | Micropollutant |
| MWCO | Molecular weight cut-off |
| NEU | Neutral hydrophilic acids |
| NF | Nanofiltration |
| NOM | Natural organic matter |
| PAC | Powdered activated carbon |
| PWF | Pure water flux |
| RO | Reverse Osmosis |
| SHA | Slightly hydrophobic acids |
| SUVA | Specific UV absorbance |
| TMP | Transmembrane pressure |
| TOC | Total organic carbon |
| UF | Ultrafiltration |

| | |
|-------------------------|-------------------------|
| UV₂₅₄ | UV absorbance at 254 nm |
|-------------------------|-------------------------|

| | |
|---------------|--------------------------------|
| UV-vis | UV visible (spectrophotometer) |
|---------------|--------------------------------|

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|------------|------------------------|
| VHA | Very hydrophobic acids |
|------------|------------------------|

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|-------------|----------------------------|
| WWTP | Wastewater treatment plant |
|-------------|----------------------------|

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1 Introduction

The United Nations' Sustainable Development Goals (SDGs), a.k.a. *The Global Goals* were adopted in 2015 to prioritize progress in terms of global peace and prosperity. SDG 6 is one of the goals which focuses on water and sanitation (JMP, 2021). Even though most of Europe has safely managed drinking water sources, their deterioration over the recent decades has been a major issue. The increase in population creates stress on the existing water resources along with the increase in agricultural and industrial demands. Water being a circular system, when a pollutant is introduced, it stays within the system provided that it is neither removed nor transformed. Due to complexity of the system, it is near impossible to track a specific pollutant and therefore, it is important to limit the ingress. There are multiple points of entry for pollutants to the waterbodies. They can be classified as point sources and non-point sources. Point sources include industries and unsecured landfills whereas non-point sources include agriculture, rain-water from road surfaces, etc. The point sources generally release pollutant in concentrated form whereas non-point sources are diffused. Wastewater treatment plants being a major point source, if not treated properly, could be destructive to the well-being of receiving waterbody (Metz and Ingold, 2014).

Natural organic matter (NOM) is a mixture of various compounds in concentrations ranging from ng/L to mg/L. The composition is not completely understood due to plethora of compounds and therefore, it is impossible to establish the physico-chemical understanding of them as well (Sillanpää, 2015). In domestic wastewater treatment plants (WWTPs), organic matter is identified as total organic carbon (TOC). In freshwater sources, NOM is associated with TOC directly due to natural origins but in WWTP, some of the organic matter may not have natural origin but still referred as TOC. In WWTP, a significant amount of organic carbon is removed in primary and secondary treatment but due to limitations of these processes, their complete removal is not possible. It is important to remove TOC from the influent in order increase the effectiveness of advanced treatment intended to remove compounds present in low concentrations referred to as micropollutants.

A micropollutant is a compound which has adverse effect on the environment even at lower concentrations. Unlike macro-pollutants like nitrogen and phosphorus, micropollutants have complex removal processes and require specialized identification techniques. The treatment of wastewater is a well-regulated field in the Europe. With various standards put forward by the European Union and by respective countries, they are insufficient and the future of regulations related to micropollutants are dependent on research. Therefore, enforcing standards for micropollutant is a difficult task due to substantial gap in the knowledge about the processes and effectiveness of existing treatments (Barbosa *et al.*, 2016). A study by Wilkinson John *et al.* (2022) indicated that the highest cumulative concentration of 61 active pharmaceutical micropollutants were observed in African countries followed by Asian countries, presumably due to lack of treatment. Due to their stable nature and biological impact on aquatic life, the presence of pharmaceuticals in waterbodies needs to be addressed on an urgent basis.

Currently, most of the wastewater treatment plants are not equipped with the technologies focused on removal of micropollutants. Various stable pharmaceutical compounds have found to persist even after the biological treatment (Caliman and Gavrilescu, 2009; Verlicchi *et al.*, 2012; Margot *et al.*, 2013; Baresel *et al.*, 2017). Therefore, research in specialized treatment option is a prime focus for various countries around the world. Ozone and activated carbon are two of

the major treatment options available for removal of pharmaceuticals from the wastewater (Eggen *et al.*, 2014). Ozone being an oxidizer, it enables complete oxidization of some micropollutants and is able to achieve lower concentrations compared to activate carbon. But ozone is selective oxidizer and partially oxidized compounds (byproducts) require an additional treatment step. Furthermore, the formation of some byproducts such as bromate, trihalomethane, etc. can increase the toxicity of the treated effluent compared to influent (Margot *et al.*, 2013).

On contrary, activated carbon was found to be effective on various micropollutants and removes the compounds completely by the process of adsorption. The removal of micropollutants is a function of not only the quantity of organic carbon but also the properties of these compounds. Molecular size, solubility, surface charge, etc. affects the competition for the active adsorption sites ultimately influencing the performance of activated carbon towards the micropollutants (Velten *et al.*, 2011; Zietzschmann *et al.*, 2014). Low molecular weight compounds are often strong competitors and interfere more with the adsorbability of the micropollutants rather than the high molecular weight compounds (Zietzschmann, 2016). The removal based on the molecular size exclusion would decrease the DOC concentration but it does not give an insight about the other fractions present in the sample. Therefore, this research investigates the effect on adsorbability of pharmaceuticals due reduction in DOC which obtained using size exclusion and exclusion based on hydrophobicity/hydrophilicity of the DOMs present in the wastewater.

1.1 Objectives of the research

The organic carbon is often used as an indicator for investigating the activated carbon or ozone dose for efficient removal of micropollutants. The main aim of the research was to develop better understanding of the matrix of organic carbon present in the biologically treated wastewater. Therefore, this research focuses on the two matrices based on size exclusion and solubility fractions, and its impact on the removal of micropollutants. To fulfil this aim, the research was divided into three objectives, as follows

- Evaluate the effect on dissolve organic carbon due to removal by size exclusion
- Evaluate the effect on dissolve organic carbon due to fractionation based on hydrophobic and hydrophilic compounds
- Develop understanding about the effect of these matrices on adsorption of pharmaceutical micropollutants using activated carbon

2 Background

In this section, the background concepts and information related to study are provided in 5 subsections. First, the presence of natural organic matter along with its characteristics and treatment options are explained followed by the presence of micropollutants, their importance and treatment options. Later, the basic concepts of membrane filtration, fractionation of natural organic matter and adsorption with activated carbon are explained.

2.1 Organic matter

Organic matter in the water or wastewater has multiple sources. In drinking water, it is referred to as natural organic matter (NOM) because of its natural origin. But in case of wastewater, the sources may not be limited to natural activities but anthropogenic activities as well and therefore, is referred to as total organic matter (TOM). In this study, specific UV absorbance and resin fractionation methods are used which are mostly used in characterising NOMs in drinking water. But similar characterization of TOM using these methods is possible. Hence, in this subsection, NOMs and its characterization methods are introduced followed by TOM. The quantification of both NOM in drinking water and TOM in wastewater is done as total organic carbon (TOC). Even though it is the most common method to quantify organic matter (Winterdahl, 2013), it does not provide about a detailed understanding about the matrix present and their possible behaviours within the treatment process (Sillanpää *et al.*, 2015).

TOC is of high interest because it can adversely affect the performance of unit processes in water and wastewater treatment plants. Additionally, they can introduce undesirable characteristics to the water such as odour, colour, smell and taste. Especially in treatment plants units like chlorination and ozonation, the formation of disinfection byproducts (DBPs) is one of the major issues and they may work as a carrier for heavy metals and other toxic pollutants. Therefore, characterization and quantification of TOC is important during the design and operation of the units to optimize their performance.

2.1.1 Natural organic matter in drinking water

In recent years, several countries have reported the presence of NOM in the drinking water source. NOM is a complex matrix of organic compounds which has origin majorly from but not limited to plants, animals and microorganisms. Their ubiquitous nature is due to the interaction between bio and geosphere through the hydrological cycle (Sillanpää, 2015). It involves both particulate and dissolved compounds which vary in their physicochemical characteristics (Davis, 2010). Usually, the sources of the NOMs are

- Aquatic environment – Animal faeces, decomposed leaves, etc.
- Terrestrial environment – Algal growth, dead fish, etc.

(Filella, 2009; Tchobanoglous *et al.*, 2014a). The quality and quantity of NOMs are dependent on several factors such as catchment area, season of the year, amount of precipitation, climatic conditions, type of vegetation, etc.(Sillanpää *et al.*, 2015). Due to the complex synthesis and degradation processes of NOMs, most of them are not yet identified and can be assumed to be in large numbers in a sample of water. Therefore, there is very little hope for identification and complete separation of all of the NOMs. These compounds are identified as functional groups since the quantification of each chemical compound is impossible. The technological

advancement in the field of analytical chemistry has introduced sophisticated methods for the estimation of different compounds. However, cost and time required for the evaluations is high.

2.1.2 Characteristics of NOMs and specific UV absorbance (SUVA)

NOMs can be divided into two major categories; Hydrophobic and hydrophilic compounds. Hydrophilic compounds consist of aliphatic and nitrogenous compounds. Whereas, the largest fraction in hydrophobic compounds is humic substances. They are of special importance because of their resistance to the biological treatment processes and these are the precursor to the formation of DBPs. Humic substances are further categorized as humic acid (HA), fulvic acid (FA) and humin (Sillanpää *et al.*, 2015).

Specific UV absorbance (SUVA) is a number used to identify the hydrophobicity and hydrophilicity of NOMs in the water sample. It is a ratio of UV absorbance at 254 nm and DOC of the water sample. The higher SUVA indicates presence of higher molecular weight (HMW) compounds in the sample. SUVA greater than 4 indicates high hydrophobic compounds, 2 to 4 indicates a mixture of hydrophobic and hydrophilic compounds and less than 2 indicate hydrophilic compounds of lower molecular weight (LMW) are dominant in the water (Edzwald and Tobiason, 1999). In the recent decade, the new UV-vis spectroscopic methods have been used to quantify NOMs; colour (436 and 400 nm) and UV (280 and 254 nm) (Uyguner-Demirel and Bekbolet, 2011). However, some of the functional groups present in water especially from humic substances are not easily distinguishable within an identifiable absorption spectrum. Therefore, even though SUVA and other spectroscopic methods are good for coarse identification and quantification, they do not provide detailed quality parameters of NOMs such as functional groups (Sillanpää *et al.*, 2015). The use of SUVA and the fractions are majorly used in characterising NOMs in drinking water but in this study, the same methods are used for characterising TOMs in wastewater.

2.1.3 Total organic matter in wastewater

As mentioned before, in wastewater, the sources of organic material often include anthropogenic sources such as industries and commercial activities. Therefore, collectively it is termed as TOM which has bigger and more complex matrix of compounds compared to NOMs. TOM entails particulate and dissolved fractions which are referred to as particulate organic carbon and dissolved organic carbon (DOC). In wastewater treatment, removal of particulate organic carbon is comparatively easy and generally happens in primary treatment units of conventional treatment train whereas the significant removal of dissolved organic carbon (DOC) occurs in subsequent treatment units.

Even if some of the DOMs do not contribute to any toxicity, they act as carriers to toxic substances such as heavy metals, microbial species and other compounds which could potentially increase the toxicity of the sample. Such as in some cases, their interactions with metals increase the toxicity of the sample (Ravichandran, 2004 cited in Winterdahl, 2013). Also, if disposed without treatment, they can depreciate dissolved oxygen of the receiving waterbody which can lead to eutrophic conditions.

2.1.4 Treatment options for removal of DOMs

As it presents a matrix of compounds with different properties, single process alone is not sufficient to remove all compounds. Starting from primary treatment, the DOMs are removed in every step of the treatment train. Biological treatment is one of the major removal steps for DOMs. In the tertiary and quaternary treatment units, various other options are available for removal of DOMs.

In wastewater treatment plant, coagulation is usually used for removal of phosphorus (post-P precipitation) but it can, to a certain extent, remove organic matter. A study by Sharp *et al.* (2006) suggest the coagulant requirement depends upon the molecular weight of the compound. DOM with higher molecular mass tend to require lower doses whereas the lower molecular mass compounds might increase the dosing requirements. But the major focus being phosphorus, the doses may not be optimized for removal of organic matter.

The use of membranes can be an effective way for removal of DOM but is costly. Due to presence of high organics, the use of nanofiltration or reverse osmosis in wastewater treatment is not ideal due to fouling issues (Fonseca Couto *et al.*, 2018). Ion exchange resins have found to efficiently remove charged compounds regardless of their affinity towards water (Bolto *et al.*, 2002). Since the charge on the compound is an important factor in performance, it is more likely that the residual fraction represents neutral/uncharged compounds. A study by Kim and Symons (1991) indicated that the use of anion resins can significantly reduce precursor compounds to trihalomethane which can be beneficial for treatment options such as ozonation or advanced oxidation.

Advanced oxidation (AO) for removal of organic matter is a well investigated treatment process. It includes processes such as ozonation with hydrogen peroxide or UV (Sillanpää and Matilainen, 2015). Oxidation with hydroxyl radicals produce reaction rate several times higher than that of ozone which makes it one of most effective oxidants. Two of the major problem with these processes are the formation of byproducts and high treatment cost (Suty *et al.*, 2004). Additionally, complete oxidation of organic carbon is not practicable from AO processes in operational conditions but it certainly enables transformation of high molecular weight compounds to low molecular weight hydrophilic compounds which are partially oxidized (Sillanpää *et al.*, 2018).

2.2 Micropollutants in wastewater

In last couple of decades, many researchers have raised concerns over increasing concentration of Micropollutants (MPs) in the surface waters. micropollutants are compounds, organic or inorganic, which even at concentrations in ng/L can have negative impact on organisms. The presence of MPs in the wastewater is mostly due to anthropogenic activities including but not limited to agriculture, industrial processes and domestic use. Depending upon the use, they are categorised as pharmaceuticals, personal care products, pesticides, endocrine disrupting agents and illicit drugs (Hofman and Teo, 2021).

For pharmaceuticals, the impact on the human due to unintended consumption can be injurious to the overall health. Furthermore, some of these compounds may undergo physico-chemical transformations while in aquatic environment and increase the possibility of adverse effects. Biomagnification over a large time period, probably only identifiable after a couple of generations, may induce irreversible health conditions (Santos *et al.*, 2010). Major identified concerns for these compounds are infertility, partially developed sexual organs, loss or alteration of sexual activities, birth defects, increased chances of cancer and other chronic disorders (Caliman and Gavrilescu, 2009). Even with the advancement in technologies, assessment of impact of MPs in aquatic environment is a difficult, time consuming and expensive task.

The wastewater treatment plants are a crucial link between the urban and natural environment. They are intended to work as a filter and isolate pollutants from contaminating aquatic settings. Various chemicals used in the domestic and industrial processes eventually end up at the

treatment plants (Reemtsma *et al.*, 2006). An approximation in 2012 suggests that about 143,000 commercial compounds were registered in Europe (Hofman and Teo, 2021). Due to this large set of compounds, the identification of the transformation byproducts of these compounds is impossible. One step forward to control the release of the MPs, European Union in 2000 published a water policy followed by identifying 33 priority substances in 2008 and later published a list of 45 priority compounds for monitoring along with treatment options (Barbosa *et al.*, 2016) but these policies do not impose any discharge standards for micropollutants (Metz and Ingold, 2014; Kosek *et al.*, 2020). Most of the WWTPs are designed and operated based on the discharge standards imposed by the regulatory agencies such as EU and, in Swedish context, Naturvårdsverket. Due to the lack of data on various MPs, in most of the cases, governments follow precautionary principle for their policy development and regulatory enforcement. Even for the known MPs, a standalone removal process is insufficient, let alone the unknown compounds and their response to the treatment (Santos *et al.*, 2010). But the development in assessment techniques such as high-performance liquid chromatography, mass spectrophotometry, etc. has enabled researchers to identify compounds which are at extremely low concentrations such as ng/L. To enhance the removal of the MPs, the reaction kinetics need to be investigated in details and should be used to optimization of treatment processes (Schwarzenbach *et al.*, 2006).

As a right step forward, in 2016, Switzerland was the first country which implemented policies to reduce the release of MPs into natural environment (Luterbacher, 2016) and an initial cost benefit analysis done by Logar *et al.* (2014) concluded that the upgradation of 100 wastewater treatment plants to meet the standards is beneficial. The selection of treatment plants to upgrade for micropollutant removal is a complex task. Cimbritz and Mattsson (2018), in Swedish context, suggested that for small treatment plants (< 8000 population equivalence), it is cost effective to divert the wastewater into larger plants for treatment of MPs.

2.2.1 Existing treatment options for removal of MPs

The removal of MPs is not only a function of treatment process but the physio-chemical properties of the MPs (Zietzschmann *et al.*, 2015). In the removal of MPs, three basic mechanisms are involved; physical removal, chemical transformation and degradation. Removal by sorption on sludge or activated carbon (i.e. sorption) are two of the examples of physical removal. Ozonation and biological treatment are the examples of transformation and degradation as both degrade some compounds whereas some are transformed into a byproduct.

Most of the wastewater treatment plants (WWTPs) in the world are equipped with biological treatment processes. The main objective of these processes is to remove the macro-pollutants such as nitrogen and phosphorus from the wastewater. Some of the MPs are removed in the treatment by means of sorption on the activated sludge, complete degradation, transformation and, to a very small extent, volatilization. During the same process, other MPs also go through physical and chemical transformation (Luo *et al.*, 2014). Hybrid suspended-biofilm processes, according to Edefell *et al.* (2021) and Falås *et al.* (2013), have increased degradation rates for certain MPs compared to conventional biological processes. Furthermore, membrane bioreactor processes also been found to have increased removal efficiencies for some micropollutants (Martin Ruel *et al.*, 2010). However, a long term study by Margot *et al.* (2013) concluded that the most persistent compounds like carbamazepine, diclofenac and metoprolol had less than 10% removal in the biological treatment. Additionally, a comprehensive review by Verlicchi *et al.* (2012), who compiled the research done on 264 WWTPs located all around the world, concluded that a standalone biological treatment is insufficient. Review also concluded that even

some compounds were removed, a significant number of MPs persisted in the effluent and some were observed to have negative removal. But secondary treatment is an important step in the treatment process as its inadequate removal of DOC would significantly affect the performance of advanced treatment units intended for removal of MPs. Therefore, Baresel *et al.* (2017) concluded that the additional treatment for MPs should be considered when the primary and secondary treatment produce satisfactory performance.

Tertiary and/or advanced treatment options in wastewater are mostly used for removal of MPs. Nowadays, some of the advanced treatment options are referred to as quaternary treatment. Presently, most promising treatment options for removal of MPs are membrane filtration, activated carbon, advanced oxidation or combination of these technologies. In case of micropollutant removal by membrane filtration, performance of membrane filtration is influenced by various factors such as membrane fouling, relative hydrophobicity and dipole movement. In general, the removal of MPs from the membrane filter can be estimated using molecular weight cut-off (MWCO) but this is not a standardized characterising technique (Söderman, 2017). MWCO can be defined as a rejection rate of 90% for a specific molecular weight by the membrane (Madsen, 2014). Since fouling and scaling being a major problem, it increases TMP and significantly affects the MWCO. Furthermore, there are several challenges associated with membranes such as its operational life, optimal low-cost membrane design and energy requirements (Zularisam *et al.*, 2006). The treatment of retentate is also an important factor to consider for membrane filtration. Therefore, a use of coarse membranes intended for removal of DOC is more likely to aid improving the performance of oxidative or adsorptive treatment units.

Ozonation for MP removal is one of the most extensively researched technologies. Complete degradation of various MPs by oxidation is favourable but partial oxidation of compounds present a challenge as multiple oxidation pathways for a single compound can yield numerous byproducts. Due to some of the byproducts such as bromate and trihalomethane, the toxicity of the effluent can increase compared to influent. Even though some of the byproducts are biologically stable, most of them can be removed with biological post-process (Margot *et al.*, 2013).

Another one of the most promising technologies is adsorption by activated carbon because of its complete removal of MPs from liquid phase. As adsorption is dependent on the availability of active sites on the adsorbent, the competition between the compounds plays an important role in the removal. It is reported that the HMW DOC fractions are less competitive but can interfere with the interaction between active sites and MPs. LMW DOC fractions are highly competitive compounds to adsorb efficiently (Newcombe *et al.*, 1997; de Ridder *et al.*, 2011; Velten *et al.*, 2011; Zietzschmann *et al.*, 2014).

2.3 Membrane Filtration

Membrane filtration is a method of removal of solids by size exclusion. Membrane is a semi-permeable synthetic material which works as a sieve allowing a certain size solid to pass through and retains others. Membranes can be classified by various ways. But mainly they are classified based on the size excluded by the membrane. Microfiltration (MF) works in the range of 70 to 2000 nm, ultrafiltration (UF) in 8 to 200 nm, nanofiltration (NF) in 0.9 to 10 nm and reverse osmosis (RO) in 0.1 to 2 nm (Tchobanoglous *et al.*, 2014b). The main driving force for the membrane operation is the difference of hydrostatic pressure between the membrane feed side and permeate side. the operating pressure can differ based on the process and material used. Operating pressure for microfiltration can be around 0.5 to 1 bar whereas for reverse osmosis, around 10 to 100 bars (Madsen, 2014). Membrane are further classified based on their

configuration; tubular, spiral and hollow fine-fibre, based on the operation mode; crossflow and dead-end, and lastly, based on their material (Tchobanoglous *et al.*, 2014b).

One of the most important considerations in membrane filtration is fouling. Fouling accounts for the solutes retained on the feed side that can block pores and provide additional resistance to the passage of permeate which leads to increase in trans-membrane pressure (TMP). There are two types of fouling; reversible and irreversible. Reversible can easily be removed by backwashing or chemical treatment but irreversible accounts for permanent loss of flux and reduced life of the membrane. The fouling is also classified into four mechanisms; complete pore blocking, partial pore blocking, internal pore blocking and cake layer formation. Scaling is another problem which occurs especially in NF and RO membranes due the feed side solute concentration exceeds the level of saturation. This hinders the path of flow and increases TMP and can ultimately lead to physical damage to the membranes. Furthermore, fouling control is an complex issue and a single parameter such as DOC cannot represent the possible interactions of DOM with the membrane (Gorczyca, 2018). Therefore, a thorough understanding of the process under specific conditions must be established before implementation of membrane processes.

Even after their appearance in late 50s, membranes have been a part of industrial treatment trains but not the municipal treatment plants. Now, stringent removal requirements necessitate the use of membranes in domestic wastewater treatment. In general, the size of MPs lies around 1nm (i.e., about 1000 kDa) (Madsen, 2014). Therefore, the use of microfiltration and ultrafiltration for removal of MPs may not be useful and tighter membranes might be required. Since NF and RO membranes require high TMP, in municipal applications, it is beneficial to use loose membranes such as MF and UF in combination with another processes. Furthermore, the use of NF and RO is costly and they are heavily associated with the fouling issues (Fonseca Couto *et al.*, 2018).

2.4 Fractionation of DOM

Characterisation of DOMs is a difficult task because identification of each compound requires isolation and separation which is nearly impossible. Even though DOMs have different origins and each have unique structure, they share some common physical or chemical properties. Based on these properties, the fractionation of DOMs is possible. Resin fractionation is a rapid method to isolate and separate the DOMs based on their hydrophobicity and hydrophilicity. Water being a polar solvent creates a solvent-solute bonds with some compounds which are identified as hydrophilic while hydrophobic compounds are unable to create such bonds and are the partially separated from solvent phase. pH of the solvent is an important factor in this ion exchange method. In acidic conditions, Van der Waals forces are dominant whereas in neutral or basic conditions hydrophobic fraction stays in aqueous phase and is hard to remove (Piper *et al.*, 2010). Resins benefit from this mechanism to remove hydrophobic fraction from the liquid phase.

To remove hydrophilic fractions, Leenheer (1981) initially proposed the use of resins. Later, Malcolm and MacCarthy (1992) concluded that the use of XAD-8 and XAD-4 resins can remove most of the hydrophobic fractions from the sample. The hydrophobic and hydrophilic fractions are later divided into very hydrophobic fraction (VHA), slightly hydrophobic fraction (SHA), charged hydrophilic fraction (CHA) and neutral hydrophilic fraction (NEU). At pH of 8, Bolto *et al.* (1999) used IRA-958 (first introduced by Croué *et al.* (1999)) for removal of charged hydrophilic compounds and also suggested that the neutral hydrophilic fraction was not removed by any of the resins.

2.5 Adsorption and use of activated carbon in WWTP

Adsorption is a process of one substance accumulating on the surface of another. It is an operation of mass transfer when substances changes phases, in case of wastewater, from liquid to solid. Adsorption is a complex process with various mechanisms working together but is divided into two classes; physical adsorption and chemisorption. (Crittenden *et al.*, 2012). The factors influencing the adsorption process can be divided into 3 parts; Characteristics of adsorbent, Characteristics of adsorbate and Characteristics of adsorption environment (solution). The characteristics of adsorbent include its physical properties such as not only porosity and surface area but the accessibility of the adsorbate molecules to the meso- and micropores. In case of the activated carbon, the mineral matter content and surface chemistry has been found to be important (Moreno-Castilla, 2004; Alves *et al.*, 2018). The physico-chemical properties of the adsorbate (i.e. MPs) such as charge, molecular weight, affinity towards adsorbent, functional group and polarity are important factors. Additionally, hydrophobic compounds are generally easy to remove because hydrophilic compounds have stronger solvent-solute bonds. In case of activated carbon, the characteristics of solvent include pH, ionic strength and temperature of the solution in case of activated carbon (Aktaş and Çeçen, 2011).

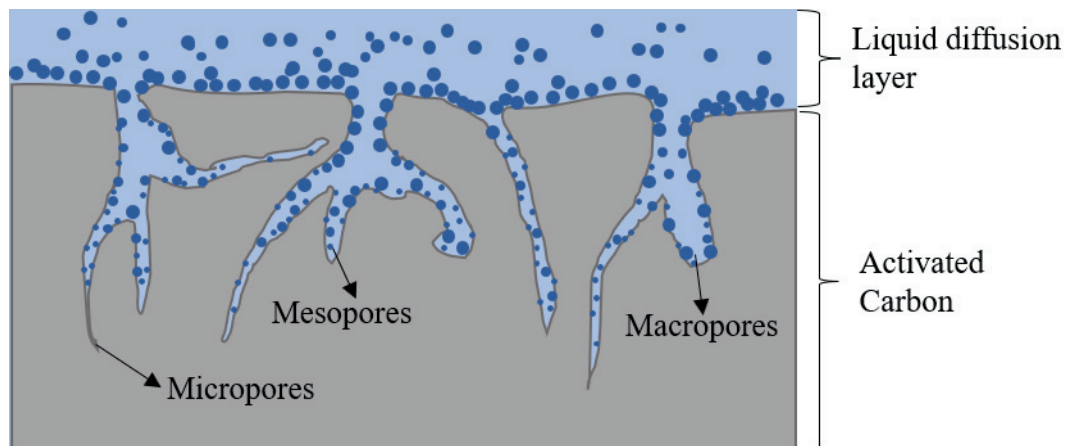


Figure 2.1. Illustrative diagram representing different pore sizes in the activated carbon

Activated carbon (AC) is an amorphous material that has high porosity and high surface area. Even though the name 'Activated Carbon' has a short history, its use however was reported even in 3750 BC. According to a review by Çeçen (2011), the first mention of use of carbon refers back to Hindu literature in 450 BC for purification of drinking water. Nowadays, activated carbon has established its importance and is widely used as an advanced treatment option for the removal of organic contaminants from drinking water and wastewater which can contribute to smell, taste, colour and odour.

It is produced using two main processes; Carbonization followed by activation at high temperatures. It possesses a highly porous nature with a surface area of 600 to 2000 m²/g (Sillanpää and Bhatnagar, 2015). According to the International Union of Pure and Applied Chemistry (IUPAC), the pores of the activated carbon are divided into three sections; macropores (> 50 nm), mesopores (2 to 50 nm) and micropores (< 2 nm) (Fitzer *et al.*, 1995), see Figure 2.1.

There are two types of AC used in the treatment processes; granular activated carbon (GAC) and powdered activated carbon (PAC). The average size of GAC ranges from 0.2 to 0.5 mm whereas PAC ranges from 15 to 25 µm (Aktaş and Çeçen, 2011). GAC is widely used as a filter in the advanced steps of the treatment train for its easy separation from the liquid phase and comparative

easy regeneration. GAC is mainly used after secondary treatment whereas PAC, on the other hand, is used in conjunction with biological treatment for removal of non-biodegradable compounds and requires proper separation technique. Also, Regeneration of PAC is a difficult process. The use of GAC or PAC is decided based on the process description and required efficiency among other factors. In terms of adsorption, PAC has shown faster kinetics than GAC. But to achieve equilibrium condition, PAC often requires recirculation which leads to higher contact times and lower effluent pollutant concentrations whereas GAC, in stationary filtration setup, can achieve equilibrium but with higher effluent pollutant concentrations (Kårelid *et al.*, 2017a;b; Real *et al.*, 2017).

3 Material and Methodology

In this section, the methods and materials used for the research are stated. For the study three experimental setups were used; Membrane filtration assembly, setup for adsorption studies and fractionation setup. For the research, the wastewater was collected from Källby wastewater treatment plant (WWTP) located in the south-west part of Lund. It receives wastewater from the city of Lund serving about 120,000 residents. In 2015, the daily flow was reported to be 31,000 m³/day. The treatment train include screening, grit chamber, primary sedimentation and biological treatment followed by post-precipitation for extended phosphorus removal (VASyd, 2016). The samples for the experiments were collected at secondary sedimentation tank.

The research was divided into three studies. Initially, six membranes, two microfiltration and four ultrafiltration membranes, were selected and the effect of filtration on the performance of adsorption was evaluated. It was expected that removal of compounds having molecular weight more than MWCO could improve the performance of activated carbon. In the second study, three ultrafiltration membrane permeates were used with three pharmaceutical micropollutants. Later, as the solubility of organic matter affect the competition for active adsorption sites, a comparative study with filtered and unfiltered samples were conducted and the effect of removal of hydrophobic and hydrophilic compounds was evaluated.

3.1 Experimental setup and materials

3.1.1 Membrane Filtration

In this study, a crossflow filtration unit with sheet membranes was used (as shown in Figure 3.1). The same assembly was previously used by Al-Rudainy *et al.* (2017). The feed water was stored in a 15 L tank connected with temperature controlled (MCM, Shinko Technos Co. Ltd., Osaka, Japan) immersed heater (Backer, Elektro-Värme AB, Sweden). A frequency converter (ELEX 4000, Bergkvist & Company AB, Gothenburg, Sweden) connected to positive displacement pump (Hydra-cell D25XL, Wanner, Minneapolis, USA) was used to achieve required flowrate. Two digital pressure gauges (DCS40.0AR, Trafag AG, Bubikon, Switzerland) were connected on the feed and retentate line and the average of these two pressures was considered as the transmembrane pressure (TMP). To reach the required pressure, a valve was connected on the retentate line along with a digital flowmeter (FCH-34-PP-Chemical, B.I.O-Tech e.K., Vishofen, Germany) to evaluate crossflow velocity (CFV). To calculate flux, permeate sample collection bottles were placed on a weighing scale (PL6001-1, Mettler Toledo Inc., Ohio, USA) and it was assumed that the specific gravity of the permeate is 1000 kg/m³. The surface area of the membranes was 19.6 cm². In this setup, 3 different membranes can be used at a same time and it was assumed the difference in TMP and CFV between the 3 membranes was assumed to be negligible. All of the membrane units are of same dimensions. Due to same dimensions, the crossflow depth at all of the membranes is same. Therefore, to maintain CFV, the flow was monitored. All of the membranes used were made by Alfa Laval (Lund, Sweden). Different membranes were used in each study, they are mentioned in the respective subsections of the methodology.

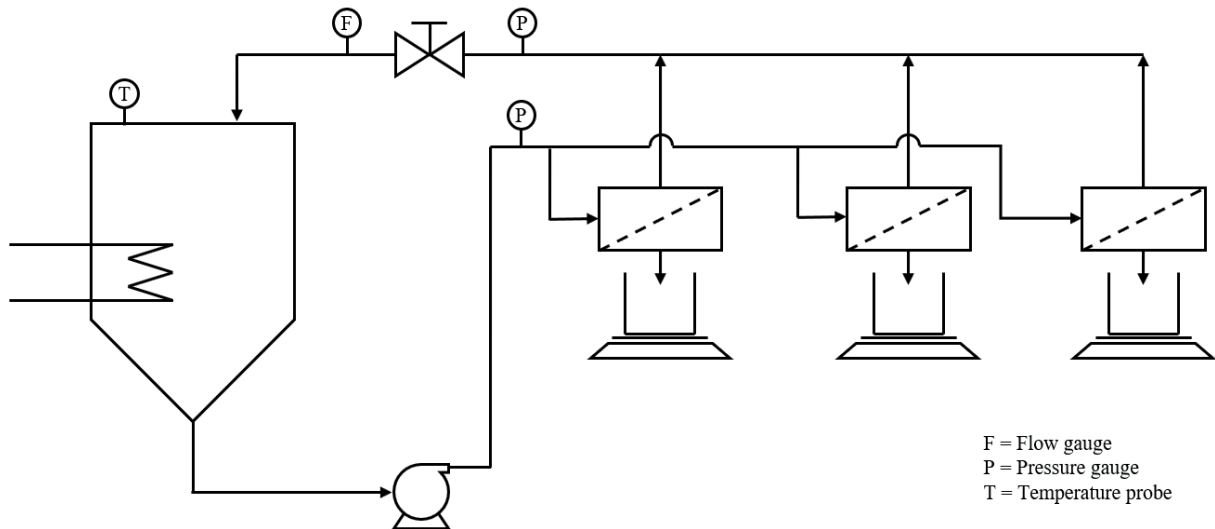


Figure 3.1. Experimental filtration setup.

The cleaning of the membrane is an importance step before start of the filtration process. The process is carried out at a higher temperature rated by cleaning chemical concurrent with the membrane (recommended) operating limits. In this study, the membranes used were cleaned using chemical from Ultrasil 110 (Ecolab AB, Älvsjö, Sweden). The solution was rated for the dosage ranging from 0.05% to 1% with pH range from 10.8 to 11.2. Considering the data sheets from the membranes and cleaning agent, the cleaning is done for temperature of 50°C with 30 minutes of contact time. Initially, 4 L of deionised (DI) water at room temperature was used and the temperature was slowly increased to 50°C at 1 bar TMP to avoid shocking the membranes. After reaching the temperature, 25g of Ultrasil 110 was mixed with 1 L of DI water heated to 50°C. This solution was added in the feed tank and recirculated, making the concentration of the 5 L solution to 0.5%. After 30 minutes, the solution was drained and the system was rinsed with DI water to remove residual cleaning agent and slowly bring the assembly to room temperature. Then, pure water flux (PWF) was evaluated using DI water and reaching the predefined pressure and CFV.

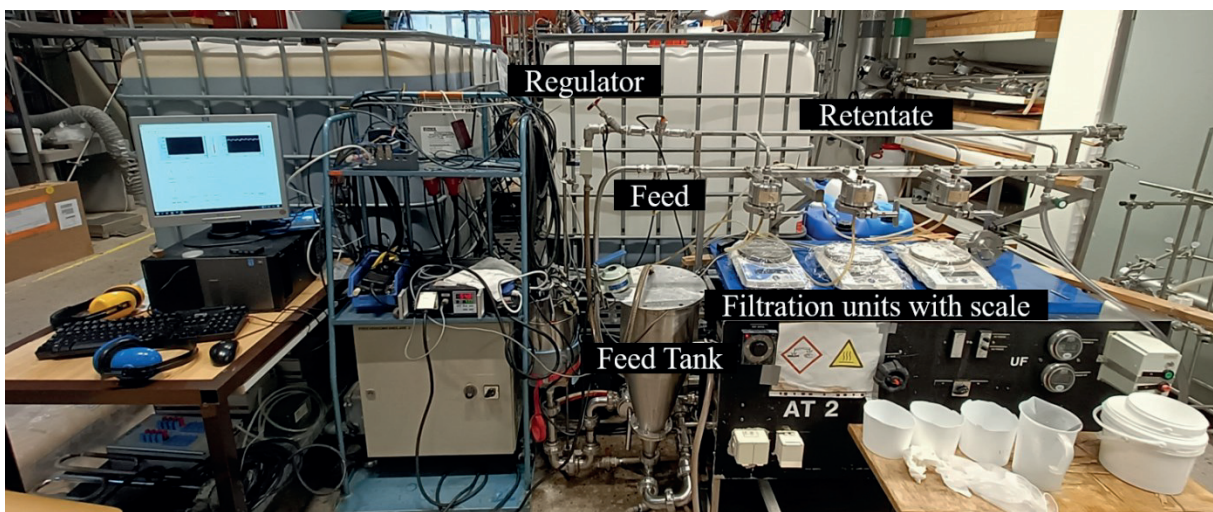


Figure 3.2. Filtration assembly.

The cleaning process is repeated multiple times until PWF is found similar between the consecutive cycles. Additionally, organic carbon was evaluated between every PWF measurement

to identify any additional interference due to insufficient cleaning process. DOC was analysed on a TOC analyser (TOC-L, Shimadzu Europa GmbH, Germany) fitted with auto sampler (ASL, Shimadzu Europa GmbH, Germany). After cleaning process, the assembly was rinsed with DI water multiple times to remove any residual chemical used during the cleaning. The assembly (Figure 3.2) was then used for filtration of the sample collected from the WWTP. Initially, the retentate and permeate was recirculated. After reaching required TMP and CFV, the permeates were collected in glass bottles of required volume. During the filtration process, the change in TMP over time was recorded using LabVIEW (National Instruments). The recorded data was further studied to evaluate sudden change in flux which could indicate leakages and/or other problems.

3.1.2 Resin fractionation of NOMs and UV-vis spectral scan

To study the NOMs fractions, resin fractionation is one of the fastest and most cost-effective method available. As mentioned earlier, it is a simplistic way to define the NOMs as hydrophobic and hydrophilic. Using this method, different fractions of the NOMs can be separated and further evaluated as needed.

Three sets of resin columns were used in the study. The setup used for the study was previously used by Karlsson (2018) for fractionation of NOMs in the drinking water. Three types of resins from SIGMA ALDRICH CHEMIE GMBH (Steinheim, Germany) were used; Superlite DAX-8, Amberlite XAD-4 and Amberlite IRA958 chloride. As previously mentioned in section 2.4, XAD resins (including DAX-8 and XAD-4) are used for adsorption of hydrophobic compounds whereas IRA is used for removing charged hydrophilic compounds and the filtrate from IRA contains only neutral hydrophilic fraction (NEU). Amberlite XAD-8 is no longer sold commercially and is replaced by Superlite DAX-8, hence used in this study. The bed volume (BV) of each column was selected to be 15mL. The DAX was used in removal of very hydrophobic compounds (VHAs) at 2 pH, XAD for slightly hydrophobic compounds (SHAs) at 2 pH and IRA for charged hydrophilic compounds (CHAs) at 8 pH. A peristaltic pump (ECOLINE VS-MS/CA8-6, ISMATEC, Wertheim, Germany) was used to ensure flow of 3 mL/min. The water was pumped from bottle through columns using a peristaltic pump. A representative column setup is illustrated in Figure 3.3. For ease of operation, the actual setup included 4 columns in each set (as illustrated in Figure 3.4). Each sample was passed through 2 columns to collect more filtrate without any desorption and regeneration.

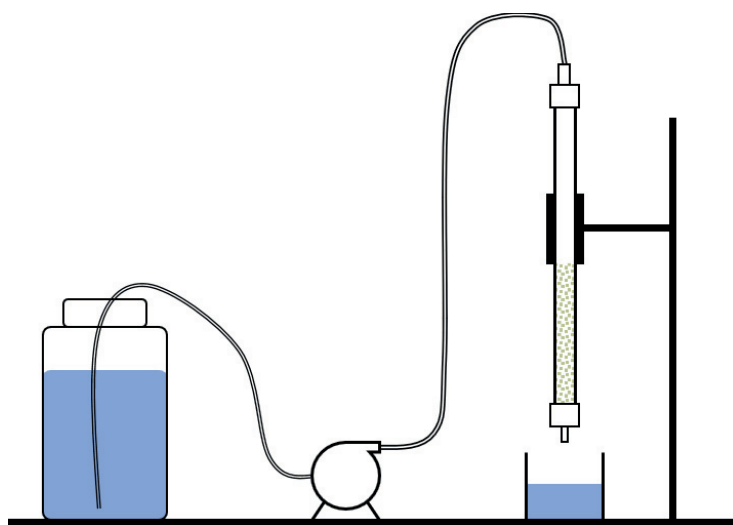


Figure 3.3. Fractionation assembly with resins in the column.

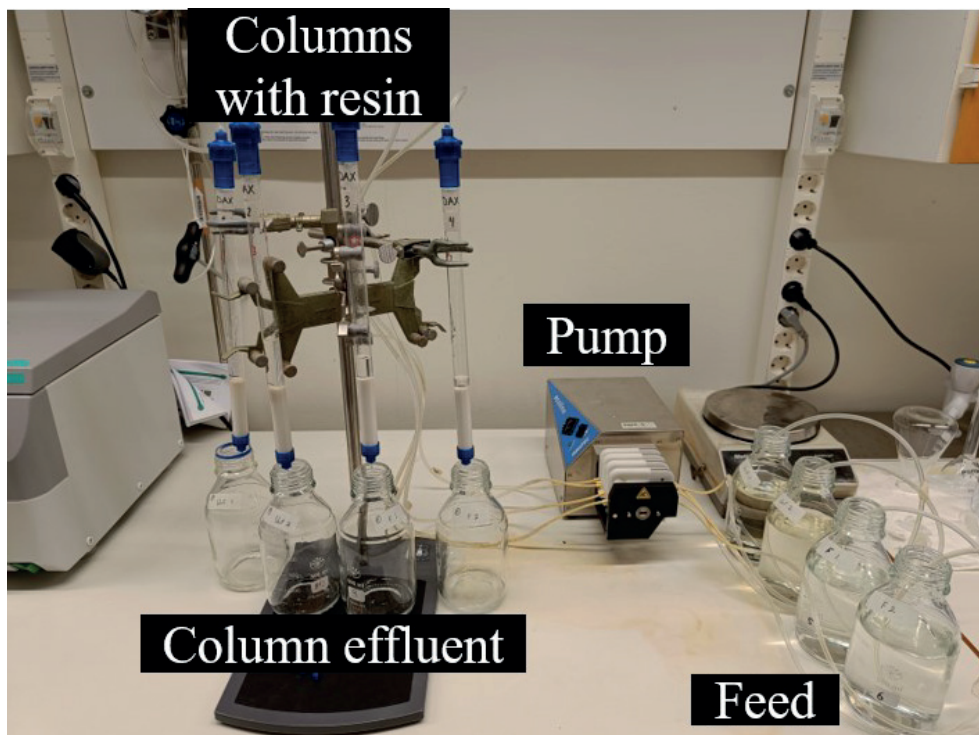


Figure 3.4. Columns used for the fractionation of NOMs.

Pre-cleaning of the resins is an important process especially for DAX as it is a salt imbibed resin. Initially, the resins are washed with DI water. Double the BV i.e. 30mL of HPLC grade methanol was used to wash by continuous stirring for one hour. Then the same process was repeated with HPLC grade acetonitrile. The resins were washed with DI water and transferred to the columns. Lastly, the column was rinsed with 2 BV of DI water to displace remaining traces of acetonitrile.

After precleaning, all of the resins need to undergo a desorption and regeneration process. Initially, for DAX and XAD, the desorption was done using 0.1M NaOH. Four BV of NaOH was pumped through the columns and then the column was rinsed with DI water. Regeneration was done using four BV of 0.1M HCl. For IRA, same procedure was followed except the desorption was done with 1M NaOH and 1M NaCl and regeneration with 1M HCl and 1M NaCl. All of the flow rates were set to 3 mL/min. Desorption and regeneration was done after fractionation studies as well. Both the precleaning and desorption-regeneration methods are based on the research done by Leenheer (1981), Piper *et al.* (2010) and Karlsson (2018).

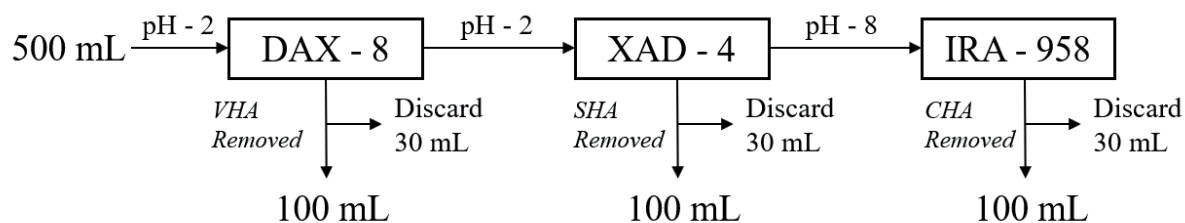


Figure 3.5. Process of fractionation. Diagram redrawn with permission from Stina Karlsson. VHA – Very hydrophobic compounds, SHA – Slightly hydrophobic compounds and CHA – Charged hydrophilic compounds.

After desorption and regeneration, the columns were prepared for the sample. Unfiltered wastewater sample was filtered through 0.45 μm filter to avoid clogging of the column due to particulates. Then, 500 mL of sample was then passed through the first set of columns containing DAX. Initially, twice the BV of column filtrate was discarded and 470 mL of water collected out of which 100 mL (without VHA fraction) was used for further analysis. Remaining 370 mL of filtrate was used in XAD column and same process was repeated as illustrated in Figure 3.5. From XAD, the sample lacked VHA and SHA fractions. Lastly, 240 mL of sample was passed through IRA column and 210 mL of sample present with only NEU (neutral hydrophilic) fraction was collected for further studies. To calculate the concentrations of each fraction present in the sample, each filtrate was analysed for DOC on TOC analyser (see section 3.1.1) and following set of equations were used (Karlsson, 2018).

$$VHA = DOC_{\text{unfractionated sample}} - DOC_{\text{DAX filtrate}} \quad (1)$$

$$SHA = DOC_{\text{DAX filtrate}} - DOC_{\text{XAD filtrate}} \quad (2)$$

$$CHA = DOC_{\text{XAD filtrate}} - DOC_{\text{IRA filtrate}} \quad (3)$$

$$NEU = DOC_{\text{IRA filtrate}} \quad (4)$$

To study the aromatics features present in the samples, UV absorbance at 254 nm was used. The special use of UV_{254} and SUVA is established by various researchers (Sillanpää *et al.*, 2015) and therefore, these measurements were used to evaluate the dominant fractions based on SUVA. The absorbance was done using the DR6000 (Hach Lange GmbH, Düsseldorf, Germany). Furthermore, a spectral scan was done using wavelength 190 to 600 nm (in UV and visible spectrum) with an increment of 1 nm. This was used to study the change in absorbance over the spectrum for different samples of water tested in the study.

3.1.3 Synthetic radiolabelled pharmaceutical compounds

The detection of a specific compounds is a costly and time-consuming method. Therefore, in this study, synthetic compounds were used. During synthesis, specific carbon in the chain is replaced by ^{14}C . Even though synthesised compounds are radioactive, they possess same physico-chemical properties as of the original compound. Due to the radioactivity of the compounds, they can be easily analysed using a liquid scintillation unit. In this study, three pharmaceutical compounds were selected. Carbamazepine (carbonyl- ^{14}C) and diclofenac (RS-carboxyl- ^{14}C) from Hartmann Analytic (Braunschweig, Germany) and sulfamethoxazole (phenyl ring- ^{14}C) from Izotop (Budapest, Hungary), see Figure 3.6. The characteristics of the compounds are presented in the Table 3.1.

Table 3.1. Properties of the Pharmaceutical compounds used in the study

| Pharmaceuticals | Type/use | MW (g/mol) | log Kow* | log pKa* | Charge at pH 7 |
|------------------|-------------------|------------|----------|----------|----------------|
| Carbamazepine | Antidepressant | 236.27 | 2.45 | 13.9 | Neutral |
| Diclofenac | Anti-inflammatory | 296.15 | 4.51 | 4.1 | Negative |
| Sulfamethoxazole | Antibiotic | 253.24 | 0.89 | 1.8; 5.8 | Negative |

*Sourced from Margot *et al.* (2013)

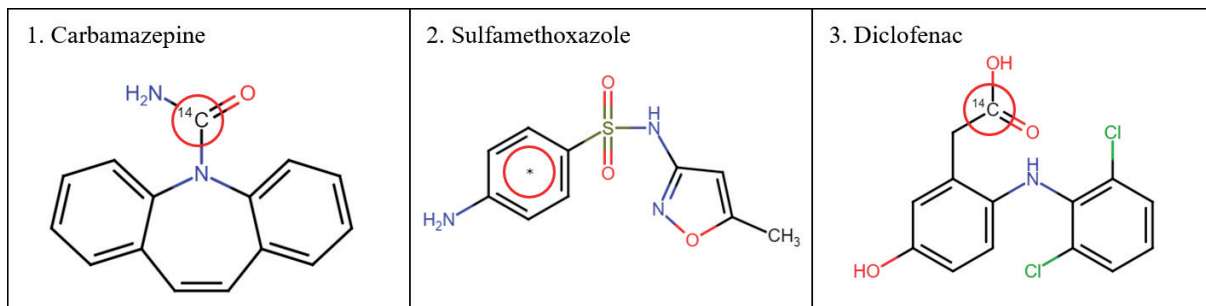


Figure 3.6. Pharmaceutical MPs used in the study with position of radiolabelled carbon shown in red circle. For Sulfamethoxazole, the radiolabelled carbon is situated in the phenyl ring indicated by *.

3.1.4 Adsorption study using PAC

The permeate from the membrane filtration was used for the adsorption studies. The permeates were spiked with synthetic radio-labelled (^{14}C) pharmaceutical compounds with concentration of $1\ \mu\text{Ci/L}$. Various high-performance polypropylene (PP) conical centrifuge tubes (VWR, Stockholm, Sweden) of either 15mL or 50mL were prepared. PAC (NORIT SAE SUPER, CABOT, Amersfoort, Netherland; particle diameter $\sim 2\ \mu\text{m}$ and BET surface area $1150\ \text{m}^2/\text{g}$) was diluted to $1\ \text{g/L}$ in DI water and kept in suspension using magnetic stirrer (MIX drive 1, 2 Mag, Munich, Germany) fitted with regulator (MIX control eco, 2 Mag, Munich, Germany) to ensure complete mix conditions. The PAC doses, pharmaceutical compounds and sample volumes were varied in each study and are mentioned in respective subsections. After addition of the PAC, the tubes are placed on a mechanical horizontal shaker (HS 501 Digital, IKA Labor-technik, Staufen, Germany) for desired length of time and samples were collected in 1 mL Eppendorf[®] tubes (Eppendorf AG, Hamburg, Germany) at different time intervals.

For analysis of the sample, the method used was similar to the one described by Betsholtz *et al.* (2021). The collected samples were centrifuged (Z 216 M, Hermle Labortechnik GmbH, Wehingen, Germany) at 13000 rpm for 5 minutes to ensure the separation of PAC and 0.8 mL supernatant was stored in the Eppendorf[®] tubes. 0.4 mL of supernatant is then mixed with 3.6 mL of liquid scintillation cocktail (Hionic-Fluor[™], Perkin Elmer, Hågersten, Sweden) in a 6 mL polyethylene vial. Prepared samples were analysed in a liquid scintillation unit (Tri-Carb 4910TR, Perkin Elmer, Hågersten, Sweden, see Figure 3.7) for radioactivity in counts per minute (CPM). The initial sample without PAC addition was analysed in triplicates and rest of the experiment samples were analysed in singles.

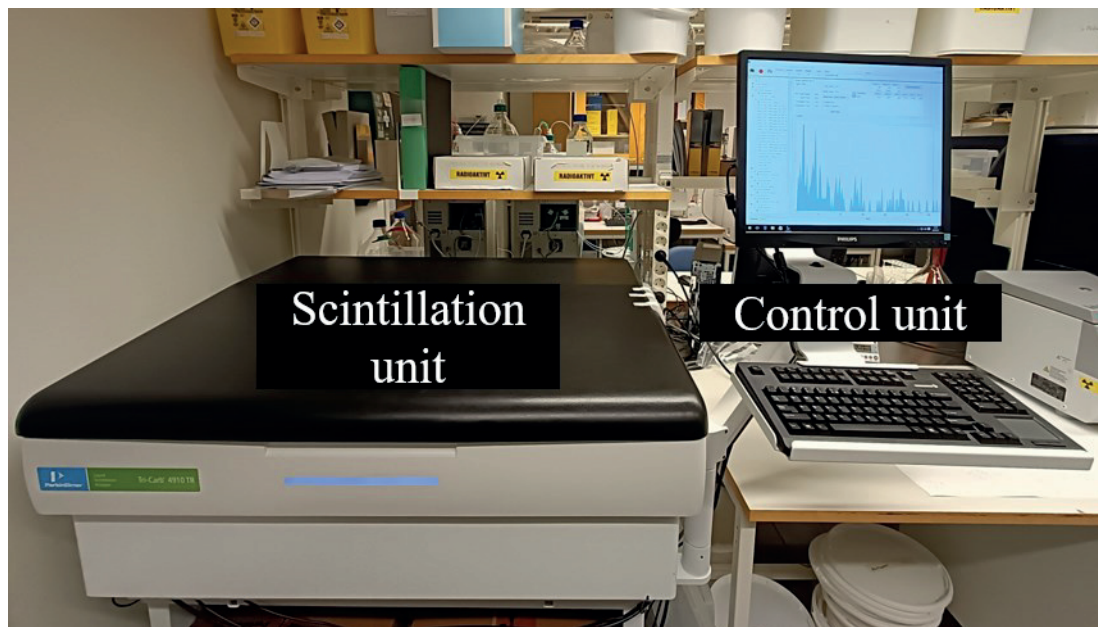


Figure 3.7. Liquid scintillation unit from Perkin Elmer

To convert CPM into the concentration of the ^{14}C -labelled pharmaceutical compounds, a conversion factor was used which was evaluated based on the specific radioactivity, molecular mass and initial concentration. Table 3.2 represents conversion factors for the ^{14}C -labelled pharmaceutical compounds. The level of quantification for liquid scintillation units was evaluated and the values lower than 45 CPM are ignored due to high possibility of interference from the natural background radiation. In this study, since the initial concentration introduced in the samples was 1000 CPM, the values ignored that are lower than 45 CPM indicate the removal efficiency of more than 95.5%.

Table 3.2. Conversion factors for the used synthetic pharmaceutical compounds based on their radioactivity

| Compound | Conversion factor ($\mu\text{g}/\mu\text{Ci}$) |
|------------------|--|
| Carbamazepine | 10.55 |
| Diclofenac | 5.29 |
| Sulfamethoxazole | 12.55 |

Note: The conversion factors were evaluated based on the radioactivity and the molecular weight of the compound.

The PAC studies were concluded with development of isotherms to study adsorption process for removal of selected compounds. An isotherm is a mathematical representation of the adsorption process of a MP with respect to its phase in the solution which has reached its equilibrium state at a constant temperature. In equilibrium state, the rate of adsorption and desorption of the MP is same. An isotherm indicates the adsorbed phase and liquid phase of the MP. In this study, Freundlich isotherm is used as it is widely used for the application of AC. It is an empirical equation and given as (Freundlich, 1909)

$$\frac{x}{m} = q_e = K_F C_e^{1/b} \quad (5)$$

Where, x is the amount of adsorbate adsorbed, m is the amount of adsorbent which is replaced by q_e which is the amount of adsorbate per unit adsorbent at equilibrium, C_e is equilibrium concentration of adsorbate in liquid phase and this equation in linear form can be rewritten as

$$\log(q_e) = \log(K_F) + \frac{1}{b} \log(C_e) \quad (6)$$

K_F and $1/b$ are Freundlich constants and represent adsorption capacity and adsorption intensity, respectively. Lower values of the slope (i.e. $1/b$) indicate that the AC is more efficient for lower doses which is highly desirable (Aktaş and Çeçen, 2011).

In this study, a MATLAB code was developed using equation 5 for easy fitting of the data to the Freundlich isotherm (see Appendix I). The constants were obtained along with the goodness of fit (R^2) values. The isotherms were not developed for the R^2 values less than 90%.

3.2 Experimental methods

3.2.1 Adsorption of pharmaceuticals in the permeates of membranes with different MWCO

This study was conducted to evaluate the effect of removal of DOMs based on size fractionation method (i.e. membrane filtration) on the adsorption of ^{14}C -labelled carbamazepine using PAC. The biologically treated wastewater (from secondary clarifier) was collected on February 2nd, 2022 from Källby WWTP. It was first filtered through 6 membranes. The cleaning of the MF and UF membranes was done on flow of 12 ± 0.2 L/min with TMP of 1 ± 0.1 bar. Their operating parameters of the membranes are mentioned in the Table 3.3.

Two permeates from membrane filtration (MF – 100 nm and UF – 5 kDa) were selected for the PAC studies in addition to unfiltered wastewater. The MWCO of selected MF membrane was high indicating that even though some compounds have been removed, a significant portion of HMW compounds (i.e. compounds with molecular weight more than 10 kDa which generally has less adsorbility towards activated carbon (Velten *et al.*, 2011)), are still present in the permeate whereas for UF membrane, most of the HMW compounds are expected to be removed. This was done to evaluate the effect on adsorption studies.

Table 3.3. Operating parameters of the membranes used in initial study

| Pore Size (nm) | MWCO (kDa) | Type | TMP (bar) | Flow (L/min) | Details |
|----------------|------------|------|-------------|--------------|---------|
| 500 | - | MF | 1 ± 0.1 | 12 ± 0.2 | MFP-5 |
| 100 | - | MF | 1 ± 0.1 | 12 ± 0.2 | MFG -7 |
| ~ 14* | 100 | UF | 1 ± 0.1 | 12 ± 0.2 | GR40PP |
| ~ 8* | 25 | UF | 2 ± 0.1 | 12 ± 0.2 | GR60PP |
| ~ 5* | 5 | UF | 2 ± 0.1 | 12 ± 0.2 | GR90PP |
| ~ 3* | 2 | UF | 4 ± 0.1 | 12 ± 0.2 | GR95PP |

Note: The values of pore sizes* for the UF membranes are approximate and obtained from Cheryan (1998). In UF terminology, these values are generally presented in molecular mass (kilo Daltons) rather than pore sizes.

All three were spiked with ^{14}C -labelled carbamazepine and 8 PAC doses (0, 2.5, 5, 7.5, 10, 16, 20 and 40 mg/L) were introduced. Samples were collected at 5 intervals (0.5, 1, 2, 6 and 24

hours). The samples were centrifuged and analysed on scintillation unit. It was found that the samples collected at 24 hours have nearly reached equilibrium condition and based on this data isotherms were developed.

3.2.2 Effect of three UF membranes on adsorption of three pharmaceuticals

The second study was designed based on the results of initial study. The wastewater from secondary clarifier was collected on March 13th, 2022 from Källby WWTP. As the results of first study indicated higher DOC removal for UF at lower PAC doses, a deviation in adsorption isotherm for the same and to further investigate the influence of fractions within a small range of MWCO, 3 UF membranes were selected for the study; 25, 5 and 2 kDa. In this study, the cleaning process of membrane was repeated thrice to ensure proper cleaning. Each cleaning was followed by a PWF with DOC measurement. After a similar value in cleaning 2 and 3 for PWF and DOC, the membranes were used for filtration of wastewater. A higher TMP of 5 ± 0.3 bar was opted in order to achieve higher flux with same flow of 12 ± 0.2 L/min. The raw wastewater was then filtered through $0.45 \mu\text{m}$ to remove suspended solids but hereon onwards mentioned as unfiltered wastewater.

In addition to the four samples (i.e. unfiltered wastewater, 25, 5 and 2 kDa permeate) deionised (DI) water and tap water from the Department of Chemical Engineering were included to study the adsorption. The tap water available was potable and sourced from Bolmen lake. All the samples were spiked with four ¹⁴C-labelled pharmaceutical compounds; Carbamazepine, sulfamethoxazole and diclofenac. As the process only measures the radioactivity in the sample, all of the compounds were introduced separately. For each compound, the different PAC doses were considered, as illustrated in Table 3.4 .

Table 3.4 based on their adsorption performance. Additionally, a study of effect on DOC was also carried out to evaluate the overall performance of the PAC doses. tap water, unfiltered wastewater and 3 UF permeates were used for the PAC study. Based on the first study, it was considered that the state of equilibrium was reached after 24 hours. Higher doses were selected for the study.

Table 3.4. Selected PAC doses for the second study in mg/L

| Carbamazepine | Diclofenac | Sulfamethoxazole | DOC |
|---------------|------------|------------------|-----|
| 0 | 0 | 0 | 0 |
| 2.5 | 2.5 | 2.5 | 10 |
| 5 | 5 | 5 | 25 |
| 7.5 | 7.5 | 7.5 | 50 |
| 10 | 10 | 10 | 75 |
| 15 | 15 | 15 | 100 |
| 20 | 20 | 20 | 150 |
| 40 | 40 | 40 | 200 |
| - | 60 | 60 | - |
| - | 80 | 80 | - |

3.2.3 Adsorption of pharmaceuticals in fractionated wastewater based on hydrophobicity/hydrophilicity

In addition to previous studies, a fractionation of DOC was done on the unfiltered wastewater and 2 kDa permeate to evaluate the effect of removal of different fractions on the adsorption

pattern of the pharmaceutical compounds. This was done using the fractionation method as mentioned in section 3.1.2. Two samples were used; Unfiltered wastewater and 2 kDa membrane permeate. The details of the fractionated samples are shown in Table 3.5.

Table 3.5. Samples used for fractionation and the fractions remained in the column permeate

| Sample | Sample filtered | Resin used | Removed fraction | Fractions remained in resin filtrate |
|---|------------------------|-------------------|-------------------------|---|
| Unfiltered sample | Unfiltered sample | DAX | VHA | SHA, CHA and NEU |
| | DAX filtrate | XAD | SHA | CHA and NEU |
| | XAD filtrate | IRA | CHA | NEU |
| Filtered (2 kDa membrane permeate) | Filtered sample | DAX | VHA | SHA, CHA and NEU |
| | DAX filtrate | XAD | SHA | CHA and NEU |
| | XAD filtrate | IRA | CHA | NEU |

Note: This table is based on the process of fractionation, illustrated in Figure 3.5.

After fractionation, it was ensured that the pH of the samples used for further investigations were brought back to 7 as it can affect the adsorption mechanisms. Later, Carbamazepine was introduced in each of the fractionated sample and 8 PAC dosed were selected; 0, 2, 4, 6, 8, 10, 15, 20 mg/L. Samples were analysed after 24 hours of contact time. Furthermore, UV spectral scan for absorbance was calculated for all the samples from wavelength 190 to 600nm (section 3.1.2).

4 Results and Discussion

In this section, the results of the different studies are presented along with relevant findings and interpretations of the results. First section establishes the results and discussion for the use of MF and UF and its effect on the PAC performance. Using the findings of the first study, second study evaluates different UF membranes to evaluate removal of three pharmaceuticals. Lastly, the effect of DOC fractions based on hydrophobicity/hydrophilicity on the PAC studies is presented.

4.1 The effect of membrane filtration on adsorption studies

In this study, initially six membrane filters were used. After studying the DOC concentrations (shown in Table 4.1), two membrane permeates were selected for PAC experiments, each from UF and MF along with unfiltered wastewater. The main objective of this study was to identify the time to reach the equilibrium state for PAC studies and to select best suited membranes for further investigations.

Table 4.1. DOC concentrations of unfiltered sample, MF permeate and UF permeate

| Samples | Pore Size (nm) | MWCO (kDa) | Type | DOC (mg/L) |
|-------------------------------|----------------|------------|------|------------|
| Unfiltered | - | - | - | 8.10 |
| Membrane filtration permeates | 500 | - | MF | 6.62 |
| | 100 | - | MF | 5.20 |
| | - | 100 | UF | 4.58 |
| | - | 25 | UF | 4.34 |
| | - | 5 | UF | 3.22 |
| | - | 2 | UF | 3.48 |

The DOC measurements (see Table 4.1) showed higher reduction for finer membranes. MF showed 18 to 35% reduction in DOC whereas for UF permeate, 43 to 60% reduction was observed. This significant reduction in DOC was considered to be an important factor in the adsorption studies with PAC studies because lower DOC concentration would reduce the competition for pharmaceutical compounds. Lowest DOC value in MF was observed for 100 nm membrane permeate and in UF was 5 kDa membrane. Therefore, these two permeates along with unfiltered wastewater sample were used for the PAC studies.

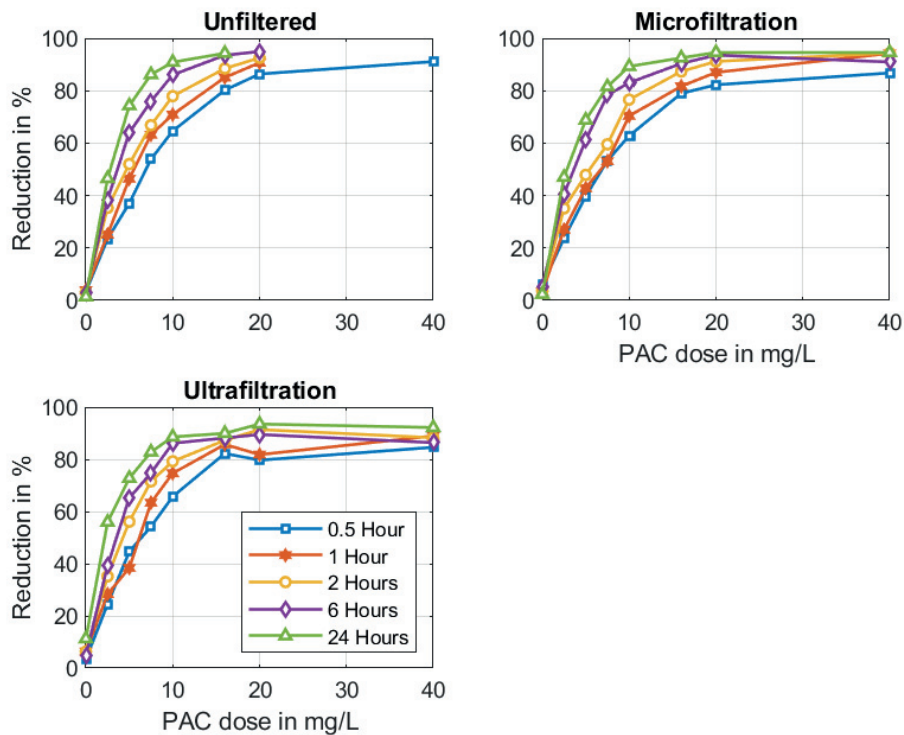


Figure 4.1. Removal of carbamazepine using PAC, comparison between contact times for each sample.

As shown in Figure 4.1, it was obvious that for higher PAC doses and contact times the respective removal efficiency increases but mainly, the study indicated that for 24-hours of contact time a near-equilibrium state was reached. The equilibrium state in activated carbon studies can be defined as a state at which the rate of desorption and adsorption of the compound being investigated is same and the concentration of the compound present in liquid phase remains constant. This was observed because for a low PAC dose of 2.5 mg/L, the removal efficiency for all three samples was observed to vary from 25% to 55% for all contact times but for the highest PAC dose of 40 mg/L, this gap was smaller and the removal was observed to be in the range of 85 to 95%. Especially, comparing the durations 6 and 24 hours, the change in percent removal for all three samples was not significant. Furthermore, at high PAC doses (>20 mg/L) the removal of micropollutant is less dependent on contact times.

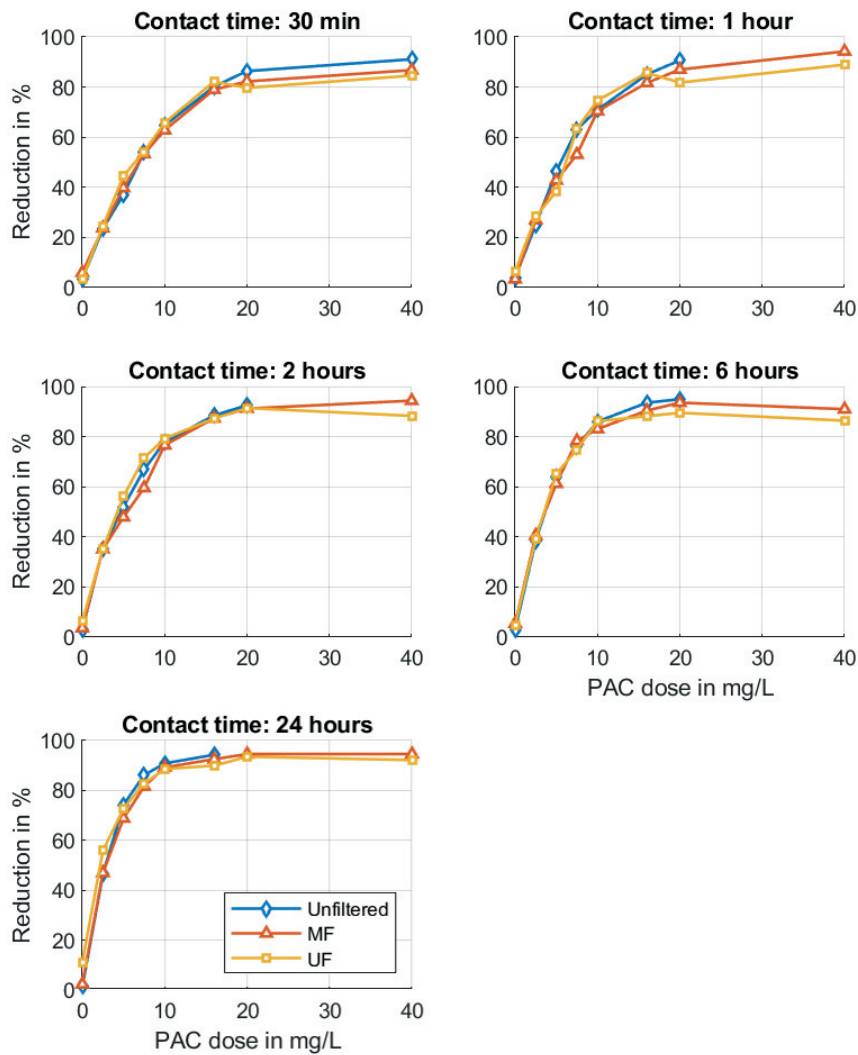


Figure 4.2. Removal of carbamazepine using PAC, comparison between unfiltered sample and two membrane permeates for each time interval.

The Figure 4.2 shows the comparison between samples for respective contact times. It indicates no significant change between the samples. For contact time of 30 minutes, more than 80% removal of carbamazepine was observed for PAC dose of 20 mg/L among all three samples used in the study whereas for contact times 1 and 2 hours it was 16 mg/L. Furthermore, with 6 hours of contact time and PAC dose of 10 mg/L, more than 80% removal of carbamazepine was found in all of the samples and as the contact time was increased to 24 hours, the PAC dose reduced to 7.5 mg/L. These findings are consistent with a study by Boehler *et al.* (2012) that concluded that for the 5 to 10 mg DOC/L in wastewater, a PAC dose of 10-20 mg/L is sufficient for more than 80% removal of MPs. Additionally, these results are consistent with the studies done by Newcombe *et al.* (1997) which suggested that the presence of HMW compounds (>30 kDa) does not have a significant impact on the removal process of LMW compounds (<500 Da).

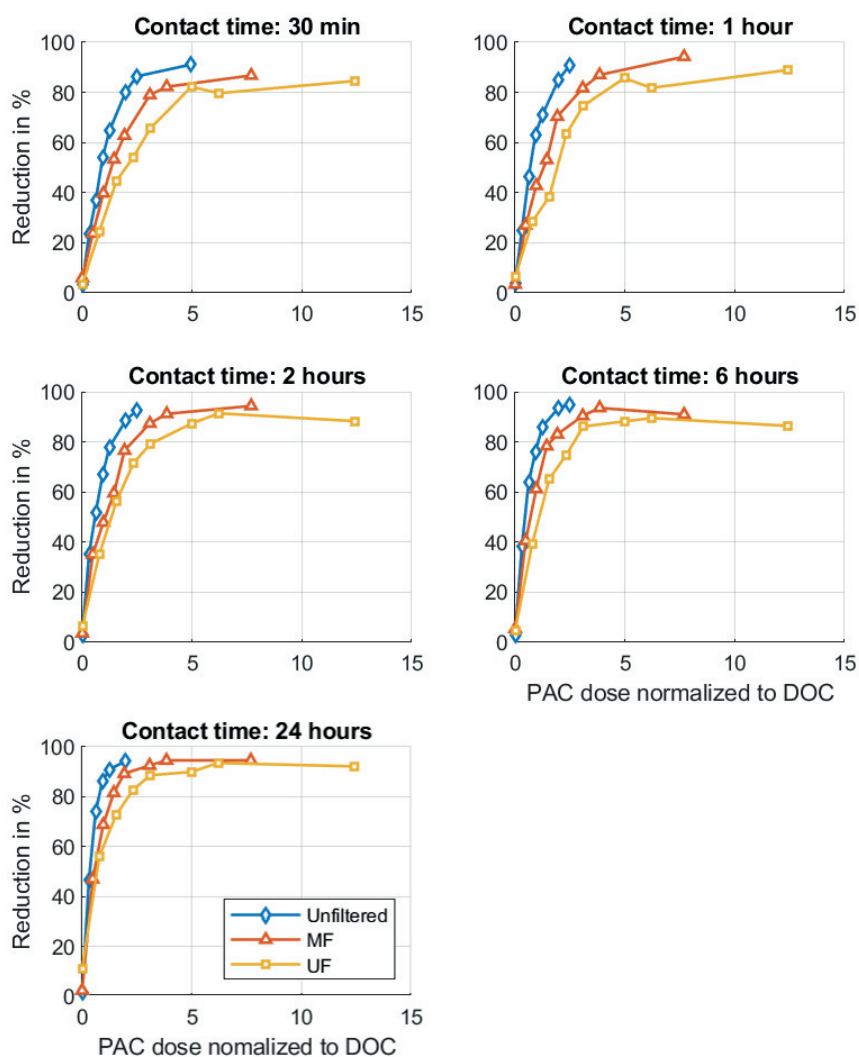


Figure 4.3. Reduction of carbamazepine with DOC normalised PAC doses and comparison between unfiltered sample and two membrane permeates for each time interval.

The DOC normalized PAC doses, Figure 4.3 illustrate that samples with high DOC concentrations present higher removal of carbamazepine. This is due to the fact that the DOC concentrations in the unfiltered wastewater is higher. As suggested by Velten *et al.* (2011) the most competition is presented by the LMW compounds (~500 up to 4000 Da), furthermore, presence of HMW compounds (>30 kDa) does not significantly affect the adsorption performance of LMW compounds (Newcombe *et al.*, 1997; Zietzschmann *et al.*, 2014). Therefore, an ideal graph should indicate that the reduction for PAC doses normalized to DOC should be the same for all samples or maybe slightly higher for UF because a portion of ‘intermediate’ molecular weight compounds (between 30 and 4 kDa) are removed. Since this is not the case, the use of DOC as a normalizing factor needs to be further investigated.

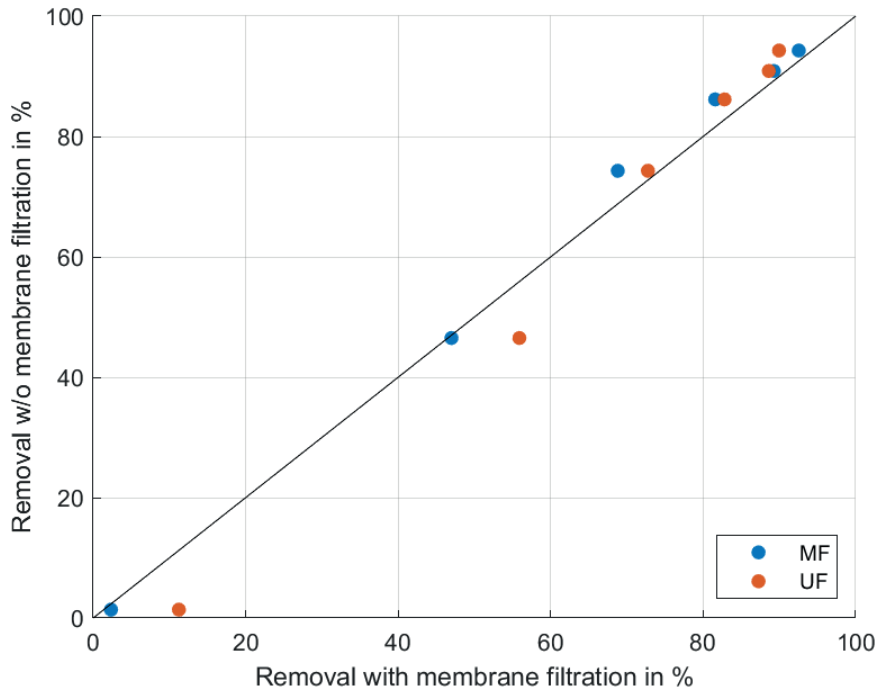


Figure 4.4. Comparison for removal of carbamazepine for filtered v/s unfiltered sample for respective PAC doses. A point on 45° line suggests that for an any given PAC dose removal in membrane permeate and unfiltered sample is same.

The comparison between the unfiltered and filtered wastewater for removal of carbamazepine, Figure 4.4, suggests that there is no significant change in reduction between the samples but for lower PAC doses a small deviation for UF permeate can be observed indicating a slightly higher removal.

4.2 Effect of UF permeates on adsorption of different pharmaceutical compounds

The previous study (Figure 4.4) indicated a slight increase in removal efficiency for the UF at lower doses. Additionally, the adsorption isotherm developed for the same (Figure II.1 in Appendix II) also showed a deviation compared to unfiltered and MF samples, hence, three UF membranes were selected for this study and PAC studies were conducted on three pharmaceutical compounds. In previous experiment, for 2 kDa membrane, very low flux was observed for TMP at 2 bars, later it was increased to 4 bars. Therefore, to produce sample with identical conditions and higher flux, TMP of 5 bars was opted and 2 litres of permeate was collected from each membrane. The study also included two more samples. DI water provided an ideal condition for the pharmaceutical compounds to adsorb onto the PAC without any interference from DOM. Furthermore, as most of the current research is based on the NOMs present in the drinking water, in this study, to develop better understanding of any similarities about the adsorption processes between freshwater (NOM) and wastewater (DOM) with respect to micropollutant removal using activated carbon, tap water was included.

Table 4.2. DOC concentration of the samples used in the second study

| Samples | MWCO | DOC (mg/L) |
|-----------------------|--------|------------|
| DI water | - | 0.02 |
| Tap water | - | 2.26 |
| Unfiltered wastewater | - | 9.09 |
| UF permeate | 25 kDa | 4.72 |
| | 5 kDa | 3.73 |
| | 2 kDa | 3.47 |

The DOC observed in the DI water (Table 4.2) was extremely low considering the fact that it is treated for research use and expected to be sparse in organic carbon. But a small amount of organic carbon is expected to be present as it is not practicable to produce carbon-free water. Compared to DI water, the DOC content in the tap water was considerably high indicating the presence of NOMs in the sample and the value was found to be consistent with the periodic testing done by VA Syd for quality purposes (VASyd, 2022). For the biologically treated wastewater (i.e. unfiltered sample) the value of DOC was observed to be slightly higher than the sample collected for the previous study (Table 4.1).

The reduction of DOC in the membrane permeates was observed to be 48, 59 and 61% for 25, 5 and 2 kDa, respectively, again similar to the reduction observed in previous study. This indicates that the molecular weight distribution of DOM in the two samples collected for first study and second study were similar and hence after membrane filtration, a significant change in percent reduction among two sampling periods was not observed.

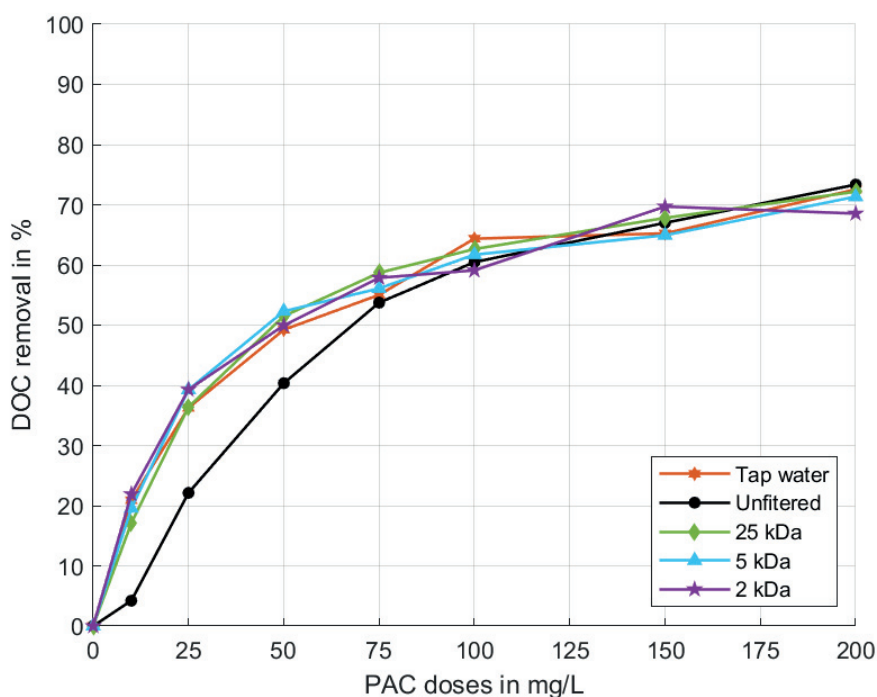


Figure 4.5. Removal of DOC for different PAC doses introduced in the samples.

In the beginning of the second study, the reduction in DOC with respect to different PAC doses was studied and the results are shown in the Figure 4.5. For the tap water and membrane permeates, similar DOC reduction was observed. For lower PAC doses, unfiltered sample shows lower removal efficiency but for higher doses, a similar pattern can be observed. This suggests that the HMW compounds (>25 kDa) at lower doses show slower affinity towards activated carbon but as the availability of PAC increases (high PAC doses), these compounds get adsorbed and show similar DOC reduction with respect to other samples. It also observed that even for higher doses such as 200 mg/L, a portion of DOC is not removed. These compounds are likely to be LMW (<500 Da) hydrophilic compounds which are less adsorbable on activated carbon (Velten *et al.*, 2011).

Later, the study was divided into three subsections which refers to three pharmaceuticals used; Carbamazepine, diclofenac and sulfamethoxazole. Among the compounds used in this study, carbamazepine responds the best to the activated carbon whereas diclofenac has lesser affinity and out of three, sulfamethoxazole displays the least affinity (Margot *et al.*, 2013). Therefore, in order to compensate for this, two additional PAC doses were introduced in the matrix for diclofenac and sulfamethoxazole, as mentioned in the Table 3.4.

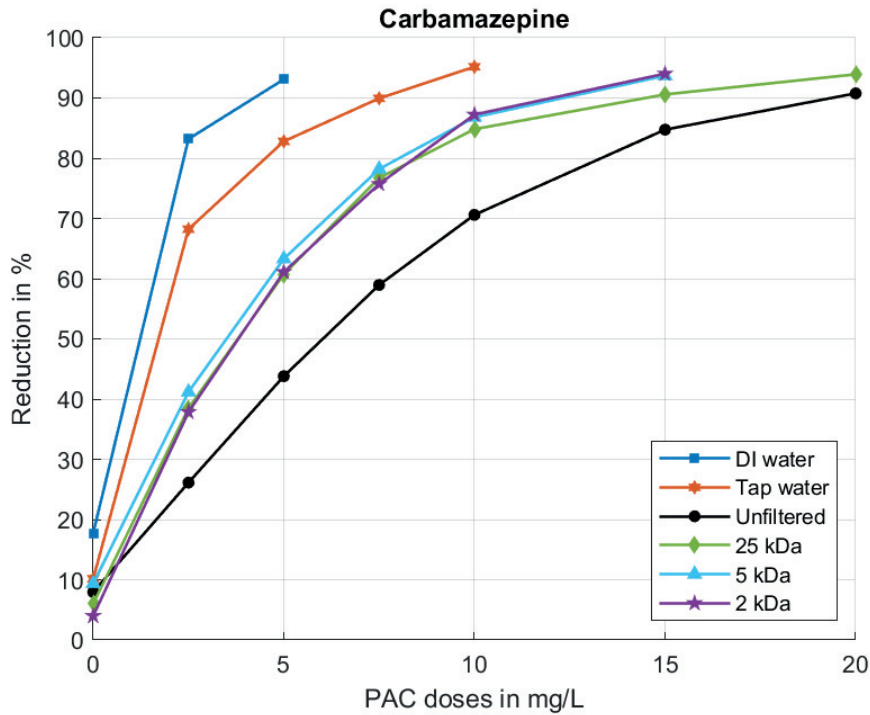


Figure 4.6. Removal of carbamazepine using PAC for DI, tap water, unfiltered wastewater and three membrane filtration permeates. Studies carried out for the doses 0 to 40 mg/L but due to limit of quantification, results at 40 mg/L are excluded and the reduction is higher than 95.5%.

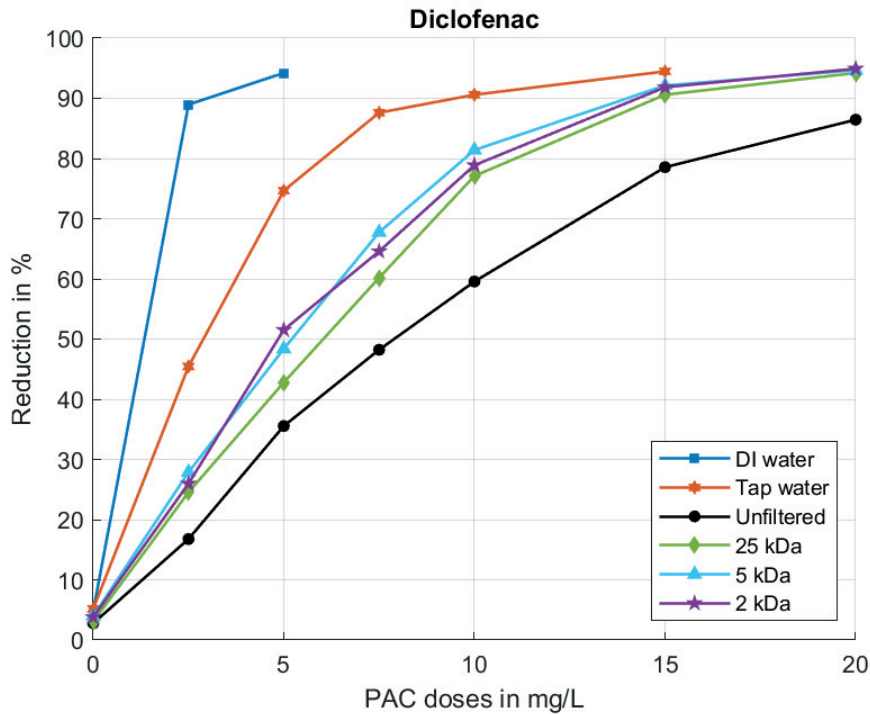


Figure 4.7. Removal of diclofenac using PAC for DI, tap water, unfiltered wastewater and three membrane filtration permeates. Studies carried out for the doses 0 to 80 mg/L but due to limit of quantification, results at 40, 60 and 80 mg/L are excluded and the reduction is higher than 95.5%.

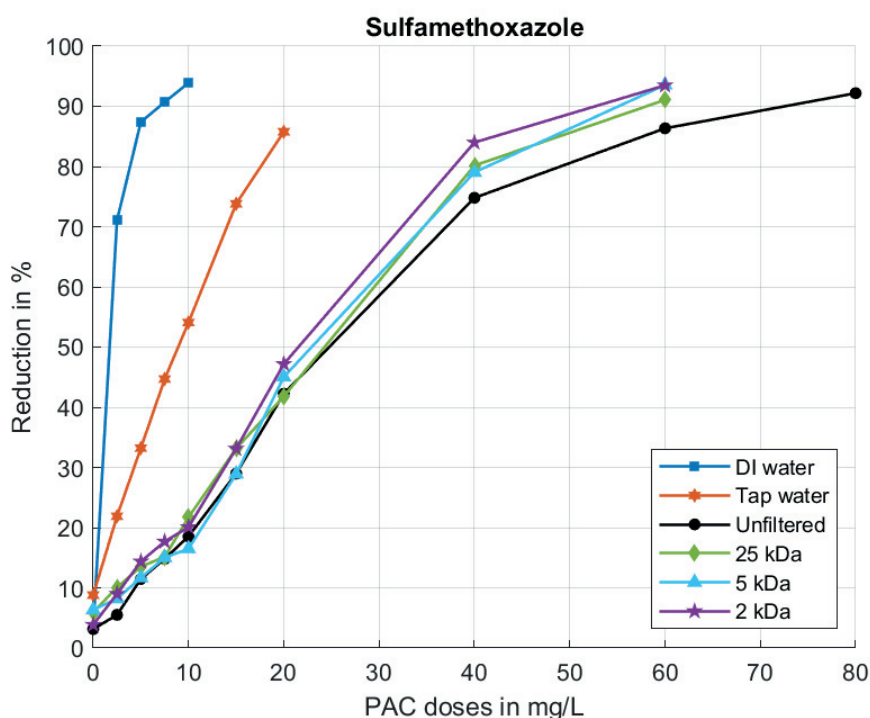


Figure 4.8. Removal of sulfamethoxazole using PAC for DI, tap water, unfiltered wastewater and three membrane filtration permeates.

Carbamazepine is a stable compound with high affinity towards the activated carbon compared to other two compounds. This can be identified using the Figure 4.6 to 4.8. For lower PAC doses, the reduction of all pharmaceuticals DI water was found to be highest among all six samples followed by tap water, membrane permeates and unfiltered wastewater, which presented lowest reduction. More than 80% reduction of carbamazepine was observed for all membrane permeates at PAC dose of 10 mg/L whereas for unfiltered wastewater, it was 15 mg/L. There was no significant variation observed among the membrane filtration permeates, especially between 25 and 5 kDa permeates, even though the difference of MWCO between the membranes is considerably big. This confirms that the competition for the active sites on activated carbon is predominantly due to low molecular weight compounds (<4 kDa).

For the diclofenac and sulfamethoxazole, a similar pattern was observed. DI water showed higher removal efficiency due to less competition followed by tap water as it does present some competition due to presence of NOM but not a significant. Compared to carbamazepine, diclofenac also shows a noticeable high removal for membrane permeates than unfiltered sample whereas in case of sulfamethoxazole, it is not observed. It was also identified that higher PAC dose were required to obtain similar reduction of Sulfamethoxazole compared to the Carbamazepine and Diclofenac in all of the samples. Comparing graphs Figure 4.6 to 4.8, for carbamazepine and diclofenac, more than 90% reduction was observed in DI water for PAC dose of 5 mg/L whereas for sulfamethoxazole, it was 7.5 mg/L. In case of tap water, more than 90% removal was achieved for carbamazepine and diclofenac at PAC dose of 10 mg/L whereas for sulfamethoxazole, it was found to be 30 mg/L. Therefore, it suggest that the negatively charged compounds show less affinity towards PAC than neutral or positively charged compounds, which supports the findings by Margot *et al.* (2013) and Alves *et al.* (2018).

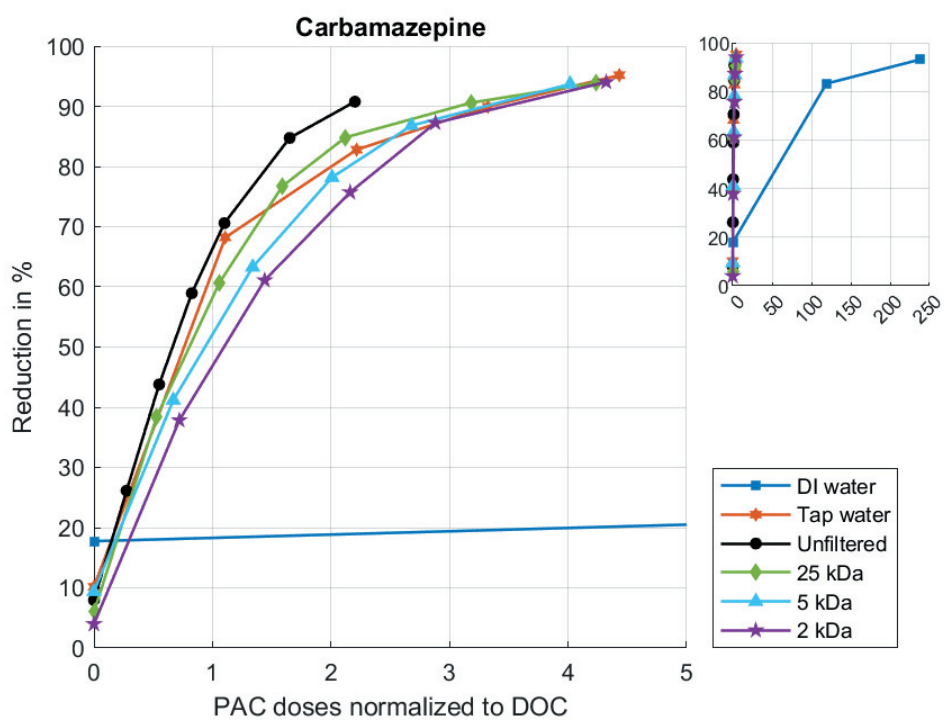


Figure 4.9. Comparison for removal of carbamazepine between five samples for DOC normalized PAC doses. Graph on the top right represents the plot for DI with same axes titles as left.

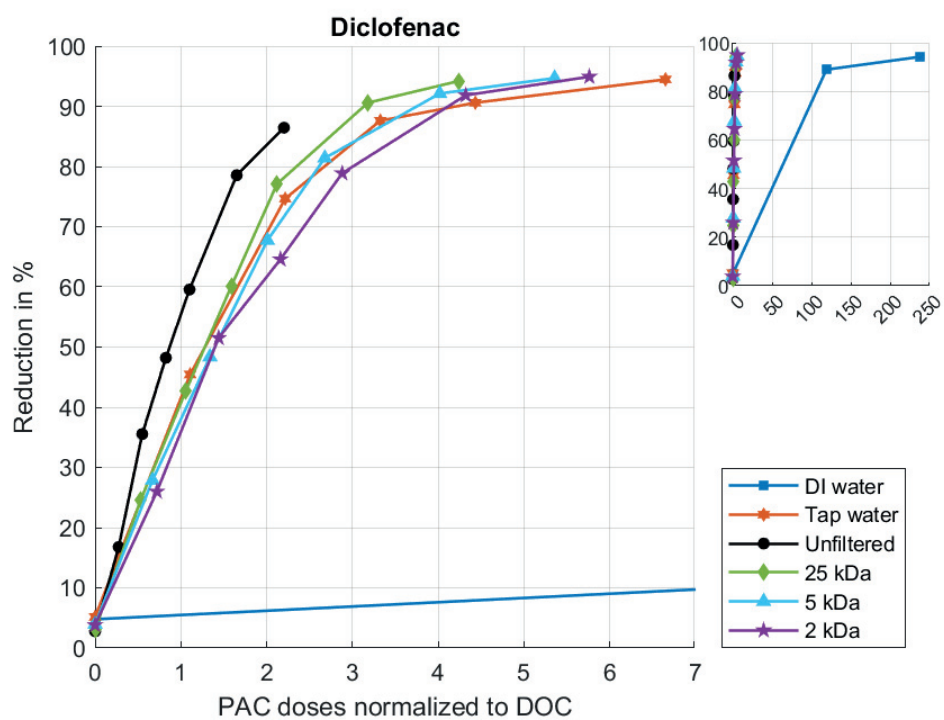


Figure 4.10. Comparison for removal of diclofenac between five samples for DOC normalized PAC doses. Graph on the top right represents the plot for DI with same axes titles as left.

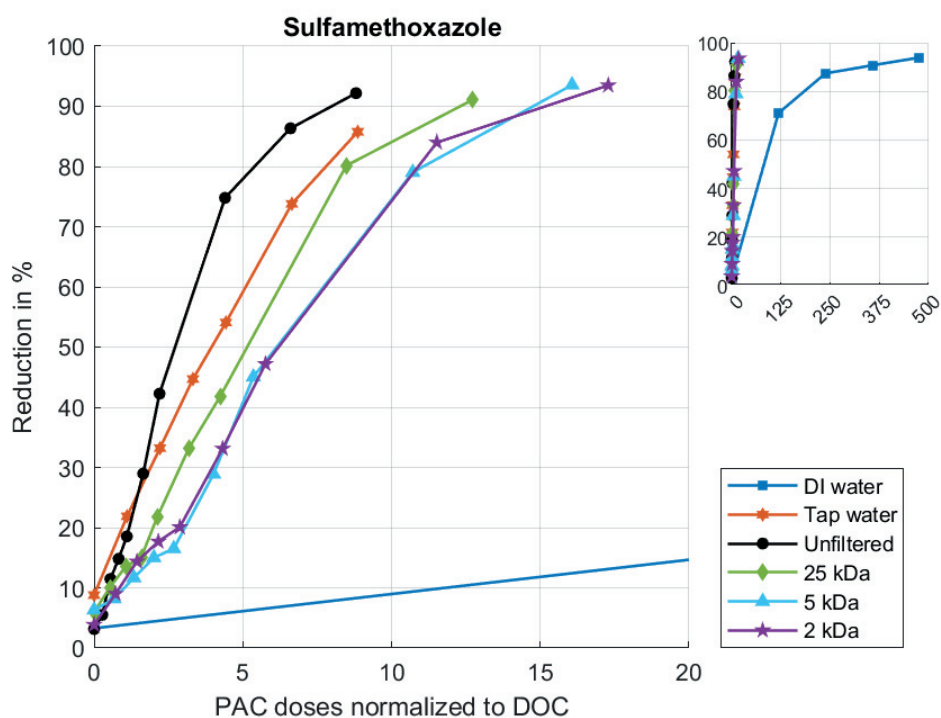


Figure 4.11. Comparison for removal of sulfamethoxazole between five samples for DOC normalized PAC dose. Graph on the top right represents the plot for DI with same axes titles as left.

In case of DOC normalized PAC doses, a similar pattern was observed as in the first study (Figure 4.3). In Figure 4.9 to 4.11, a significant gap between DI water and the rest of the samples can be observed, this is due to very low DOC concentration of 21 $\mu\text{g/L}$ (Table 4.2). The tap water plot indicates that even for lower DOC concentrations, the percent reduction of the compounds for PAC doses per mg of DOC is similar (or slightly higher in case of Sulfamethoxazole). It signifies that either similar DOC fractions are present (which is unlikely due to membrane filtration) or the competition from the different fractions is similar in the samples. But, this study, similar to previous, shows the unfiltered sample present highest removal for PAC doses normalized to DOC.

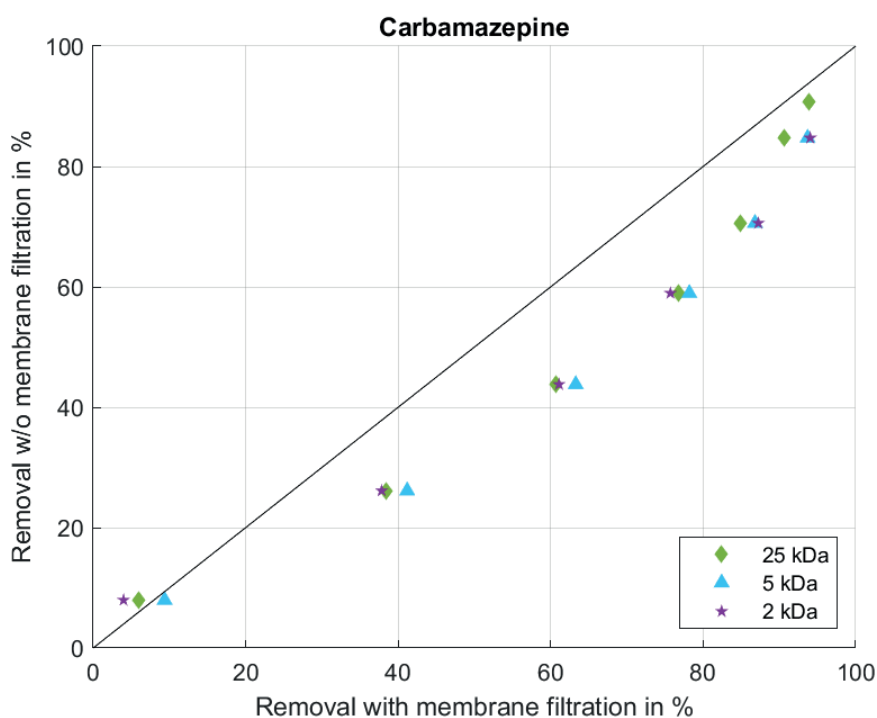


Figure 4.12. Comparison of removal of carbamazepine in unfiltered and three UF permeates for respective PAC doses. A point on 45° line suggests that for an any given PAC dose removal in membrane permeate and unfiltered sample is same.

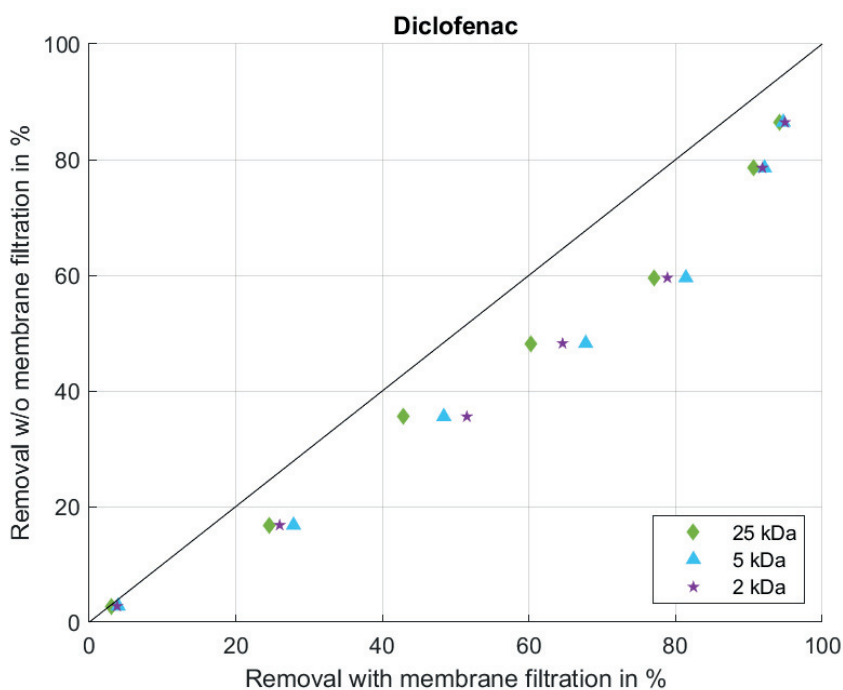


Figure 4.13. Comparison of removal of diclofenac in unfiltered and three UF permeates for respective PAC doses. A point on 45° line suggests that for an any given PAC dose removal in membrane permeate and unfiltered sample is same.

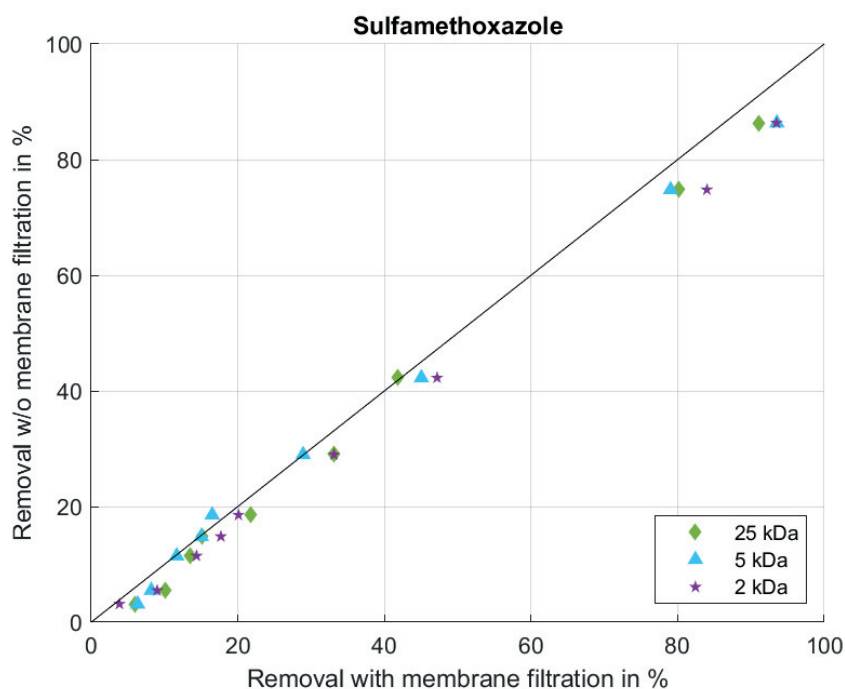


Figure 4.14. Comparison of removal of sulfamethoxazole in unfiltered and three UF permeates for respective PAC doses. A point on 45° line suggests that for an any given PAC dose removal in membrane permeate and unfiltered sample is same.

The comparison, shown in Figure 4.12 and Figure 4.13, between the removal efficiencies of carbamazepine and diclofenac for unfiltered and filtered samples indicates a bias towards the membrane permeates except for sulfamethoxazole, as almost none deviation was observed in Figure 4.14. This again indicate that the sulfamethoxazole, even after removal of significant competition, does not present a better affinity towards activated carbon.

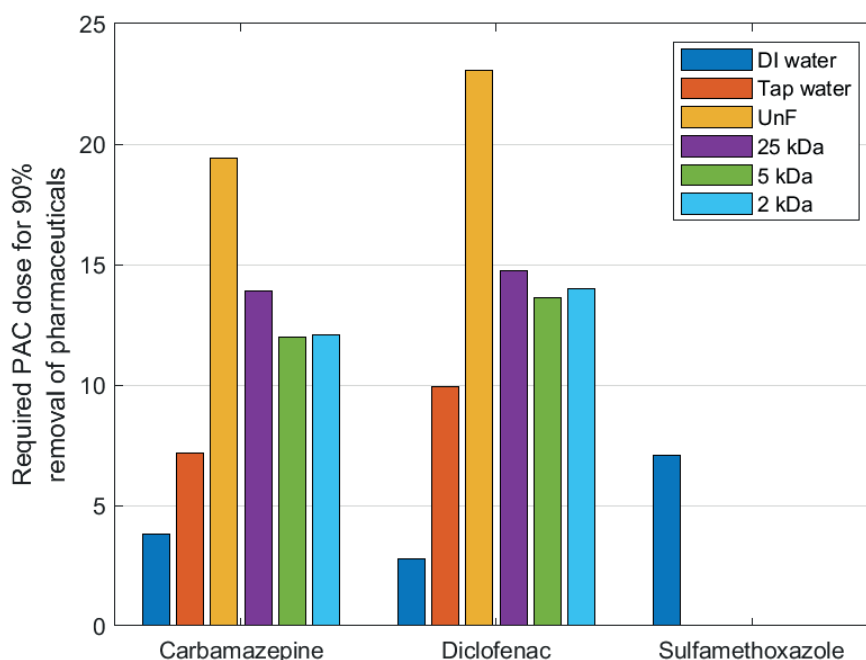


Figure 4.15. Required PAC dose in mg/L for 90% removal of three pharmaceuticals introduced in the samples. The PAC doses are evaluated based on isotherms developed from the PAC studies and are shown in Appendix II. Due to lower fit for sulfamethoxazole, the PAC doses are not estimated for samples except for DI water.

Figure 4.15 illustrate the required dose for 90% removal of respective pharmaceuticals from the five samples used in the study. For carbamazepine, the dose required for DI water was calculated to be 3.8 mg/L which indicates that even with lowest competitive conditions, approximately 20% of the dose is required compared to the dose of unfiltered sample. For tap water, the required dose increases to 7.2 mg/L which accounts for 37% of dose required for unfiltered sample. As anticipated, the required PAC dose increases due to high DOC concentration presenting superfluous competition for active sites. 30 to 40% reduction in PAC doses can be observed for membrane permeates signifying that the removal of HMW compounds (based on MWCO of each membrane) can reduce the required PAC doses.

In case of diclofenac, without any significant competition, the PAC dose required for DI water was 2.8 mg/L lower than that of carbamazepine and account for only 12% of the dose required by unfiltered sample. However, a significant jump in the dose was observed for tap water which was about 250% increase opposed to only 90% in case of carbamazepine and accounts for 43% of the dose required by unfiltered sample, slightly higher than carbamazepine. This indicates that diclofenac is a heavily affected by the presence of other compounds. This is emphasized by the fact that even though the dose required for DI water was lower compared to carbamazepine, it was about 20% higher for unfiltered sample. 35% to 40% reduction in PAC doses were observed for membrane permeates with respect to dose for unfiltered sample. The doses required for membrane permeates were slightly higher than that of carbamazepine. Additionally, for 50% removal of these pharmaceuticals, similar pattern for dosage requirements was observed in all of the samples used in the study (see Figure IV.1 in Appendix IV).

Sulfamethoxazole having a lowest (among three) affinity towards activated carbon, calculations have presented a highest PAC requirement even for DI water. Despite of having low to none competition from other compounds, Figure 4.15 depict almost 90% and 150% increase in PAC dose compared to carbamazepine and diclofenac, respectively. Due to lower fit on the isotherms, the constants for calculating the PAC doses for rest of the samples were not available but it can be speculated that the dosage requirement for the 90% removal would be significantly higher than that of its counterparts.

Recently, Edefell *et al.* (2022), who studied stratification of micropollutants in a GAC column filter, found that the carbamazepine was mostly observed in top layers of the column whereas diclofenac and sulfamethoxazole were observed in the middle and bottom layers. In the study, due to adsorption of various compounds occurs as the sample passes through the bed, competition reduces from top to bottom layer and a significant response from diclofenac and sulfamethoxazole was be observed when the competition for active sites was considerably lower (at bottom layer), concurrent with the observations of this study.

4.3 The effect of hydrophobic/hydrophilic DOM fractions on adsorption studies

Previous study indicated that the removal of DOC based on size fractionation increases the performance of the pharmaceuticals on adsorption. But the size fractionation did not present a better insight about the DOC properties and its adsorbability on activated carbon. Therefore, to understand the role of hydrophobic/hydrophilic compounds on the adsorption of pharmaceuticals, this study was designed.

Table 4.3. DOC concentration of the wastewater samples and their fractions used in the third study

| Samples | Resin | Fraction | DOC (mg/L) |
|--------------------------|-------|----------------------|------------|
| Unfiltered sample | - | Unfractionated | 8.27 |
| | DAX | w/o VHA | 5.75 |
| | XAD | w/o VHA and SHA | 4.06 |
| | IRA | w/o VHA, SHA and CHA | 3.18 |
| 2 kDa permeate | - | Unfractionated | 3.37 |
| | DAX | w/o VHA | 3.39 |
| | XAD | w/o VHA and SHA | 3.18 |
| | IRA | w/o VHA, SHA and CHA | 2.65 |

Note: w/o – without, VHA – Very hydrophobic acids, SHA – Slightly hydrophobic acids, CHA – Charged hydrophilic acids, NEU – Neutral hydrophilic acids. w/o VHA, SHA and CHA also means sample with only NEU fraction.

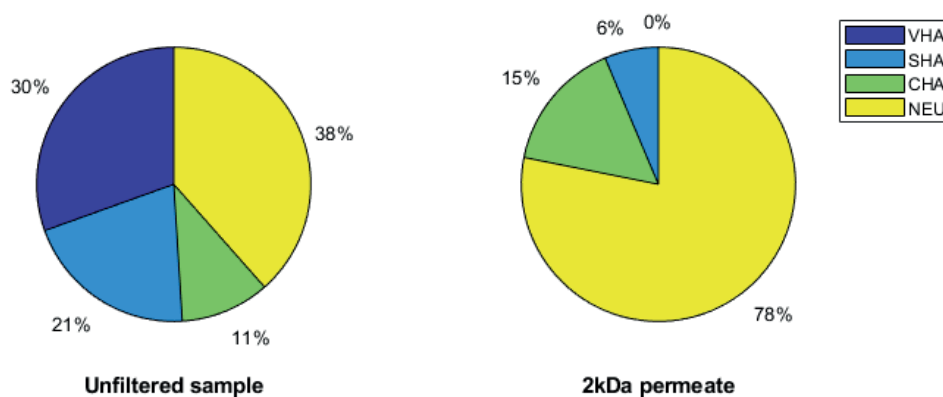


Figure 4.16. Pie chart for the percent fractions present in two samples used in the study

The values presented in Table 4.3 indicate the change in the DOC value after the fractionation using different resins followed by a pie chart (Figure 4.16) illustrating the presence of fractions in each original sample calculated based on the equations 1 to 4 (see section 3.1.2). The highest fraction present in both samples was neutral hydrophilic compounds followed by VHA in unfiltered and CHA in membrane permeate. It is obvious that a significant reduction of VHA and SHA was observed due to membrane filtration. But the DOC in unfractionated sample was lower than DAX filtrate suggesting that the VHA is absent which is not practicable. A study by Piper *et al.* (2010) recognised inadvertent leakage of DOC from DAX and XAD as a major limitation of rapid fractionation study. Therefore, even though fractionation provide valuable insight about the adsorption processes, it must be used with due regard to its limitations. For the rest of the fractions, it can be observed that reduction in SHA, CHA and NEU due to

membrane filtration is 87, 40 and 17% respectively. The high reduction in hydrophobic fraction (VHA + SHA) is an intended outcome of the study as these compounds are likely to compete the most for active sites on PAC.

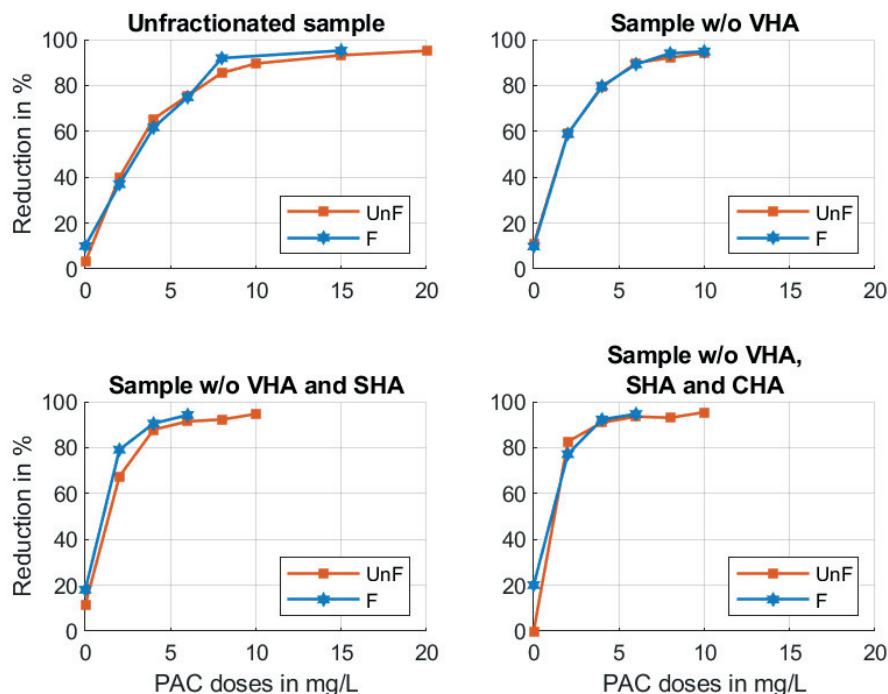


Figure 4.17. Comparison between unfiltered sample and membrane permeate with respect to each fraction for removal of Carbamazepine. UnF – unfiltered sample, F – 2 kDa permeate. w/o VHA, SHA and CHA also means sample with only NEU fraction.

The Figure 4.17 illustrates that the removal efficiency of pharmaceutical increases as the fractions are removed. Compared to previous study (Figure 4.6) where the reduction of carbamazepine between unfiltered and 2 kDa permeate was clearly identifiable, this study indicated that the removal was similar for lower doses and slightly high for higher doses as the limit of quantification was reached earlier. For samples without VHA fraction, a significant deviation between two samples was not observed but for the samples without VHA and SHA fraction, a slightly higher removal was shown by the membrane permeate. It also can be observed that at PAC dose higher than 6 mg/L, the reduction of carbamazepine is more than 95.5% in filtered sample without hydrophobic fraction (VHA and SHA). But to reach the same or higher level of reduction, for unfiltered sample, the required PAC dose was higher than 10 mg/L. A similar pattern was observed in the last fraction (NEU), i.e. sample without VHA, SHA and CHA.

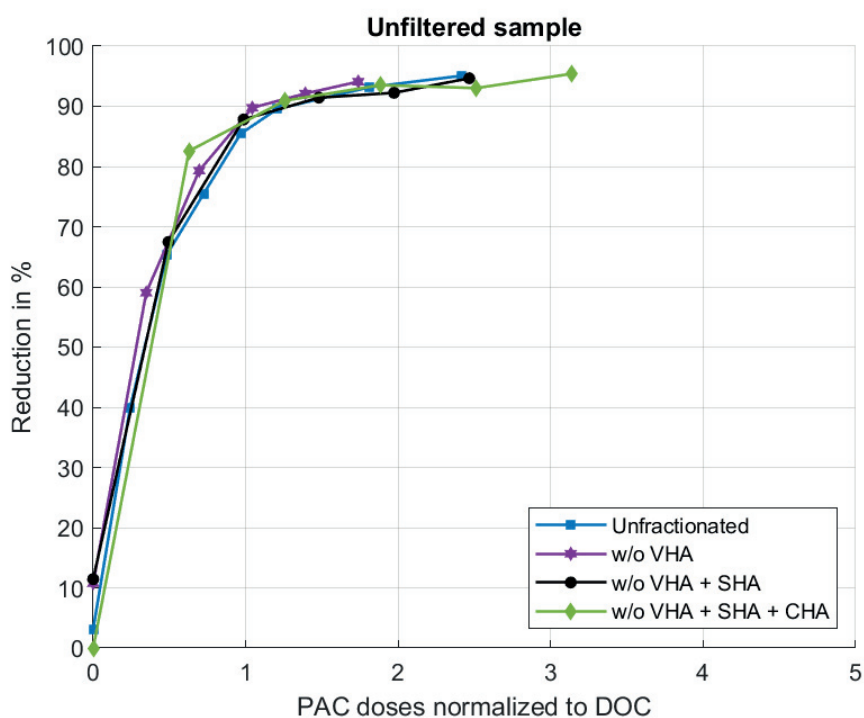


Figure 4.18. Comparison between fractions for removal of Carbamazepine for DOC normalized PAC doses in unfiltered sample. w/o VHA, SHA and CHA also means sample with only NEU fraction.

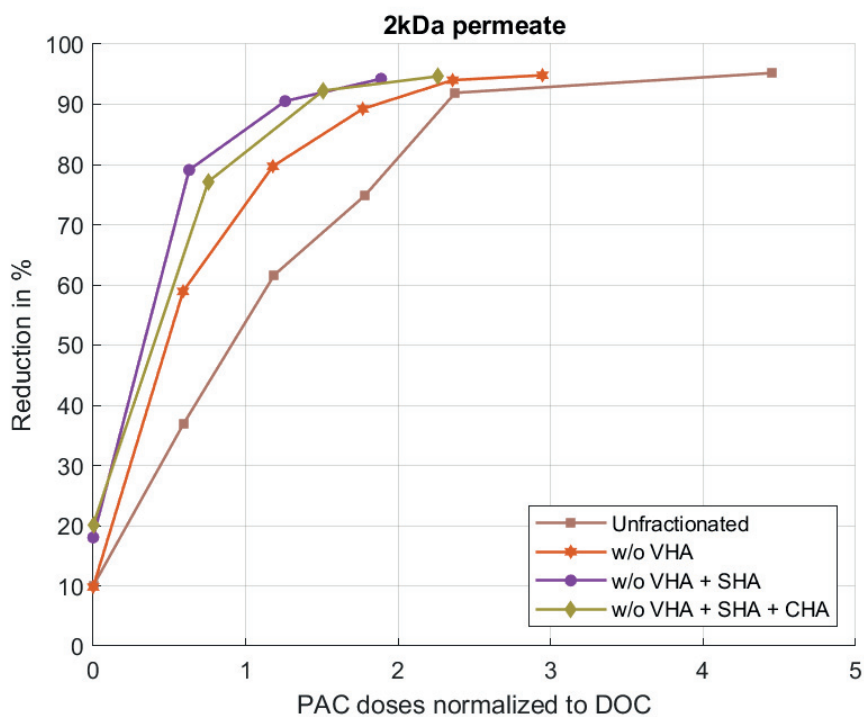


Figure 4.19. Comparison between fractions for removal of Carbamazepine for DOC normalized PAC doses in 2 kDa permeate. w/o VHA, SHA and CHA also means sample with only NEU fraction.

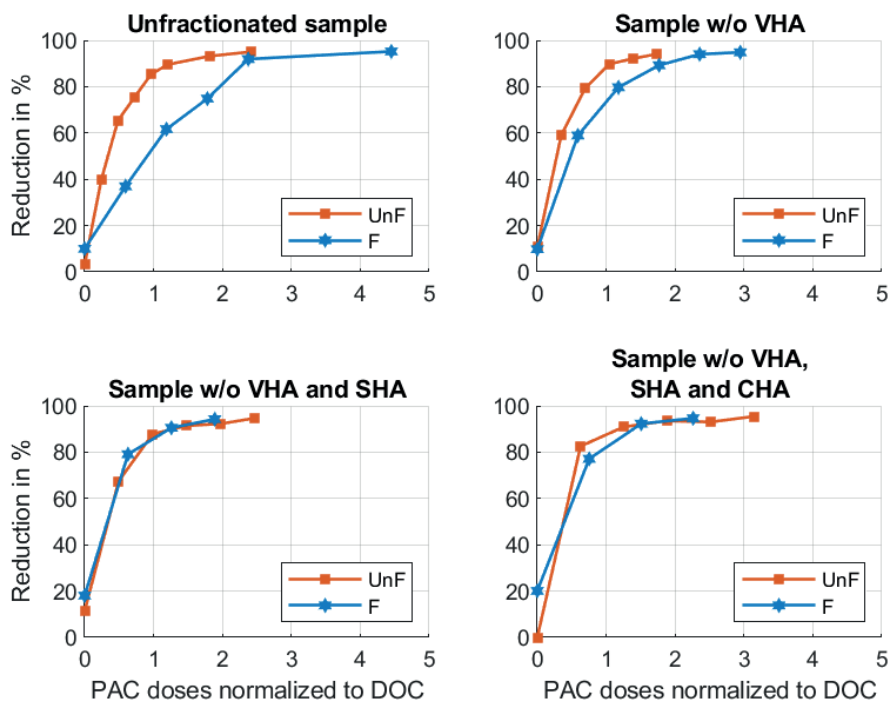


Figure 4.20. Comparison between the samples for respective fractionations for removal of Carbamazepine for DOC normalized PAC doses. UnF – unfiltered sample, F – 2 kDa permeate. w/o VHA, SHA and CHA also means sample with only NEU fraction.

For DOC normalised PAC doses, the result of unfiltered sample (Figure 4.18) shows that the removal of the unfractionated and fractionated sample is similar. This may suggest that the competition presented by the DOM for adsorption was similar with respect to the DOC concentration of sample. But for membrane permeate (Figure 4.19), as a fraction based on size exclusion was removed, the performance of PAC has improved. Here, it can be speculated that since a HMW fraction (>2 kDa) of DOC has already been removed by means of membrane filtration, the competition between the rest of the fractions is a function of their affinity towards activated carbon.

Comparing the graphs for unfiltered sample and membrane permeate for each fraction (Figure 4.20), it can be determined that the filtration process has played an important role in reducing the influence of HMW compounds (>2 kDa) and indicate that not same DOC fractions are present. Furthermore, as the hydrophobic fractions are removed from the samples, the competition between the different DOC achieve similar pattern as filtered.

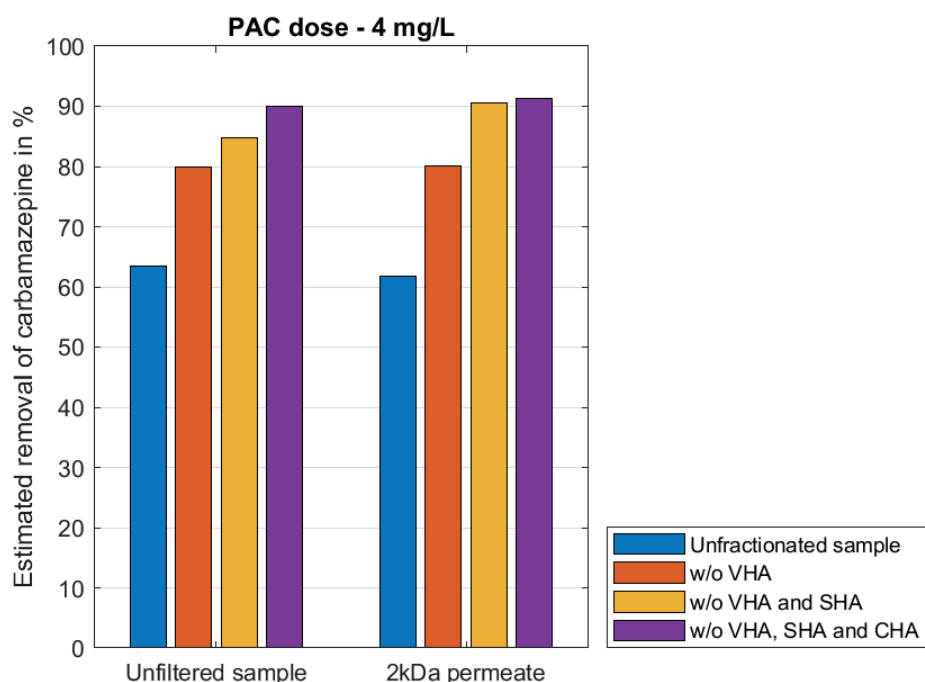


Figure 4.21. Estimated removal of Carbamazepine in the unfractionated and fractionated samples for PAC dose of 4 mg/L. w/o VHA, SHA and CHA also means sample with only NEU fraction.

Based on the constants derived from the isotherms (Table II.5 in Appendix II), a dose of 4 mg/L was evaluated for 90% removal of carbamazepine from the IRA filtration i.e. sample containing only NEU fraction. Figure 4.21 illustrate the expected removal based on a PAC dose of 4 mg/L. A similar values were observed for unfractionated samples and samples without VHA fraction along with NEU. For samples without VHA and SHA i.e. hydrophobic fraction, a significant increase was observed. This suggest that the removal of hydrophobic fraction in the membrane permeate had significant reduction in the competition for carbamazepine and it can be speculated that the fraction left in the sample had a weak affinity towards PAC. It is also possible that the membrane filtration removed some of the hydrophilic fraction which could compete with the carbamazepine presenting higher removal for the same PAC dose.

5 Conclusions

The main aim of the study was to understand how different DOC fractions in the wastewater affects the competition with pharmaceuticals for adsorption sites on activated carbon. The study indicated that the removal of HMW compounds (>25 kDa) does not have a significant impact on the performance of activated carbon towards removal of pharmaceuticals because most of the competition for active sites was presented by the LMW compounds (~500 to 4000 Da). Furthermore, considering properties of DOMs based hydrophobicity/hydrophilicity, the most competition for active sites is presented by hydrophobic compounds because its partial separation from aqueous phase.

This research also identifies the use of DOC concentrations for representing effectiveness of adsorption process has certain limitations. The removal of pharmaceuticals from wastewater correlates to various DOM fractions present and for two different wastewaters with dissimilar fractions, it may not be advantageous to use DOC as an indicator for dosing of activated carbon. Such doses should be derived after a comprehensive understanding about the different fractions present in the wastewater for efficient removal of pharmaceuticals.

6 Future Research

One of the objectives of this research was to establish comprehensive understanding about the adsorption process of activated carbon for efficient removal of pharmaceuticals. But this research was restricted to three studies and three pharmaceutical compounds. Therefore, it is recommended that wide range of micropollutants should be studied. In this study, carbamazepine diclofenac and sulfamethoxazole having neutral, negative charges at pH 7 were used. The removal of positively charged compounds should also be studied for their performance under similar conditions. As mentioned in the study, carbamazepine responds well to the activated carbon but diclofenac and sulfamethoxazole present less affinity. It would be insightful to conduct a comparative study of the compounds which has higher affinity towards activated carbon along with compounds which present higher removal with ozone. Furthermore, the research can also be extended to endocrine disrupting compounds, pesticides and other micropollutants.

Finally, for lab experimentation, the use of PAC is ideal but in practice, GAC is preferred for operational ease. In recent years, some research in magnetised PAC produced by introducing nanoparticles of iron oxides has shown promising results (Oliveira *et al.*, 2002). A research by Lompe *et al.* (2017) concluded that even though some of the micro and mesopores in the carbon matrix were observed to be blocked by these nanoparticles, a significant reduction in adsorption capacity was not observed. Therefore, magnetised PAC could be another potential candidate in advance treatment focused for removal of micropollutants but need further research and development.

References

- Aktaş, Ö. and Çeçen, F. 2011. Fundamentals of Adsorption onto Activated Carbon in Water and Wastewater Treatment. In: Çeçen, F. & Aktaş, Ö. (eds.) *Activated Carbon for Water and Wastewater Treatment*. <https://doi.org/10.1002/9783527639441.ch2>
- Al-Rudainy, B., Galbe, M. and Wallberg, O. 2017. Influence of prefiltration on membrane performance during isolation of lignin-carbohydrate complexes from spent sulfite liquor. *Separation and Purification Technology*, 187, 380-388. <https://doi.org/10.1016/j.seppur.2017.06.031>
- Alves, T. C., Cabrera-Codony, A., Barceló, D., Rodriguez-Mozaz, S., Pinheiro, A. and Gonzalez-Olmos, R. 2018. Influencing factors on the removal of pharmaceuticals from water with micro-grain activated carbon. *Water Research*, 144, 402-412. <https://doi.org/10.1016/j.watres.2018.07.037>
- Barbosa, M. O., Moreira, N. F. F., Ribeiro, A. R., Pereira, M. F. R. and Silva, A. M. T. 2016. Occurrence and removal of organic micropollutants: An overview of the watch list of EU Decision 2015/495. *Water Research*, 94, 257-279. <https://doi.org/10.1016/j.watres.2016.02.047>
- Baresel, C., Ek, M., Ejhed, H., Allard, A.-S., Westling, K. and Fortkamp, U. 2017. *Handbok för rening av mikroföroreningar vid avloppsreningsverk*[Online]. Available at: <https://www.ivl.se/publikationer/publikationer/handbok-for-rening-av-mikrofororeningar-vid-avloppsreningsverk.html> [Accessed 2022-04-14].
- Betsholtz, A., Karlsson, S., Svahn, O., Davidsson, Å., Cimbritz, M. and Falås, P. 2021. Tracking 14C-Labeled Organic Micropollutants to Differentiate between Adsorption and Degradation in GAC and Biofilm Processes. *Environmental Science & Technology*, 55, 11318-11327. <https://doi.org/10.1021/acs.est.1c02728>
- Boehler, M., Zwickenpflug, B., Hollender, J., Ternes, T., Joss, A. and Siegrist, H. 2012. Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon. *Water Science and Technology*, 66, 2115-2121. <https://doi.org/10.2166/wst.2012.353>
- Bolto, B., Abbt-Braun, G., Dixon, D., Eldridge, R., Frimmel, F., Hesse, S., King, S. and Toifl, M. 1999. Experimental Evaluation of Cationic Polyelectrolytes for Removing Natural Organic Matter from Water. *Water Science and Technology*, 40, 71-79. <https://doi.org/10.2166/wst.1999.0445>
- Bolto, B., Dixon, D., Eldridge, R., King, S. and Linge, K. 2002. Removal of natural organic matter by ion exchange. *Water Research*, 36, 5057-5065. [https://doi.org/10.1016/S0043-1354\(02\)00231-2](https://doi.org/10.1016/S0043-1354(02)00231-2)
- Caliman, F. A. and Gavrilescu, M. 2009. Pharmaceuticals, Personal Care Products and Endocrine Disrupting Agents in the Environment – A Review. *CLEAN – Soil, Air, Water*, 37, 277-303. <https://doi.org/10.1002/clen.200900038>

- Çeçen, F. 2011. Water and Wastewater Treatment: Historical Perspective of Activated Carbon Adsorption and its Integration with Biological Processes. In: Çeçen, F. & Aktaş, Ö. (eds.) *Activated Carbon for Water and Wastewater Treatment*. ISBN: 978-3-527-32471-2. <https://doi.org/10.1002/9783527639441.ch1>
- Cheryan, M. 1998. Membrane properties. *Ultrafiltration and Microfiltration Handbook*. 2nd ed. Boca Raton: CRC Press. ISBN: 9780429179112. <https://doi.org/10.1201/9781482278743>
- Cimbritz, M. and Mattsson, A. 2018. *Reningstekniker för läkemedel och mikroföroreningar i avloppsvatten : Redovisning av åtta projekt som fått medel från Havs- och vattenmiljöanslaget 2014-2017*[Online]. Göteborg. Available at: <http://urn.kb.se/resolve?urn=urn:nbn:se:havochvatten:diva-173> [Accessed 2019-11-18].
- Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J. and Tchobanoglous, G. 2012. Adsorption. *MWH's Water Treatment: Principles and Design, Third Edition*. ISBN: 9781118131473. <https://doi.org/10.1002/9781118131473.ch15>
- Croué, J.-P., Korshin, G. V. and Benjamin, M. M. 1999. *Characterization of natural organic matter in drinking water*, Denver, AWWA Research Foundation and American Water Works Association. ISBN: 1583210156 9781583210154.
- Davis, M. L. 2010. *Water and wastewater engineering : design principles and practice, Professional Edition*, McGraw-Hill. ISBN: 0071713840.
- de Ridder, D. J., Verliefde, A. R. D., Heijman, S. G. J., Verberk, J. Q. J. C., Rietveld, L. C., van der Aa, L. T. J., Amy, G. L. and van Dijk, J. C. 2011. Influence of natural organic matter on equilibrium adsorption of neutral and charged pharmaceuticals onto activated carbon. *Water Science and Technology*, 63, 416-423. <https://doi.org/10.2166/wst.2011.237>
- Edefell, E., Falås, P., Torresi, E., Hagman, M., Cimbritz, M., Bester, K. and Christensson, M. 2021. Promoting the degradation of organic micropollutants in tertiary moving bed biofilm reactors by controlling growth and redox conditions. *Journal of Hazardous Materials*, 414. <https://doi.org/10.1016/j.jhazmat.2021.125535>
- Edefell, E., Svahn, O., Falås, P., Bengtsson, E., Axelsson, M., Ullman, R. and Cimbritz, M. 2022. Digging deep into a GAC filter – Temporal and spatial profiling of adsorbed organic micropollutants. *Water Research*, 218, 118477. <https://doi.org/10.1016/j.watres.2022.118477>
- Edzwald, J. K. and Tobiasson, J. E. 1999. Enhanced Coagulation: US Requirements and a Broader View. *Water Science and Technology*, 40, 63-70. <https://doi.org/10.2166/wst.1999.0444>
- Eggen, R. I. L., Hollender, J., Joss, A., Schärer, M. and Stamm, C. 2014. Reducing the Discharge of Micropollutants in the Aquatic Environment: The Benefits of Upgrading Wastewater Treatment Plants. *Environmental Science & Technology*, 48, 7683-7689. <https://doi.org/10.1021/es500907n>

- Falås, P., Longrée, P., la Cour Jansen, J., Siegrist, H., Hollender, J. and Joss, A. 2013. Micropollutant removal by attached and suspended growth in a hybrid biofilm-activated sludge process. *Water Research*, 47, 4498-4506. <https://doi.org/10.1016/j.watres.2013.05.010>
- Filella, M. 2009. Freshwaters: which NOM matters? *Environmental Chemistry Letters*, 7, 21-35. <https://doi.org/10.1007/s10311-008-0158-x>
- Fitzer, E., Kochling, K., Boehm, H. and Marsh, H. 1995. Recommended terminology for the description of carbon as a solid (IUPAC Recommendations 1995). *Pure and Applied Chemistry*, 67, 473-506. <https://doi.org/10.1351/pac199567030473>
- Fonseca Couto, C., Lange, L. C. and Santos Amaral, M. C. 2018. A critical review on membrane separation processes applied to remove pharmaceutically active compounds from water and wastewater. *Journal of Water Process Engineering*, 26, 156-175. <https://doi.org/10.1016/j.jwpe.2018.10.010>
- Freundlich, H. 1909. *Kapillarchemie: eine Darstellung der Chemie der Kolloide und verwandter Gebiete*, Leipzig, Akademische Verlagsgesellschaft.
- Gorczyca, B. 2018. Membrane surface morphology and fouling in filtration of high DOC water. *E3S Web Conf.*, 59. <https://doi.org/10.1051/e3sconf/20185900001>
- Hofman, R. and Teo, C. J. 2021. Chapter 21 - Emerging micropollutants in municipal wastewater: occurrence and treatment options. In: Mohammad, A. W. & Ang, W. L. (eds.) *Integrated and Hybrid Process Technology for Water and Wastewater Treatment*. Elsevier. ISBN: 978-0-12-823031-2. <https://doi.org/10.1016/B978-0-12-823031-2.00026-4>
- JMP 2021. *Progress on household drinking water, sanitation and hygiene 2000-2020. Five years into SDGs*[Online]. Edited by: Who & Unicef. Available at: https://data.unicef.org/wp-content/uploads/2022/01/jmp-2021-wash-households_3.pdf [Accessed 2022-02-24].
- Kårelid, V., Larsson, G. and Björleinius, B. 2017a. Effects of recirculation in a three-tank pilot-scale system for pharmaceutical removal with powdered activated carbon. *Journal of Environmental Management*, 193, 163-171. <https://doi.org/10.1016/j.jenvman.2017.01.078>
- Kårelid, V., Larsson, G. and Björleinius, B. 2017b. Pilot-scale removal of pharmaceuticals in municipal wastewater: Comparison of granular and powdered activated carbon treatment at three wastewater treatment plants. *Journal of Environmental Management*, 193, 491-502. <https://doi.org/10.1016/j.jenvman.2017.02.042>
- Karlsson, S. 2018. *Fractionation of NOM in water from the treatment process at Ringsjöverket*. Lund University. <http://lup.lub.lu.se/student-papers/record/8955472> [Accessed 2021/12/21]
- Kim, P. H. S. and Symons, J. M. 1991. Using Anion Exchange Resins to Remove THM Precursors. *Journal AWWA*, 83, 61-68. <https://doi.org/10.1002/j.1551-8833.1991.tb07267.x>
- Kosek, K., Luczkiewicz, A., Fudala-Książek, S., Jankowska, K., Szopińska, M., Svahn, O., Tränckner, J., Kaiser, A., Langas, V. and Björklund, E. 2020. Implementation of advanced micropollutants removal technologies in wastewater treatment plants (WWTPs) - Examples

- and challenges based on selected EU countries. *Environmental Science & Policy*, 112, 213-226. <https://doi.org/10.1016/j.envsci.2020.06.011>
- Leenheer, J. A. 1981. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environmental Science & Technology*, 15, 578-587. <https://doi.org/10.1021/es00087a010>
- Logar, I., Brouwer, R., Maurer, M. and Ort, C. 2014. Cost-Benefit Analysis of the Swiss National Policy on Reducing Micropollutants in Treated Wastewater. *Environmental Science & Technology*, 48, 12500-12508. <https://doi.org/10.1021/es502338j>
- Lompe, K. M., Menard, D. and Barbeau, B. 2017. The influence of iron oxide nanoparticles upon the adsorption of organic matter on magnetic powdered activated carbon. *Water Research*, 123, 30-39. <https://doi.org/10.1016/j.watres.2017.06.045>
- Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., Liang, S. and Wang, X. C. 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of The Total Environment*, 473-474, 619-641. <https://doi.org/10.1016/j.scitotenv.2013.12.065>
- Luterbacher, C. 2016. Are systems designed to remove micropollutants from wastewater treatment plants enough to protect lakes and rivers? That's what the Swiss government is betting on. *SWI swissinfo*, Published on 2016-10-11, https://www.swissinfo.ch/eng/pollution--_stepping-up-wastewater-treatment/42465310. [Accessed 2022-05-11]
- Madsen, H. T. 2014. Chapter 6 - Membrane Filtration in Water Treatment – Removal of Micropollutants. In: Søgaaard, E. G. (ed.) *Chemistry of Advanced Environmental Purification Processes of Water*. Amsterdam: Elsevier. ISBN: 978-0-444-53178-0. <https://doi.org/10.1016/B978-0-444-53178-0.00006-7>
- Malcolm, R. L. and MacCarthy, P. 1992. Quantitative evaluation of XAD-8 and XAD-4 resins used in tandem for removing organic solutes from water. *Environment International*, 18, 597-607. [https://doi.org/10.1016/0160-4120\(92\)90027-2](https://doi.org/10.1016/0160-4120(92)90027-2)
- Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., de Alencastro, L. F., Abegglen, C., Thonney, D., Chèvre, N., Schärer, M. and Barry, D. A. 2013. Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? *Science of The Total Environment*, 461-462, 480-498. <https://doi.org/10.1016/j.scitotenv.2013.05.034>
- Martin Ruel, S., Esperanza, M., Choubert, J. M., Valor, I., Budzinski, H. and Coquery, M. 2010. On-site evaluation of the efficiency of conventional and advanced secondary processes for the removal of 60 organic micropollutants. *Water Science and Technology*, 62, 2970-2978. <https://doi.org/10.2166/wst.2010.989>
- Metz, F. and Ingold, K. 2014. Sustainable Wastewater Management: Is it Possible to Regulate Micropollution in the Future by Learning from the Past? A Policy Analysis. *Sustainability*, 6. <https://doi.org/10.3390/su6041992>
- Moreno-Castilla, C. 2004. Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon*, 42, 83-94. <https://doi.org/10.1016/j.carbon.2003.09.022>

- Newcombe, G., Drikas, M. and Hayes, R. 1997. Influence of characterised natural organic material on activated carbon adsorption: II. Effect on pore volume distribution and adsorption of 2-methylisoborneol. *Water Research*, 31, 1065-1073. [https://doi.org/10.1016/S0043-1354\(96\)00325-9](https://doi.org/10.1016/S0043-1354(96)00325-9)
- Oliveira, L. C. A., Rios, R. V. R. A., Fabris, J. D., Garg, V., Sapag, K. and Lago, R. M. 2002. Activated carbon/iron oxide magnetic composites for the adsorption of contaminants in water. *Carbon*, 40, 2177-2183. [https://doi.org/10.1016/S0008-6223\(02\)00076-3](https://doi.org/10.1016/S0008-6223(02)00076-3)
- Piper, C., Jefferson, B. and Jarvis, P. 2010. *Development of a rapid fractionation tool for natural organic matter*. Master of Sciences, Cranfield University. https://dspace.lib.cranfield.ac.uk/bitstream/handle/1826/5628/Piper_Claire_Thesis_2010.pdf?sequence=1&isAllowed=y [Accessed 2022-03-28]
- Ravichandran, M. 2004. Interactions between mercury and dissolved organic matter—a review. *Chemosphere*, 55, 319-331. <https://doi.org/10.1016/j.chemosphere.2003.11.011>
- Real, F. J., Benitez, F. J., Acero, J. L. and Casas, F. 2017. Adsorption of selected emerging contaminants onto PAC and GAC: Equilibrium isotherms, kinetics, and effect of the water matrix. *Journal of Environmental Science and Health, Part A*, 52, 727-734. <https://doi.org/10.1080/10934529.2017.1301751>
- Reemtsma, T., Weiss, S., Mueller, J., Petrovic, M., González, S., Barcelo, D., Ventura, F. and Knepper, T. P. 2006. Polar Pollutants Entry into the Water Cycle by Municipal Wastewater: A European Perspective. *Environmental Science & Technology*, 40, 5451-5458. <https://doi.org/10.1021/es060908a>
- Santos, L. H. M. L. M., Araújo, A. N., Fachini, A., Pena, A., Delerue-Matos, C. and Montenegro, M. C. B. S. M. 2010. Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment. *Journal of Hazardous Materials*, 175, 45-95. <https://doi.org/10.1016/j.jhazmat.2009.10.100>
- Schwarzenbach, R. P., Escher, B. I., Fenner, K., Hofstetter, T. B., Johnson, C. A., von Gunten, U. and Wehrli, B. 2006. The Challenge of Micropollutants in Aquatic Systems. *Science*, 313, 1072-1077. <https://doi.org/10.1126/science.1127291>
- Sharp, E. L., Jarvis, P., Parsons, S. A. and Jefferson, B. 2006. Impact of fractional character on the coagulation of NOM. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 286, 104-111. <https://doi.org/10.1016/j.colsurfa.2006.03.009>
- Sillanpää, M. 2015. Chapter 1 - General Introduction. In: Sillanpää, M. (ed.) *Natural Organic Matter in Water*. Butterworth-Heinemann. ISBN: 978-0-12-801503-2. <https://doi.org/10.1016/B978-0-12-801503-2.00001-X>
- Sillanpää, M. and Bhatnagar, A. 2015. Chapter 7 - NOM Removal by Adsorption. In: Sillanpää, M. (ed.) *Natural Organic Matter in Water*. Butterworth-Heinemann. ISBN: 978-0-12-801503-2. <https://doi.org/10.1016/B978-0-12-801503-2.00007-0>

Sillanpää, M. and Matilainen, A. 2015. Chapter 6 - NOM Removal by Advanced Oxidation Processes. In: Sillanpää, M. (ed.) *Natural Organic Matter in Water*. Butterworth-Heinemann. ISBN: 978-0-12-801503-2. <https://doi.org/10.1016/B978-0-12-801503-2.00006-9>

Sillanpää, M., Matilainen, A. and Lahtinen, T. 2015. Chapter 2 - Characterization of NOM. In: Sillanpää, M. (ed.) *Natural Organic Matter in Water*. Butterworth-Heinemann. ISBN: 978-0-12-801503-2. <https://doi.org/10.1016/B978-0-12-801503-2.00002-1>

Sillanpää, M., Ncibi, M. C. and Matilainen, A. 2018. Advanced oxidation processes for the removal of natural organic matter from drinking water sources: A comprehensive review. *Journal of Environmental Management*, 208, 56-76. <https://doi.org/10.1016/j.jenvman.2017.12.009>

Söderman, O. 2017. *Membrane screening to identify optimal properties when separating organic matter from Bolmen water*. Lund University. <http://lup.lub.lu.se/student-papers/record/8903148> [Accessed 2022-01-25]

Suty, H., De Traversay, C. and Cost, M. 2004. Applications of advanced oxidation processes: present and future. *Water Science and Technology*, 49, 227-233. <https://doi.org/10.2166/wst.2004.0270>

Tchobanoglous, G., Metcalf, Eddy, Burton, F. L. and Stensel, H. D. 2014a. *Wastewater engineering : treatment and resource recovery, 5th edition, Vol. 1*, McGraw-Hill. ISBN: 9781259010798.

Tchobanoglous, G., Metcalf, Eddy, Burton, F. L. and Stensel, H. D. 2014b. *Wastewater engineering : treatment and resource recovery, 5th edition, Vol. 2*, McGraw-Hill. ISBN: 9781259010798.

Uyguner-Demirel, C. S. and Bekbolet, M. 2011. Significance of analytical parameters for the understanding of natural organic matter in relation to photocatalytic oxidation. *Chemosphere*, 84, 1009-1031. <https://doi.org/10.1016/j.chemosphere.2011.05.003>

VASyd 2016. *Källby wastewater treatment plant*[Online]. Available at: https://www.vasyd.se/-/media/Dokument_ny_webb/Avlopp/Avloppsreningsverk-och-pumpstationer/KallbyReningsverkEnglish201609Webb.pdf [Accessed 2022-04-12].

VASyd 2022. *Vattenkvalitet i Lunds kommun - Orter som vanligtvis får vatten från sjön Bolmen*[Online]. Available at: https://www.vasyd.se/-/media/Dokument_ny_webb/Vattenrapporter/2021-2/Lund-Bolmen-DV-2021-2.pdf [Accessed 2022-04-26].

Velten, S., Knappe, D. R. U., Traber, J., Kaiser, H.-P., von Gunten, U., Boller, M. and Meylan, S. 2011. Characterization of natural organic matter adsorption in granular activated carbon adsorbers. *Water Research*, 45, 3951-3959. <https://doi.org/10.1016/j.watres.2011.04.047>

Verlicchi, P., Al Aukidy, M. and Zambello, E. 2012. Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a

secondary treatment—A review. *Science of The Total Environment*, 429, 123-155.
<https://doi.org/10.1016/j.scitotenv.2012.04.028>

Wilkinson John, L., Boxall Alistair, B. A., Kolpin Dana, W., Leung Kenneth, M. Y., Lai Racliffe, W. S., Galbán-Malagón, C., Adell Aiko, D., Mondon, J., Metian, M., Marchant Robert, A., Bouzas-Monroy, A., Cuni-Sanchez, A., Coors, A., Carriquiriborde, P., Rojo, M., Gordon, C., Cara, M., Moermond, M., Luarte, T., Petrosyan, V., Perikhanyan, Y., Mahon Clare, S., McGurk Christopher, J., Hofmann, T., Kormoker, T., Iniguez, V., Guzman-Otazo, J., Tavares Jean, L., Gildasio De Figueiredo, F., Razzolini Maria, T. P., Dougnon, V., Gbaguidi, G., Traoré, O., Blais Jules, M., Kimpe Linda, E., Wong, M., Wong, D., Ntchantcho, R., Pizarro, J., Ying, G.-G., Chen, C.-E., Pérez, M., Martínez-Lara, J., Otamonga, J.-P., Poté, J., Ifo Suspense, A., Wilson, P., Echeverría-Sáenz, S., Udikovic-Kolic, N., Milakovic, M., Fatta-Kassinou, D., Ioannou-Ttofa, L., Belušová, V., Vymazal, J., Cárdenas-Bustamante, M., Kassa Bayable, A., Garric, J., Chaumot, A., Gibba, P., Kunchulia, I., Seidensticker, S., Lyberatos, G., Halldórsson Halldór, P., Melling, M., Shashidhar, T., Lamba, M., Nastiti, A., Supriatin, A., Pourang, N., Abedini, A., Abdullah, O., Gharbia Salem, S., Pilla, F., Chefetz, B., Topaz, T., Yao Koffi, M., Aubakirova, B., Beisenova, R., Olaka, L., Mulu Jemimah, K., Chatanga, P., Ntuli, V., Blama Nathaniel, T., Sherif, S., Aris Ahmad, Z., Looi Ley, J., Niang, M., Traore Seydou, T., Oldenkamp, R., Ogunbanwo, O., Ashfaq, M., Iqbal, M., Abdeen, Z., O’Dea, A., Morales-Saldaña Jorge, M., Custodio, M., de la Cruz, H., Navarrete, I., Carvalho, F., Gogra Alhaji, B., Koroma Bashiru, M., Cerkvénik-Flajs, V., Gombač, M., Thwala, M., Choi, K., Kang, H., Ladu John, L. C., Rico, A., Amerasinghe, P., Sobek, A., Horlitz, G., Zenker Armin, K., King Alex, C., Jiang, J.-J., Kariuki, R., Tumbo, M., Tezel, U., Onay Turgut, T., Lejju Julius, B., Vystavna, Y., Vergeles, Y., Heinzen, H., Pérez-Parada, A., Sims Douglas, B., Figy, M., Good, D. and Teta, C. 2022. Pharmaceutical pollution of the world’s rivers. *Proceedings of the National Academy of Sciences*, 119.
<https://doi.org/10.1073/pnas.2113947119>

Winterdahl, M. 2013. *Intra-Annual Variability of Natural Organic Matter in Boreal Streams*. Doctoral thesis, Sveriges lantbruksuniversitet.
<http://urn.kb.se/resolve?urn=urn:nbn:se:slu:epsilon-e-820> [Accessed 2022-05-10]

Zietzschmann, F. 2016. *Impacts of background organic matter on organic micro-pollutant adsorption onto activated carbon*. Doctoral Thesis, Technische Universität Berlin.
<http://dx.doi.org/10.14279/depositonce-5475>

Zietzschmann, F., Mitchell, R. L. and Jekel, M. 2015. Impacts of ozonation on the competition between organic micro-pollutants and effluent organic matter in powdered activated carbon adsorption. *Water Research*, 84, 153-160.
<https://doi.org/10.1016/j.watres.2015.07.031>

Zietzschmann, F., Worch, E., Altmann, J., Ruhl, A. S., Sperlich, A., Meinel, F. and Jekel, M. 2014. Impact of EfOM size on competition in activated carbon adsorption of organic micro-pollutants from treated wastewater. *Water Research*, 65, 297-306.
<https://doi.org/10.1016/j.watres.2014.07.043>

Zularisam, A. W., Ismail, A. F. and Salim, R. 2006. Behaviours of natural organic matter in membrane filtration for surface water treatment — a review. *Desalination*, 194, 211-231.
<https://doi.org/10.1016/j.desal.2005.10.030>

Appendix I

MATLAB (R2022a) code developed for fitting Freundlich isotherms on the data points obtained from the PAC studies.

```
f1 = figure();
c =
{'#0072BD', '#D95319', 'k', '#77AC30', '#4DBEEE', '#7E2F8E', '#9332A8', '#A89A32'};
d = {'s', 'h', 'o', 'd', '^', 'x', '+', '*'};
z = 7; %to eliminate PAC dose of 0 mg/L
e = {'-', '--', '-.', ':', '-.', '-.', '-.', ':'};
%assigning colours and other visual effects
for n = 1:8 %based on data series
    clear x y
    [x, y] = prepareCurveData(s(1:z,n),sr(1:z,n));
```

Fit data to the model

```
ft = fittype( 'k*x^(1/b)', 'independent', 'x', 'dependent', 'y' );
opts = fitoptions('method','NonlinearLeastSquares','MaxIter',100000);
opts.Display = 'off';
opts.Robust = 'off';
[fitresult, gof] = fit( x, y, ft, opts);
rsquare(n) = gof.rsquare; %extract fit
k(n) = fitresult.k; %extract constants
b(n) = fitresult.b;
```

Plot fit with data.

```
hold on %plotting data points
plot(xData,yData,d{n},MarkerFaceColor=c{n},MarkerSize=4);
x = 0.2:0.1:8;
y = k(n)*x.^(1/b(n)); %extrapolating based on constants
plot(x,y,LineStyle=e{n},Color=c{n},LineWidth=1.5);
hold off
```

Label axes

```
xlabel( 'Equilibrium Concentration in \mug/L', 'Interpreter', 'tex' )
ylabel( '\mug PhC adsorbed/mg PAC ', 'Interpreter', 'tex' )
grid on
end
legend({'', 'UnF', '', 'UnF-DAX', '', 'UnF-XAD', '', 'UnF-IRA', '', 'F', '', 'F-DAX', '', 'F-XAD', '', 'F-IRA'}, Location='southeast', NumColumns=2)
```

Save figure and data

```
const = array2table([rsquare' k' b]);
const.Properties.VariableNames = {'Rsqaure', 'K', 'b'};
saveas(f1, 'third_Isotherm_Fractionation', 'png')
writetable(const, 'constants.csv', Delimiter=',')
```


Appendix II

In this section, all the isotherm plots are presented. The isotherms were developed for the data points where the goodness of fit (R^2) was observed to be greater than 90%. For lower fits, the isotherms were not developed. The goodness of fit for each plot is provided in the table along with the Freundlich constants shown the equation 1.

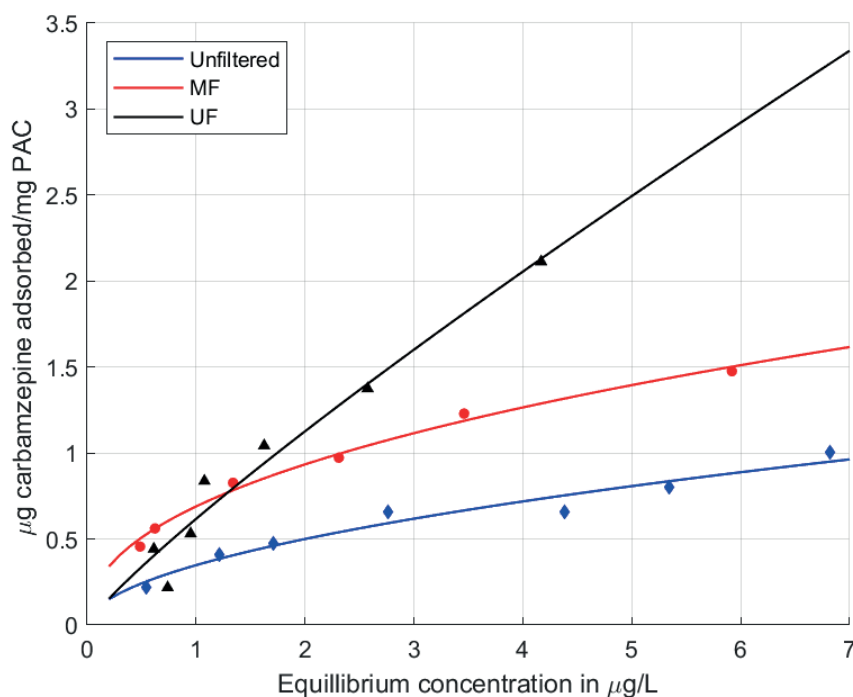


Figure II.1. Isotherm for the adsorption of Carbamazepine on unfiltered and two membrane permeates for the first study

Table II.1. Freundlich parameters for the isotherms plotted in Figure II.1

| Sample | R^2 (%) | K_F | b |
|------------|-----------|--------|--------|
| Unfiltered | 95.32 | 0.3480 | 1.9112 |
| MF | 99.08 | 0.6895 | 2.2839 |
| UF | 95.45 | 0.6174 | 1.1527 |

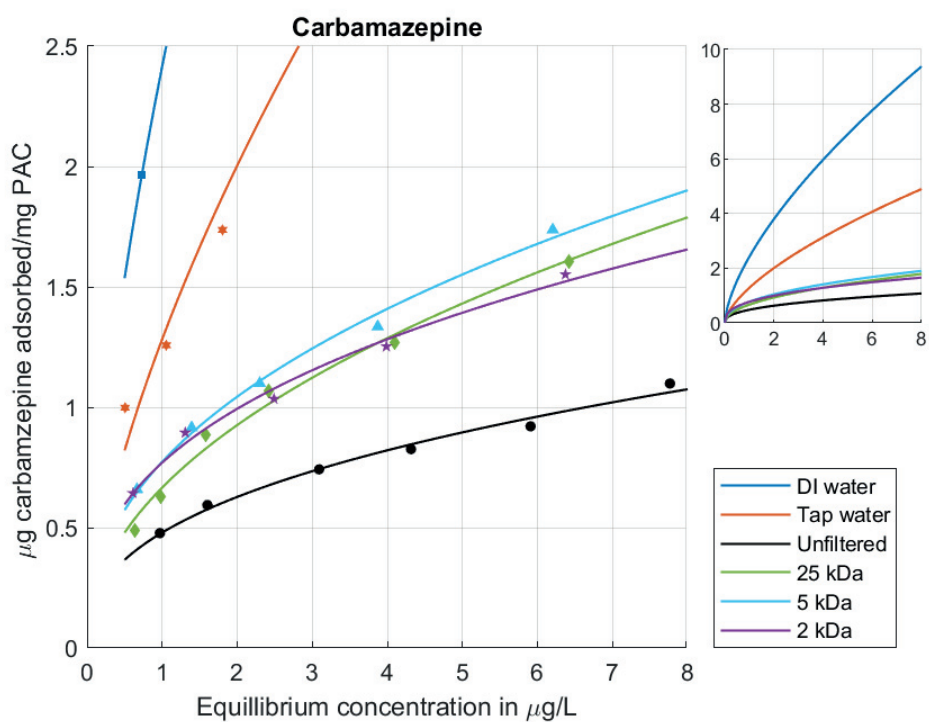


Figure II.2. Isotherm for the adsorption of Carbamazepine developed from the results of the second study

Table II.2. Freundlich parameters for the isotherms plotted in Figure II.2

| Sample | R ² (%) | K _F | b |
|----------------------|--------------------|----------------|--------|
| DI water | 100 | 2.4149 | 1.5326 |
| Tap water | 97.10 | 1.2823 | 1.5523 |
| Unfiltered | 98.70 | 0.4794 | 2.5760 |
| UF - 25 kDa permeate | 98.81 | 0.6663 | 2.1058 |
| UF - 5 kDa permeate | 99.29 | 0.7735 | 2.3125 |
| UF - 2 kDa permeate | 98.87 | 0.7698 | 2.7159 |

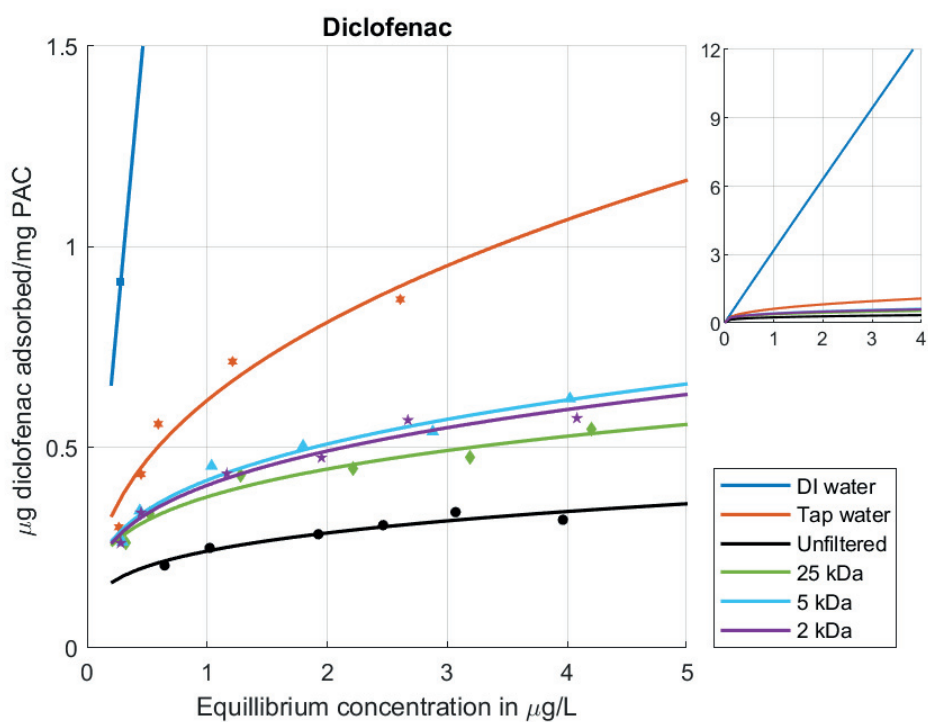


Figure II.3. Isotherm for the adsorption of Diclofenac developed from the results of the second study

Table II.3. Freundlich parameters for the isotherms plotted in Figure II.3

| Sample | R ² (%) | K _F | b |
|----------------------|--------------------|----------------|--------|
| DI water | 100 | 3.1944 | 1.0142 |
| Tap water | 94.57 | 0.6172 | 2.5289 |
| Unfiltered | 91.91 | 0.2415 | 4.0471 |
| UF - 25 kDa permeate | 95.29 | 0.3767 | 4.1079 |
| UF - 5 kDa permeate | 96.69 | 0.4181 | 3.5457 |
| UF - 2 kDa permeate | 96.19 | 0.4055 | 3.6251 |

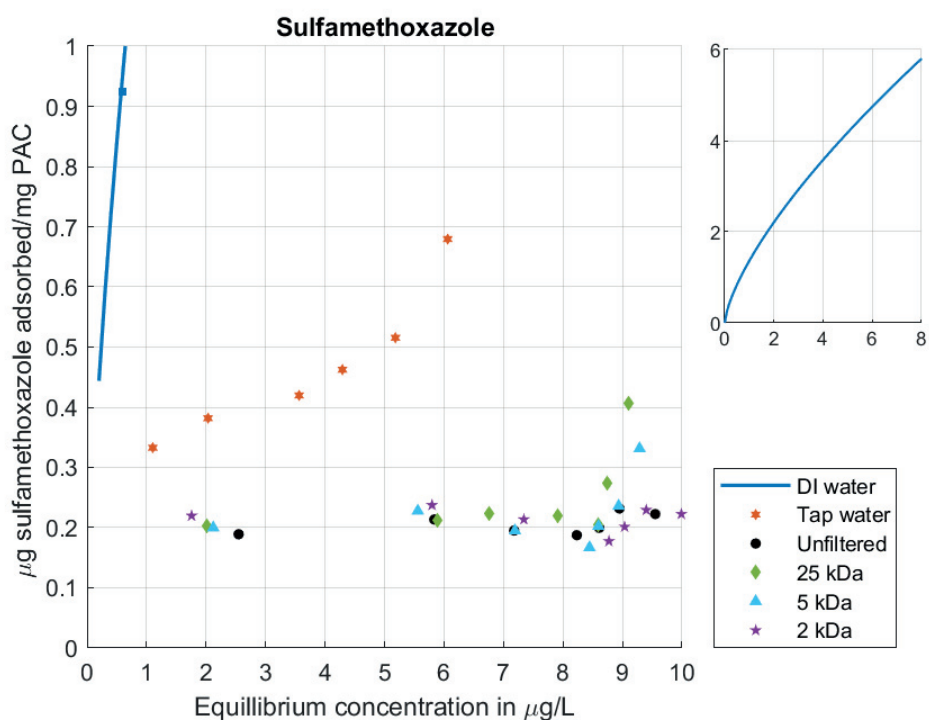


Figure II.4. Isotherm for the adsorption of Sulfamethoxazole developed from the results of the second study

Table II.4. Freundlich parameters for the isotherms plotted in Figure II.4

| Sample | R ² (%) | K _F | b |
|----------------------|--|----------------|--------|
| DI water | 96.62 | 1.3620 | 1.4356 |
| Tap water | Not fitted due to low goodness of fit (R ² < 90%) | | |
| Unfiltered | | | |
| UF - 25 kDa permeate | | | |
| UF - 5 kDa permeate | | | |
| UF - 2 kDa permeate | | | |

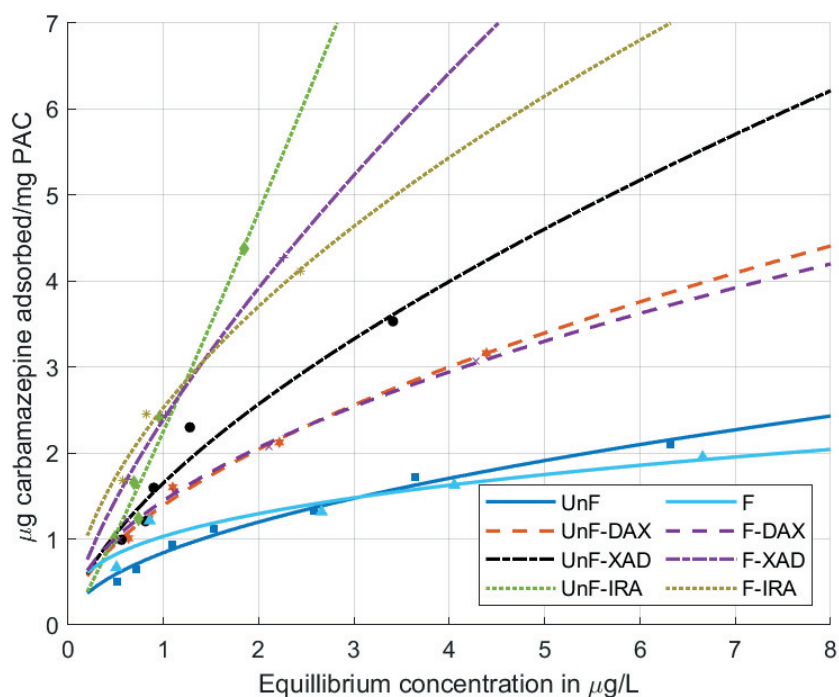


Figure II.5. Isotherm for the adsorption of Carbamazepine developed for the different fractions evaluated in the third study. UnF – unfiltered sample, F – 2 kDa permeate. DAX – w/o VHA, XAD – w/o VHA and SHA, IRA – w/o VHA, SHA and CHA. w/o VHA, SHA and CHA also means sample with only NEU fraction.

Table II.5. Freundlich parameters for the isotherms plotted in Figure II.5

| Sample | Resin | R ² (%) | K _F | b |
|-------------------|-------|--------------------|----------------|--------|
| Unfiltered sample | - | 98.13 | 0.8412 | 1.9600 |
| | DAX | 99.09 | 1.3918 | 1.8036 |
| | XAD | 94.68 | 1.6529 | 1.5702 |
| | IRA | 94.25 | 2.2353 | 0.8945 |
| 2 kDa permeate | - | 96.96 | 0.9655 | 2.6684 |
| | DAX | 99.45 | 1.4470 | 1.9516 |
| | XAD | 91.53 | 2.1117 | 1.1437 |
| | IRA | 97.87 | 2.5283 | 1.8105 |

Note: DAX – without VHA, XAD – without VHA and SHA, IRA – without VHA, SHA and CHA.

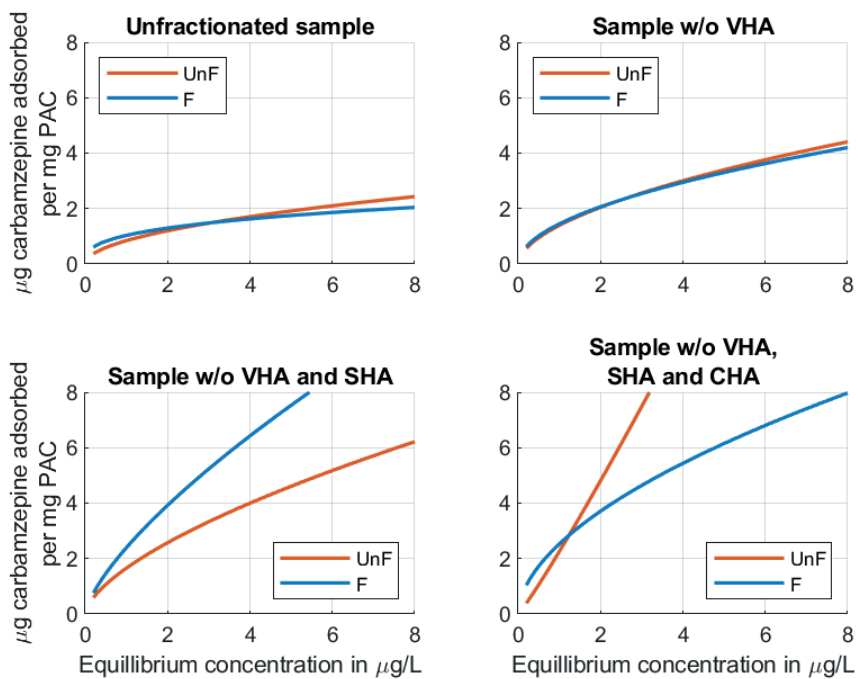


Figure II.6. Comparison of adsorption isotherms between the different fractionated samples of unfiltered sample and 2 kDa permeate. w/o VHA, SHA and CHA also means sample with only NEU fraction.

Appendix III

In this section, different UV spectral scans are presented.

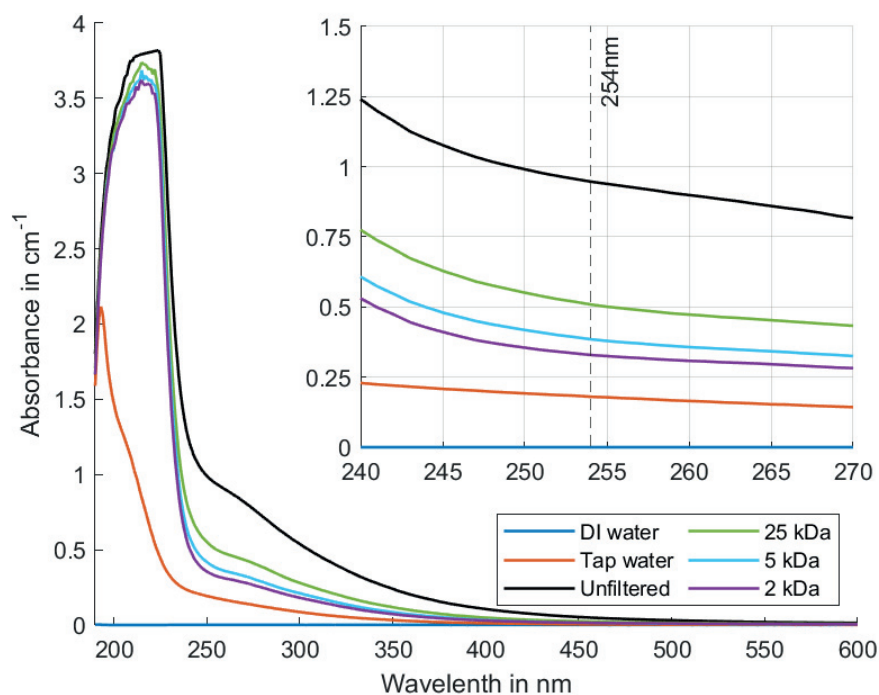


Figure III.1. UV-vis spectral scan for the UF membrane permeates used in the second study along with DI and tap water.

Table III.1. Absorbance at UV_{254} and $SUVA$ for the samples used in the second study.

| Sample | UV_{254} | $SUVA$ | Dominant fraction* |
|----------------------|------------|--------|--------------------|
| DI water | 0 | 0 | - |
| Tap water | 0.180 | 7.98 | Hydrophobic |
| Unfiltered | 0.947 | 10.42 | Hydrophobic |
| UF - 25 kDa permeate | 0.509 | 10.79 | Hydrophobic |
| UF - 5 kDa permeate | 0.385 | 10.31 | Hydrophobic |
| UF - 2 kDa permeate | 0.329 | 9.47 | Hydrophobic |

Note: Dominant fraction is determined based on $SUVA$.

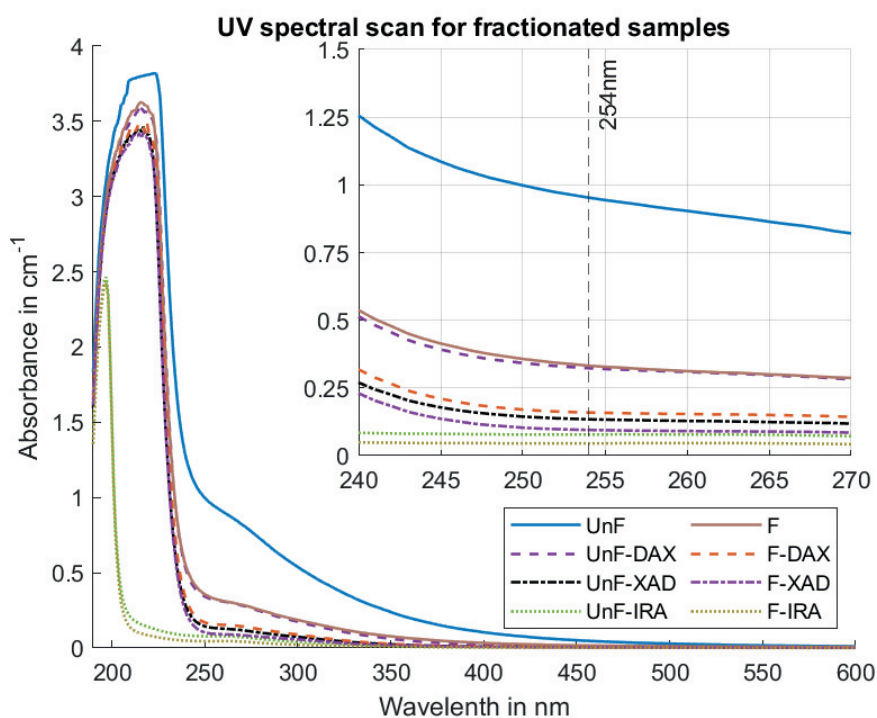


Figure III.2. UV-vis spectral scan for unfractionated and fractionated samples derived from the 2 samples used in the third study. UnF – unfiltered sample, F – 2 kDa permeate. DAX – w/o VHA, XAD – w/o VHA and SHA, IRA – w/o VHA, SHA and CHA. w/o VHA, SHA and CHA also means sample with only NEU fraction.

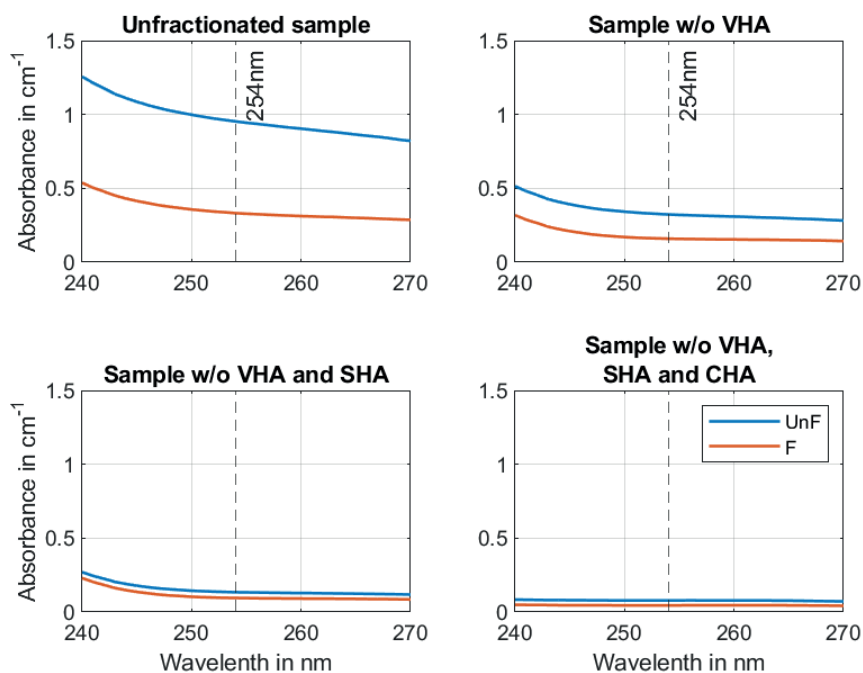


Figure III.3. Comparison between filtered and unfiltered samples for respective fraction for UV-vis spectral scan. UnF – unfiltered sample, F – 2 kDa permeate. w/o VHA, SHA and CHA also means sample with only NEU fraction.

Table III.2. Absorbance at UV_{254} and $SUVA$ for the samples used in the third study.

| Sample | Resin | UV_{254} | $SUVA$ | Dominant fraction* |
|--------------------------|-------|------------|--------|--------------------|
| Unfiltered sample | - | 0.953 | 11.51 | Hydrophobic |
| | DAX | 0.323 | 5.61 | Hydrophobic |
| | XAD | 0.134 | 4.21 | Hydrophobic |
| | IRA | 0.078 | 2.44 | Mixed |
| 2 kDa permeate | - | 0.332 | 9.85 | Hydrophobic |
| | DAX | 0.159 | 4.68 | Hydrophobic |
| | XAD | 0.095 | 2.99 | Mixed |
| | IRA | 0.045 | 1.70 | Hydrophilic |

Note: Dominant fraction is determined based on $SUVA$. DAX – without VHA, XAD – without VHA and SHA, IRA – without VHA, SHA and CHA. w/o VHA, SHA and CHA also means sample with only NEU fraction.

Appendix IV

In this section, graphs illustrating PAC dose required for 50% removal of pharmaceutical compounds are provided.

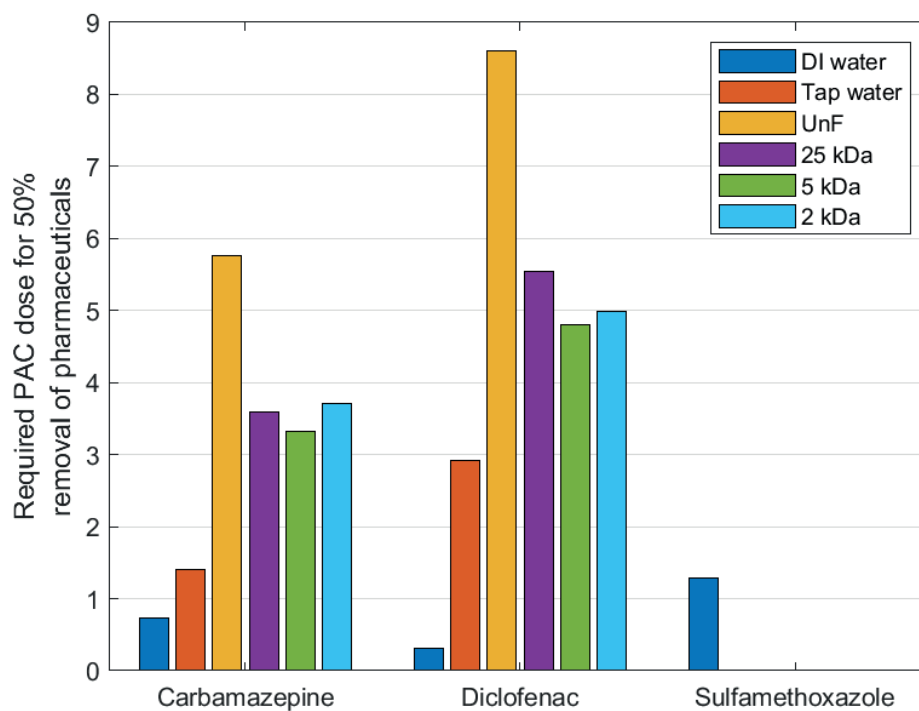


Figure IV.1. Required PAC dose for 50% removal of three pharmaceutical compounds used in second study.

Appendix V

In this section, some additional graphs relevant to the text are presented. Figure V.1 illustrates that as the fractions are removed from the samples, the competition from the DOM reduces effectively increasing removal of pharmaceutical i.e. carbamazepine in this case. To further understand the removal performance, the comparison shows in Figure V.2 suggest that the removal of VHA and SHA, for lower doses of PAC, a small increase in removal of carbamazepine can be observed for membrane permeate.

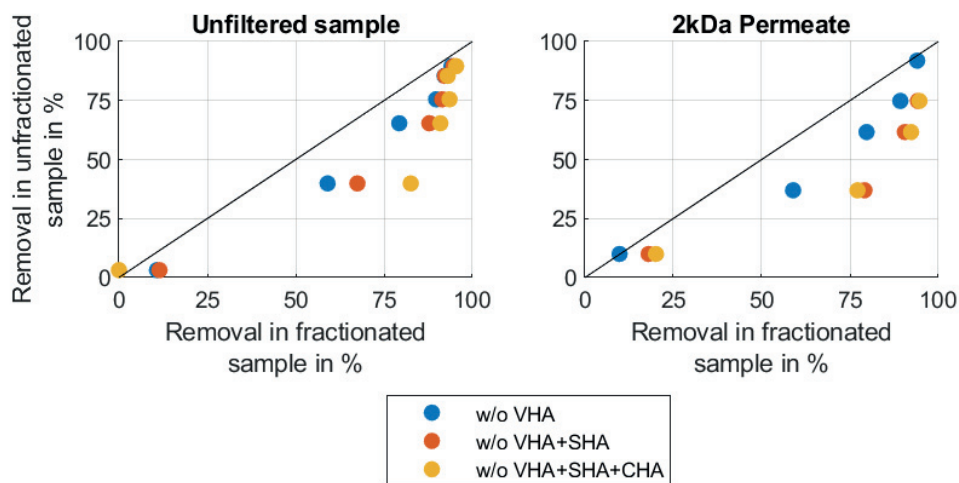


Figure V.1. Comparison between unfractionated and fractionated samples for removal of Carbamazepine. w/o VHA, SHA and CHA also means sample with only NEU fraction.

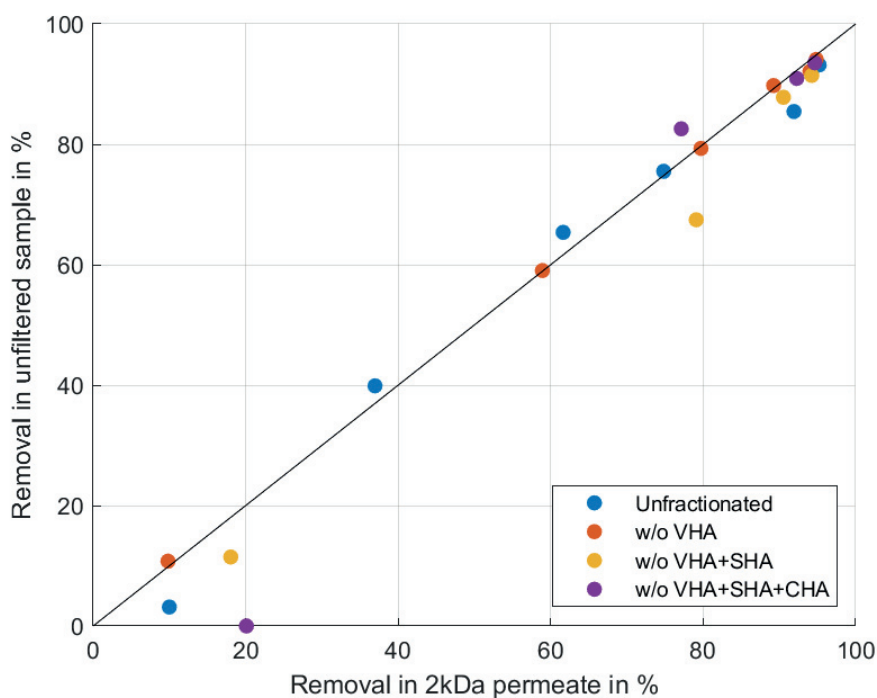


Figure V.2. Comparison between the fractions of unfiltered sample and 2kDa permeate in removal of Carbamazepine for respective PAC doses. w/o VHA, SHA and CHA also means sample with only NEU fraction.

