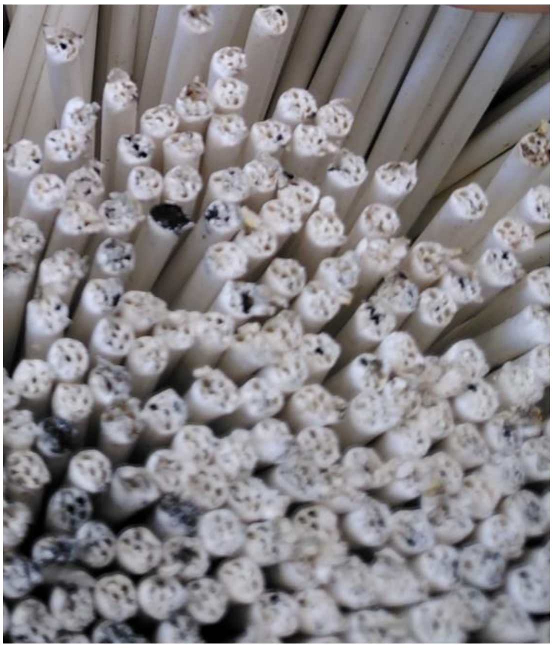

ENHANCING PERFORMANCE OF ULTRAFILTRATION WITH INLINE DOSING OF COAGULANT AND POWDERED ACTIVATED CARBON

Effect on fouling and removal of organic micropollutants including poly- and perfluoroalkyl substances

ABSTRACT

Addition of coagulant with PAC-UF showed to be effective to prevent irreversible fouling, with direct surface water treatment. However, coagulation is responsible for blocking of capillaries. Removal of OMP including PFAS was much lower compared to other PAC-UF systems and therefore PAC-UF with simultaneous and continuous inline dosing of PAC is not a good set-up and adjustments in set-up should be made in order to make this configuration work. Possible improvements are increase of filtration time between backwash and dosing sequence of PAC and coagulant.

Anna Griffioen-Vis

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Enhancing performance of ultrafiltration with inline dosing of coagulant and powdered activated carbon

Effect on fouling and removal of organic micropollutants including poly- and perfluoroalkyl substances

By

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Abstract

In this study simultaneous and continuous inline dosing of PAC and coagulant in UF was investigated. Surface water was directly treated with PAC-UF and performance of the system was assessed by looking at membrane fouling and OMP removal. There is increasing stress on water quantity and quality in drinking water sources. Organic micropollutants present in source waters together with stricter regulations for OMP in drinking water, raises the need for adequate OMP removal by drinking water treatment plants. Advanced water treatment systems are needed to remove OMP such as pharmaceuticals, per- and polyfluoroalkyl substances (PFAS) and industrial and consumer products (ICP). Combining adsorption and membrane processes in one technique, hybrid membrane processes, enhances performance of OMP removal by membrane processes. Powdered activated carbon (PAC) combined with coagulation and ultrafiltration (UF) is a possible treatment technique for surface water.

Permeability in UF-membranes remains steady, when dosing coagulant. Only a small increase in irreversible fouling of 0.2-0.7*10^9 $m^{-1}h^{-1}$ is visible. Different coagulant dosing (1.2 and 3.2 mg/l), as well as different PAC doses (6-15 mg/l)) or a filtration time increase (30 minutes) all have irreversible fouling in the same order of magnitude. However, absence of coagulant dosing causes irreversible fouling to increase to 8.7*10^{10} $m^{-1}h^{-1}$ and can not be easily reversed with a chemically enhanced backwash (CEB). Inline dosing of PAC alone causes an irreversible fouling of 11.4*10^{10} $m^{-1}h^{-1}$ and highest increase in reversible fouling of 11.7*10^{10} $m^{-1}h^{-1}$. Addition of coagulant (1.2 mg/l) lowers reversible fouling compared to no dosing, on the other hand addition of PAC to coagulant shows no clear increase or decrease in reversible fouling. Coagulation has a negative effect on capillary blocking, an increase of 4-8% compared to no coagulant or adsorbent. PAC and no dosing did not influence pore blocking.

Highest removal of low to good adsorbable OMP was 10-63% for continuous and simultaneous dosing of 12 mg PAC/l and 1.2 mg $FeCl_3$/l. Increasing filtration time (30 to 60 min) showed highest removal efficiency of 75% of Sotalol and 5-Methyl-1H-Benzotriazole, both good adsorbable OMP. Removal of PFAS varies between a few percent and 37%. Increasing contact time (from 25 to 200 seconds) of PAC with water before the membrane did not affect removal efficiency as did pre-coating of PAC. Additionally, continuous dosing of coagulant (1.2 mg/l) with PAC (10 mg/l) has a negative impact on OMP adsorption including PFAS. With a higher PAC dose (15 mg/l) removal efficiency was not affected.

Addition of coagulant with PAC-UF showed to be effective to prevent irreversible fouling, with direct surface water treatment. However, coagulation is responsible for blocking of capillaries even resulting in a small decrease of permeability. Removal of OMP including PFAS was much lower compared to other PAC-UF systems and therefore PAC-UF with simultaneous and continuous inline dosing of PAC is not a good set-up. Adjustments in set-up should be made in order to make this configuration work. Possible improvements are increase of filtration time between backwash and dosing sequence of PAC and coagulant.

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Abbreviations

AC	activated carbon
CEB	chemically enhanced backwash
DOC	dissolved organic carbon
EFSA	European food safety authority
FeCl3	Iron chloride
FFMP	forward flush membrane pressure difference
FO	forward osmosis
GAC	granular activated carbon
ICP	industrial and consumer products
IEX	ion exchange resins
MF	microfiltration
NF	nanofiltration
NOM	natural organic matter
OMP	organic micropollutants
PAC	Powdered activated carbon
PAC-UF	Powdered activated carbon combined with ultrafiltration
PFAS	per- and polyfluoroalkyl substances (abbreviations different PFAS appendix A1)
RO	reverse osmosis
SS	suspended solids
TMP	transmembrane pressure
UF	ultrafiltration

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1 Introduction

1.1 Production of drinking water by Dunea

Drinking water company Dunea produces drinking water from dune water. Pre-treated surface water is infiltrated in the dunes which is abstracted after a retention time of approximately two months, managed aquifer recharge. The, the water receives post-treatment at the locations of Katwijk, Scheveningen and Monster. Water infiltrated in the dunes consists of rainwater and pre-treated river water. Water from the Meuse is taken in at a side branche in which it settles for six weeks. In this side branch removal of phosphate and settling of suspended solids (SS) is enhanced through dosing iron sulphate (FeSO4). In Brakel the water is taken in, where in spring and summer micro-strainers are used to remove algae and larvae. The water is then transported to Bergambacht and pretreated with rapid sand filtration. (*Hoe wordt uw drinkwater gemaakt? | Dunea Duin & Water*, n.d.)

The water quality in the river Meuse is affected by climate change in the whole Meuse basin (Rozemeijer et al., 2021). Due to climate change more low discharge periods are expected (Rozemeijer et al., 2021). During lower discharges the concentrations of organic micropollutants (OMP) increase compared to normal conditions (van Vliet et al., 2008). Therefore, drinking water companies have to prepare for higher concentrations of organic micropollutants (OMP) in their source waters.

1.2 Problem statement

Worldwide freshwater resources are under increasing stress due to climate change, urbanization, agricultural activities, rapid growth of population and industrialization (Holland et al., 2015; Rosa et al., 2018; van Vliet et al., 2008). As industries use synthetic organic chemicals in goods, products and daily life, these chemicals also reach surface waters (Tröger et al., 2021). Major sources of chemicals in the environment are wastewater treatment plants, hospitals, agriculture and industries (Ahmad et al., 2010; Loos et al., 2009; Tröger et al., 2021; van Wezel et al., 2018). Awareness and attention increase on OMP, also called contaminants of emerging concern (CEC), in drinking water sources (Kim et al., 2022; Tröger et al., 2021). However, conventional water treatment technologies such as sand filtration and flocculation are inefficient in removing CEC (Margot et al., 2013; Stackelberg et al., 2007; Westerhoff et al., 2005; Yoon et al., 2006). Simultaneously, water quality requirements are becoming stricter for different contaminants (Schrenk et al., 2020).

There is an increasing concern on the potential effects OMP can have on human health through drinking water (Tröger et al., 2021). OMP include pesticides, pharmaceuticals, per- and polyfluoroalkyl substances (PFAS) and other chemical compounds which are found in drinking water sources (Tröger et al., 2021; Wang et al., 2020). A large survey of European wastewater effluent and river water showed that a wide range of polar organic chemical contaminants was present in concentrations ranging from nanograms to milligrams (Loos et al., 2009, 2013). In every drinking water source a different unique combination of OMP is present. Even though on individual level the effect can not be detected, a negative effect on health is detected for the combinations of these OMP (Schwarzenbach et al., 2006). In the last few years, attention goes to a new important group of OMP which are PFAS. PFAS are detected in drinking water samples all over the world (Tröger et al., 2021). Human exposure to PFAS happens through various ways, via food, air, clothing, and for a small part drinking water (Schrenk et al., 2020). Due to scientific opinion on the risks of PFAS for human health the European Food Safety Authority (EFSA) introduced a new safety threshold of tolerable weekly intake of 4.4 ng/kg body weight (Schrenk et al., 2020). This new safety threshold led to a new target threshold for drinking water of 4.4 ng/l PFOA equivalent (PEQ) (Aa van der et al., 2021). Perfluorooctanoic acid (PFOA) equivalent means the total of different PFAS based on their relative toxicity compared to PFOA (Aa van der et al., 2021). Treatment technologies which are effective for other OMP have difficulty removing PFAS such as advanced oxidation, biodegradation, aerobic and anaerobic biological treatment due to the strong chemical bonds (Crone et al., 2019; Sáez et al., 2008; Thompson et al., 2011). Anion exchange resins, high pressure membranes and activated carbon (AC) are effective technologies, that are commonly used in drinking water treatment, in removing PFAS (Ching et al., 2020; Crone et al., 2019; Siegers et al., 2021; Wang et al., 2020; Yadav et al., 2022). Due to posing health risks by OMP and a possible increase in concentrations of OMP it is important to strive for a high removal of OMP in drinking water treatment plants to ensure safe drinking water.

As conventional treatment systems are inadequate to remove OMP more advanced water treatment systems are needed (Stackelberg et al., 2007; Westerhoff et al., 2005; Yoon et al., 2006). Adsorption is a promising method for the removal of both organic and inorganic contaminants, such as PFAS, in drinking water and wastewater treatment due to its practical operation, cost-efficiency, flexibility and broad applicability (Crone et al., 2019; Kim et al., 2022). The removal of PFAS with AC has been researched extensively for long chain PFAS (Crone et al., 2019). However, there are still research gaps when considering short chain PFAS, which are upcoming and difficult to remove (Zhang et al., 2019). Moreover, research on the competition between other contaminants and PFAS is lacking (Crone et al., 2019; Zhang et al., 2019). Most research is done on laboratory scale and with synthetic water, more research is needed with natural water (Zhang et al., 2019).

Membrane processes have been commonly used for water and wastewater treatment as well, as they have high recoveries, low chemical use, easy scale up and a small footprint (Gora et al., 2011; Kim, Chu, et al., 2022). Ultrafiltration (UF) is an established technology for drinking water production due to the decrease in maintenance costs, high permeate flux and retention of particulates and pathogens (K. Li et al., 2020). However, UF does not reach high efficiencies in the removal of OMP (Kim et al., 2018).

Integrated membrane processes, where membranes are combined with adsorption, such as powdered activated carbon combined with UF (PAC-UF) have been used to increase the contaminant removal of conventional membrane processes (Kim et al., 2022; Löwenberg et al., 2017; Stoquart et al., 2012; Viegas et al., 2021). UF pores are small enough to effectively retain all PAC, which makes it suitable for hybrid treatment systems (Löwenberg et al., 2014). Previous studies have shown that PAC-UF can remove different organic and inorganic contaminants from water (Kim et al., 2022; Löwenberg et al., 2017; Siegers et al., 2021; Stoquart et al., 2012; Viegas et al., 2021).

In a PAC-UF system, membrane fouling is complicated due to the participation of adsorbent particles (K. Li et al., 2020). Some studies mention a positive effect off PAC dosing on the membrane performance (Campinas et al., 2010; Löwenberg et al., 2014a), while other studies showed a negative effect with for example a lower flux (K. Li et al., 2020; Lin et al., 1999; Schwaller et al., 2021; Stoquart et al., 2012). Some papers describe research on the addition of a coagulant to reduce membrane fouling and increase the flux of PAC-UF (Löwenberg et al., 2014; Christoph Schwaller et al., 2021; Seckler et al., 2013). PAC-UF systems also differ in set-up, as some mention a separate buffer tank where the PAC is dosed (Lin et al., 1999; Löwenberg et al., 2014; Stoquart et al., 2012). There are some studies where PAC is dosed directly on the UF, also called inline dosing (Schwaller et al., 2021; Siegers et al., 2021). However, inline PAC and coagulant addition have not been studied on pilot scale. Furthermore, heterogeneous fouling such as capillary blocking has not been studied on pilot scale and not with the addition of PAC and coagulant. As such, data on fouling over a longer period than a few cycles is missing for inline dosing of PAC and coagulant. Removal efficiency of OMP with surface water and inline dosing of PAC and coagulant in UF is also missing. As most research is done on laboratory scale and with synthetic water, more research is needed with raw water (Zhang et al., 2019).

Although recently several studies have been published on integrated UF processes (Cheng et al., 2021; Echevarría et al., 2020; Huang et al., 2021; Kim et al., 2022; K. Li et al., 2020; Lohwacharin et al., 2021; Schwaller et al., 2021), a research gap exists on the performance of combined adsorbent and UF systems at pilot scale on OMP removal with the addition of a coagulant. Research is inconclusive and missing when considering fouling of an UF with inline dosing of coagulant and adsorbent. Furthermore, the removal of OMP such as PFAS with PAC-UF has potential (Kim et al., 2022; Wu et al., 2020). Thus much is still unknown considering the removal of PFAS with the combined process of PAC-UF and coagulant. Inline dosing of PAC in UF enhances performance of UF through additional OMP removal. Additionally, inline dosing of coagulant is added to prevent fouling. Inline dosing of PAC and coagulant can be easily integrated in existing treatment of drinking water companies. Compared to other alternatives for the removal of OMP, PAC-UF has a low footprint and a flexible set-up which can be easily adjusted to influent water composition. However, there are contradicting results on the effect

PAC in combination with coagulant have on fouling and OMP removal (Altmann et al., 2015; Löwenberg et al., 2014; Schwaller et al., 2021; Siegers et al., 2021). Furthermore, research on pilot-scale is missing on PAC-UF systems (Löwenberg et al., 2017; Siegers et al., 2021).

1.3 Research question and objectives

The general objective of this research is to determine the retention of different OMP and fouling of coagulation-adsorption-UF systems for direct surface water treatment at pilot scale. Furthermore, this study aims to gain insight in the effect of combining coagulation and adsorption on OMP removal and fouling. Thus, the purpose of this research is to answer the following research question:

- What is the effect of inline dosing of coagulant and PAC in UF on fouling and the removal of OMP including PFAS for direct surface water treatment?

Where the sub-questions of this study are:

i. What is the effect of varying dosing concentrations of PAC and coagulant on the fouling of an UF system?
ii. What is the removal of OMP including PFAS with varying dosing concentrations of PAC and coagulant in an integrated UF system?
iii. What effect have varying PAC dosing modes on the removal of OMP including PFAS in an integrated UF system?

In order to answer these objectives this study includes a literature review and pilot-scale experiments. Recently several studies have been published on integrated ultrafiltration systems (Cheng et al., 2021; Echevarría et al., 2020; Huang et al., 2021; Kim et al., 2022; K. Li et al., 2020; Lohwacharin et al., 2021; Schwaller et al., 2021). Different combinations with UF are mentioned such as pre-coating of the membranes, addition of oxidation, addition of coagulants, addition of adsorbents and combinations of aforementioned treatment technologies. Therefore, a literature review is included in chapter two in which these upcoming combined ultrafiltration treatment systems are studied. Chapter two starts with background information on OMP, secondly adsorbents, membranes and hybrid membrane systems are discussed. At the end mechanisms such as adsorption and fouling are explained. In chapter three materials and methods for the pilot study are given. Set-up of the pilot is described and background information on materials is given. Secondly, methods for fouling experiments and removal experiments are explained. In chapter four results for inline dosing of PAC and coagulant in UF are presented and discussed. Different variations of a coagulant combined with PAC were tested at pilot scale. Retention of different contaminants was measured as well as fouling of UF by looking at fouling of the membrane surface and capillary blocking. In chapter 5 the conclusion and recommendations on inline dosing of PAC and coagulant in UF is given.

2 Techniques present for OMP removal

In this chapter background information on the organic micropollutants tested in this research is given. Furthermore, different techniques for the treatment of direct surface water containing organic micro pollutants are discussed. At last the different water treatment mechanisms which are present with inline UF are explained.

2.1 Organic micro pollutants

In this paragraph the occurrence of organic micro pollutants in surface water and health risk are discussed. Additionally, background information is given on different groups of micro pollutants, which are measured in this paper. A substance is called an OMP, which can also be called emerging contaminant, when at least one synthetic chemical reaction of natural substances took place (İlyasoglu et al., 2022; Luo et al., 2014). An OMP is manmade and can pose a threat even when present in low levels in water (Arslan et al., 2017; Luo et al., 2014). There are different classes of organic micropollutants: pharmaceuticals, endocrine disruptive chemicals, personal care products, agricultural chemicals, detergents, surfactants, PFAS, additives, industrial and personal consumer products (ICP) and disinfection by-products (İlyasoglu et al., 2022; Ojajuni et al., 2015).

2.1.1 Occurrence organic micropollutants

Today, more than 400.000 chemicals are registered and regulated[1]. These OMP end up in surface water through various routes. Main entry routes are wastewater effluent, hospitals, intensive agriculture and industries (Arslan et al., 2017; Loos et al., 2013; Tröger et al., 2021; van Wezel et al., 2018). A large survey of European wastewater effluent and river water showed that a wide range of polar organic chemical contaminants was present in river water in concentrations ranging from nanograms to milligrams (Loos et al., 2009, 2013). Raw water sources used for drinking water contain a wide range of OMP (Tröger et al., 2021). Different studies have performed a suspect and non-target screening approach in which a wide range of OMP have been investigated and found in surface water and drinking water (Kolkman et al., 2021; Tröger et al., 2021; Q. Wang et al., 2022, Y. Wang et al, 2022). Harmful effects are seen on living organisms by low concentrations of OMP in the environment (Arslan et al., 2017; Rahman et al., 2009). Toxicity can be either acute or chronic, especially chronic toxicity is widely acknowledged at present environmental concentrations (Arslan et al., 2017). In every drinking water source a different unique combination of OMP is present. These combinations of OMP can have a negative effect on health even though on individual level the effect can not be detected

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[1] American Chemical Society (CAS). (n.d.). *Regulated Chemicals - CHEMLIST - Find whether a substance is regulated and by what agency*. Retrieved from https://www.cas.org/support/documentation/regulated-chemicals

(Schwarzenbach et al., 2006). Due to often incomplete metabolism by human and animal bodies, part of these pharmaceuticals end up in wastewater treatment plants (Tijani et al., 2016). Pharmaceuticals and their metabolites eventually end up in surface waters (Loos et al., 2009; Tijani et al., 2016; Tröger et al., 2021).

Climate change creates more extreme weather patterns, therefore more droughts are expected (Rozemeijer et al., 2021). The water quality in the rivers such as the Meuse is affected by these droughts (Rozemeijer et al., 2021). The concentrations of OMP increase during droughts due to lower discharges of the river (van Vliet et al., 2008). Consequently, in the future higher OMP concentrations are expected in drinking water sources.

2.1.2 PFAS

PFAS are chemicals which contain at least the polyfluorinated formula CnF2n+1- (Buck et al., 2011). PFAS consists of 42 subfamilies, of which the relevant subfamilies for this study are explained in this report (Buck et al., 2011). PFAS are divided into perfluorinated compounds and polyfluorinated compounds, of which the latter consists of only partly fluorinated carbon chains (Pancras et al., 2018). Important perfluorinated compounds are perfluorinated sulfonic acids (PFSA) and perfluorinated carbonic acids (PFCA). Polyfluorinated compounds often have an ethylgroup between the fluorinated compounds and the functional group (Pancras et al., 2018). Most polyfluorinated compounds are precursors of PFSA and PFCA (Lindstrom et al., 2011). PFSA and PFCA represent only 25% of total PFAS present in wastewater, others are precursors (Houtz et al. 2012). In water most PFAS dissociate in anions and cations (Wang et al., 2011). Mainly PFAS consist of a hydrophobic tail and hydrophilic head (sulfonate, carboxylate). Due to these amphiphilic properties they are ideal to use as surfactants. In contrast to more general known surfactants PFAS tails also have lipophobic properties. PFAS accumulate at interfaces of water and air and form micelles (Vierke et al, 2013).

For more than 50 years, PFAS have been used in various applications such as cooking pans, clothes, fire extinguishing water, carpets, paints and more (Zhang et al., 2019). This is due to their unique properties such as chemical stability and lowering the surface tension, which makes fabric waterproof (Paul et al., 2009). Even though PFAS have these unique properties it is nowadays widely known that for instance perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are toxic, bioaccumulative, and widely spread and persistent through our environment (Murray et al., 2019; Zhang et al., 2019). They enter the aqueous environment through plastics, aqueous film forming foam (AFFF), industrial resins and sealants as well as industrial discharges (Murray et al., 2019). Human exposure to PFAS happens through various ways, via food, air, clothing, and for a small part drinking water (Schrenk et al., 2020). Due to scientific opinion on the risks of PFAS for human health the EFSA introduced a new threshold of tolerable weekly intake of 4.4 ng/kg body weight (Schrenk et al., 2020). This new safety threshold led to a new target threshold for drinking water of 4.4 ng/l PFOA equivalent (PEQ) (Aa van der et al., 2021).

2.2 Treatment technologies for OMP removal including PFAS from surface water

In this section different treatment technologies for the removal of OMP from surface water will be discussed. Removal, retention or degradation of OMP in drinking water treatment are influenced by several factors such as source water quality, treatment process, goals, and chemical properties of OMP (Kim, Chu, et al., 2018; Rahman et al., 2014; Snyder et al., 2003). Several studies have proven that OMP are incompletely removed by conventional water treatment plants (Appleman et al., 2014; Snyder et al., 2007; Westerhoff et al., 2005; Yoon et al., 2006). Advanced water treatment technologies are capable of enhancing the removal of OMP (Ahmad et al., 2010; İlyasoglu et al., 2022; Ojajuni et al., 2015; Zhang et al., 2019). Recently PFAS have become an important group of OMP of which removal in drinking water treatment is desired. OMP are removed well by treatment technologies such as advanced oxidation, membrane processes, adsorption, biodegradation, aerobic and anaerobic biological treatment (Kim, Chu et al., 2018; Ling et al., 2020; Snyder et al., 2003).

However, advanced oxidation, biodegradation, aerobic and anaerobic biological treatment technologies have difficulty removing PFAS due to the strong C-F bonds (Crone et al., 2019). On the other hand, membrane technologies, adsorption technologies, and destructive technologies are effective in removing PFAS (Ching et al., 2020; Crone et al., 2019; Wang et al., 2020; Yadav et al., 2022). The goal of this section is to review treatment techniques which are efficient in the removal of OMP including PFAS. Therefore only techniques known by research to remove PFAS will be discussed. Destructive technologies are capable of breaking down contaminants into less toxic products (Yadav et al., 2022). Destructive technologies show potential to remove PFAS, however these technologies have only been researched on lab scale (Yadav et al., 2022). The efficiency with the presence of environmental matrices, organic and inorganic matter, and other PFAS is unknown. Therefore this technique will not be taken into account.

2.2.1 Membrane filtration

Membrane processes have been studied widely for the removal of OMP (Kim, Chu, et al., 2018). Membrane processes include forward osmosis (FO), reverse osmosis (RO), nanofiltration (NF) and UF and microfiltration (MF). The OMP removal efficiency follows RO ≥ FO > NF > UF (Kim, Chu et al., 2018). All membrane processes will be discussed in this paragraph, OMP removal and operational performance will be reviewed.

FO

The mechanism behind FO rests on an osmotic pressure difference which is caused by a concentrated draw solution to permeate water from the feed solution to the draw solution across the membrane. On the contrary, the driving force to transport water through a semipermeable membrane for RO, NF and UF processes is a hydraulic pressure difference (Kim, Chu et al., 2018). A pilot-scale with wastewater achieved removal of 70-99% of trace organic compounds (Hancock et al., 2011). Another study found rejections of >93% of pharmaceuticals from saline water by different FO membranes (Jin et al., 2012). These are promising results, however there are no known studies on OMP removal from surface water by FO. Likewise no studies on the removal of PFAS by FO are known.

Reverse osmosis

Retention of OMP by RO is determined through interactions between solute, the solution and membrane (Kim, Chu et al., 2018). Key retention mechanisms include electrostatic interactions, steric hindrance and hydrophobic interactions between OMP and the membrane (Kim, Chu et al., 2018). Hereof, steric/size exclusion is the main mechanism for RO (Kim, Chu et al., 2018). According to a study from Huang et al. (2011) RO removal efficiencies for natural surface water vary between 92.5-99.9. Another study performed with anaerobic riverbank filtrate found that retention of neutral and moderate hydrophobic OMP was >95% (Albergamo et al., 2019). Retention for neutral hydrophilic OMP larger than 180 Da was 99% and for negatively charged OMP >99% (Albergamo et al., 2019). These findings suggest that RO is an effective treatment in removing OMP in natural water that have a molecular weight larger than the molecular weight cut-off of the membrane (Huang et al., 2011). In practice RO is never used for direct surface water treatment mainly because of membrane fouling (Cornelissen et al., 2021). A disadvantage therefore, is that pre-treatment is needed in order to prevent fouling of the membrane and it increases costs of RO (Cornelissen et al., 2021). Another disadvantage is the introduction of a concentrate stream, which consists of high concentrations of contaminants, disposing of this concentrate is a problem (Snyder et al., 2007). New research does show promising results for cost reduction, minimal pre-treatment is needed with low flux RO which reduces the costs almost three times than for conventional RO with UF pre-treatment (Cornelissen et al., 2021).

Nanofiltration

The removal of OMP in NF largely depends on the physicochemical properties of OMP, which can also be affected by the chemistry of the water (Nghiem et al., 2005). Specifically these properties are: size exclusion, electrostatic interactions, hydrophobicity, and charge (Azaïs et al., 2014; Nghiem et al., 2005; Zazouli et al., 2009). Retention of several OMP by NF are known to be influenced by fouling and pH (Azaïs et al., 2014; Nghiem et al., 2005; Zazouli et al., 2009). Another study with surface water found 44-93% retention of 52 different OMP (Yoon et al., 2006). Just as for RO, a disadvantage for NF is the concentrate stream which consists of high concentrations of contaminants, disposing of this concentrate is a problem (Snyder et al., 2007).

Ultrafiltration

UF is able to have a higher permeate flux and saves operating costs compared to RO and NF (Lin et al., 1999). Furthermore, UF has high recoveries of 90-95% and as such small wastewater streams which can partly be recycled (Gora et al., 2011). Additionally, UF is efficient in disinfection of the water removing pathogenic bacteria and even viruses (Zio et al., 2005). UF ensures high permeate water quality and compact process design (Doyen, 1997). Permeate water contained lower concentrations of 52 OMP and conventional contaminants except for a few exceptions (Yoon et al., 2006). However, UF has on overall a low removal of pharmaceuticals with inconsistent degrees of retention for pharmaceuticals (Sheng et al., 2016). Although, for NF and UF membranes high retention may still be reached due to hydrophobic (adsorption) and electrostatic (attraction) interactions (Kim, Chu et al., 2018). Organic OMP which are more volatile, less polar, and more hydrophobic are able to reach higher retention than OMP which have opposite properties (Kim, Chu et al., 2018). Increased retention is seen for waters which contain higher concentrations of organic matter, including biopolymers (Wray et al., 2014). Fouling of membranes also influences the retention of endocrine-disrupting compounds due to a change of pore size and hydrophilicity (Hu et al., 2014a). Reported OMP retentions for the treatment of natural surface water vary from <5-90% (Wray et al., 2014). Another study found, <10% for less hydrophobic, more polar and less volatile compounds and 30-80% for more hydrophobic, less polar, more volatile compounds (Yoon et al., 2006).

2.2.2 Adsorption

Adsorption is the adhesion of a liquid or solid onto another liquid or solid (adsorbent). Adsorption has been used for the removal of numerous pollutants such as pesticides, PFAS, pharmaceuticals and more OMP (Ahmad et al., 2010; Militao et al., 2021; Rahman et al., 2009; Snyder et al., 2003). The advantage of adsorption compared to other technologies is a simple design, low investment costs and ease of operation (Militao et al., 2021). Removal efficiency depends on adsorbent properties, solution conditions and physicochemical properties of OMP (Ahmad et al., 2010; Aksu et al., 2005). AC is a well-known adsorbent, however nowadays there are many different adsorbents such as ion exchange resins (IEX), inorganic adsorbents, bioadsorbents, adsorbents from waste and adsorptive membranes (Ahmad et al., 2010; Ching et al., 2020; İlyasoglu et al., 2022; Militao et al., 2021; Snyder et al., 2003; Zhang et al., 2019). At the moment activated coal is the general applied water treatment technique for PFAS containing water (Pancras et al., 2018). The most commonly applied adsorbents and adsorbents studied for PFAS removal are discussed.

Carbon adsorption

AC is able to remove a wide variety of OMP including PFAS (Militao et al., 2021; Snyder et al., 2003; Wu et al., 2020). AC is seen in different forms: granular activated carbon (GAC), PAC, carbon cloth, carbon fibers, black carbon and activated carbon composites (Ahmad et al., 2010). PAC has as advantage that a continuous fresh stream of carbon can be provided, it can also be fed seasonally and can be easily adjusted to influent concentrations (Snyder et al., 2007). The ability to remove OMP by PAC depend on PAC dose and contact time and physicochemical properties of the OMP (Nam et al., 2014; Snyder et al., 2007). The high adsorptive capacity of AC results from adsorbent properties (K. Li et al., 2020; Zhang et al., 2019). Removal for organic compounds is mainly governed by hydrophobic interactions (Snyder et al., 2003). Therefore nonpolar OMP have higher removal efficiencies (Snyder et al., 2003). PFAS also is partly removed by AC, GAC has been used in many studies to remove PFAS at bench and full scale (Rahman et al., 2014). PAC adsorption capacity for PFAS is higher than GAC adsorption capacity for PFAS (Yu, Zhang et al., 2008). AC has also shown to have low affinity for certain PFAS which makes removal below environmentally relevant concentrations more difficult (Xiao et al., 2017). AC is not specific for only OMP and also adsorbs natural organic matter (NOM), which reduces the available adsorption sites on PAC for OMP (Lebeau et al., 1998; K. Li et al., 2020; Nam et al., 2014). Pharmaceuticals were effectively removed by PAC as (Adams et al., 2002) finds removal efficiencies of 81-98% for sulfamethazine, trimethoprim and carbatox. However, Westerhoff et al. (2005) mentioned a wide range of removal from 20-69% for different OMP. Another study also showed a wide range of 5-98% removal efficiency (Westerhoff et al., 2005). Lower removal of Metformin, Gabapentin and Caffeine are found due to lower affinity for AC (Ebrahimzadeh et al., 2022; Nam et al., 2014). Other OMP have higher adsorption such as 1H-benzotriazole, 5-methylbenzotriazole, Carbamazepine and Sotalol (Ebrahimzadeh et al., 2022; Nam et al., 2014). It is shown that AC can be efficient and has potential in removing OMP (Snyder et al., 2007). However, conditions of influent water, adsorbent and adsorbate influence removal efficiency and as such not all situations are suited for adsorbent removal. Moreover, PAC has to be disposed through incineration or landfill depending on the OMP adsorbed by PAC and GAC needs to be regenerated or disposed. GAC regeneration or PAC incineration requires significant amounts of energy and PAC disposing through landfill poses environmental risks (Snyder et al., 2007).

Resins

IEX remove micropollutants from water through replacement with exchangeable charged co-ions that are present on a polymeric resins surface (Yadav et al., 2022). IEX have been used to remove various pollutants due to a small footprint, regenerative abilities and high effectiveness (Li et al., 2021). There are two classes of resins; cationic exchange resins and anionic exchange resins (Yadav et al., 2022).

Different surface and recycled waters were treated with a strong basic IEX resin (Dixit et al., 2020). A removal between 30 and 40% with a dose of 50 mg/l and complete removal of OMP with 1000 mg/l (4.5 ml/l) of which most pollutants were PFAS was achieved in the study of Dixit et al. (2020). Another study with polymeric resins reached removals of more than 90% with a dose of 5.4 ml/l and between 40-60% for 1.8 ml/l (Haddad et al., 2019). In the study of Haddad et al. (2019) surface water was pre-treated. Anionic ion exchange resins show the best performance for PFOA removal compared to GAC and non-ion exchange resin, due to PFOA being anionic at pH of natural water (Zhang et al., 2019). Hydrophobicity of the resin exchange functional group and PFAS removal show a strong relationship (Zaggia et al., 2015).

Other adsorbents

Biomass-based biochar is produced from the anoxic pyrolysis (sometimes semioxic) of different biomass sources such as for instance pine (Kennedy et al., 2021). Different surface waters were tested with PAC and pine biochar (Kennedy et al., 2021). However, PAC outperformed pine biochar for all OMP, the best result were some comparable removal efficiencies (Kennedy et al., 2021). Another study also showed poor results for pine biochars however, another biochar showed comparable results with GAC for the removal of PFOA and PFOS (Xiao et al., 2017). A molecularly imprinted polymer (MIP) is a polymer which is synthesized for specific OMP (Zhang et al., 2019). The advantages are a high affinity and selectivity towards specific targets (Yu, Deng, et al., 2008). However, if the aim is to remove many different OMP than MIP is not suitable since it is made to be selective. Inorganic adsorbents such as minerals have also been studied for the removal of PFAS. However, the adsorptive capacities are much less than for resins and AC adsorption (Zhang et al., 2019). Other more environmentally friendly alternatives compared to AC are upcoming of which one are cyclodextrin polymers (CDP) (Ching et al., 2020; Wang et al., 2020; Wu et al., 2020). Recent research shows promising results of removing NOM, organic micropollutants and PFAS with CDP (Hu et al., 2020; Ling et al., 2020; Wang et al., 2020). They have a relative rapid adsorption and higher removal efficiency for PFAS compared to AC (Wang et al., 2020). CDP show more specific affinity for certain PFAS groups while AC is more non-selective (Wang et al., 2020). According to Ling et al. (2020), CDP are promising to use in batch adsorption processes followed by ultrafiltration processes (BA-UF).

2.2.3 Integrated membrane filtration

Adsorption and membrane filtration are both commonly used treatment techniques for water and wastewater treatment (Kim et al., 2022). Especially adsorption is a well-known technique for the removal of organic micropollutants (2.2.2 Adsorption). Therefore adsorption is able to enhance the performance of membrane processes mainly by increasing contaminant removal and by reducing membrane fouling (Kim et al., 2022). The past two decades many different adsorption- membrane systems, also called hybrid membrane processes, have been studied (Kim et al., 2022; Stoquart et al., 2012). In a review of Kim et al. (2022) different studies combined processes of FO, RO, NF and UF with various organic and inorganic adsorbents such as PAC, resins biochars, zeolite nanoparticles, carbon nanotubes, ferrocyanide/mixed cellulose esters, graphene/graphene oxides, and iron oxide/hydroxide agglomerates. Different studies investigated the removal of pollutants such as pesticides, personal care products, phosphate , PFAS, NOM, and pharmaceuticals (K. Li et al., 2020; Lohwacharin et al., 2021; Löwenberg et al., 2014; Murray et al., 2019; C. Schwaller et al., 2021; Viegas et al., 2021) .

Adsorption-nanofiltration hybrid systems

Adsorption-NF hybrid systems have not been as commonly applied as adsorption-UF systems (Kim et al., 2022). The review of Kim et al mentions removal of dyes, dissolved organic carbon (DOC), detergents, and ICP. Removal for all was higher than 75%. A study of Wang et al. (2020) shows that PAC pre-treatment reduced cake layer fouling of NF membrane while pre-treatment with coagulant aggravated membrane fouling (Wang et al, 2020). For UF coagulation often has a positive effect on fouling of the membrane (Schwaller et al. 2021, Wang et al. 2020).

Adsorption-ultrafiltration hybrid systems

Most studies conducted used synthetic water and OMP removal efficiencies varied for different OMP (Kim et al., 2022). Two PAC-UF systems, a pressurized and submerged system, were tested with wastewater effluent, a removal of 60-95% of selected OMP (sulfamethoxazole, carbamazepine, mecoprop, diclofenac and benzotriazole) was achieved (Löwenberg et al., 2014). In both cases PAC dosing was 20 mg/l and coagulant dosing was 4 mg Fe/l, with a 2 hour contact time for PAC. Another study used activated biochar as adsorbent and found removal efficiencies of 42%, 53% and 41% for ibuprofen, 17α-ethinyl estradiol and carbamazepine respectively (Kim et al., 2018). In this study synthetic water (including humic acid) was dosed with 10 mg pine biochar/l with a contact time of 4 hours. The biochar-adsorbent was compared with a PAC-UF system which showed a higher removal efficiency of 6-9%. This was due to PAC being more hydrophobic, having a higher surface area, and higher pore volume (Kim et al., 2018). In another study PAC-UF was compared with a MIL101(Cr) metal-organic framework-UF which showed a higher removal of 2-8% (for ibuprofen and 17α-ethinyl estradiol) depending on NOM composition (Kim et al., 2020). This difference between PAC and MIL101(Cr) was ascribed to higher pore volume of MIL101(Cr). Schwaller et al. (2021) showed removal efficiencies lower than 60% with inline dosing of 15 mg PAC/l and coagulant. Highest removal efficiencies were seen for 30 mg PAC/l with pre-coating of coagulant 33%, 84% and 93% for poor, medium and good adsorbable trace organic compounds (Schwaller et al., 2021). Treated wastewater was used as influent water with DOC of 4.0 ±0.4 mg/l. Margot et al. (2013) tested PAC-UF in a pilot with wastewater effluent (DOC 7.3 ±1.9 mg/l) for over a year. OMP removal on average was >80%

compared with raw wastewater with a PAC dose of 10-20 mg/l. Compared to oxidation by ozone PAC-UF was higher in cost, however PAC-UF removal of OMP was better and had a higher total disinfection of the effluent (Margot et al., 2013).

Addition of PAC increases membrane fouling due to deposition of PAC on membrane surfaces (Kim et al., 2022). Addition of PAC lowered the flux compared to UF with activated biochar in the study of (Kim, et al., 2018). Normalized fluxes of MIL101(Cr)-UF were higher than for PAC-UF however, both normalized fluxes are lower than for UF only (Kim et al., 2020). Both adsorbents therefore act as foulants.

Adsorption-microfiltration hybrid systems

The combination of MF with adsorption is an economic way to enhance OMP removal, ensure a more reliable disinfection capacity, and is an easy barrier for PAC retention (Viegas et al., 2021). A high removal efficiency of pesticides was achieved by a study of Viegas et al. (2021) (≥93%) with 10-12 mg PAC/l, however NOM addition required a higher dose with inline dosing of PAC in UF. Two different surface waters with a DOC level of 1.3 and 1.8 mg C/l were used as influent water. Furthermore inline dosing of PAC had lower removal efficiencies than PAC dosing in a reactor tank with high A254-absorbing NOM (Viegas et al., 2021). On the other hand PAC inline dosing is more cost-effective even when 50% higher dosing than contact tank dosing of PAC (Viegas et al., 2021).

Coagulant addition in UF

For more than 20 years the addition of coagulation prior to UF has been studied to increase removal of organics and reduce membrane fouling (Doyen et al., 2003; Kimura et al., 2005.; Peleato et al., 2017; Tang et al., 2019). Results of coagulant addition varied from no effect to a positive effect (Doyen, 1997). Coagulant can be dosed inline or as a pre-treatment with flocculation and sedimentation (Doyen et al., 2003; Kimura et al., 2005). Coagulation as a pre-treatment reduced reversible membrane fouling, however irreversible fouling was not reduced (Kimura et al., 2005). Inline dosing of coagulant without flocculation and sedimentation showed a reduction in irreversible fouling compared to no coagulation with low doses of coagulant (<1 mg/l alum) (Peleato et al., 2017; Tang et al., 2019). Inline dosing is suggested to be more effective due to a loose cake layer which forms on the membrane surface compared to coagulation including sedimentation (T. Li et al., 2020). Low doses of inline coagulant increases cake porosity from 37% to 93% (Doyen et al., 2003). Furthermore, coagulant addition ensures a steady transmembrane pressure (TMP) over time however when dosing was stopped TMP rose steeply (Doyen et al., 2003). Dosing of coagulant during the first part of a filtration cycle is enough to ensure the positive effects of coagulant dosing in UF as mentioned before (Doyen et al., 2003). An optimal range of coagulant dosing was observed by Peleato et al. (2017), indicating that from a certain point higher doses of coagulant increase irreversible fouling.

The addition of coagulant in combination with an adsorbent and NF, UF or MF has been introduced as well (Bu et al., 2019; Schwaller et al., 2021; Siegers et al., 2021). Schwaller et al (2021) and Bu et al. (2019) both show a positive effect on the increase of the transmembrane pressure. Dosing sequence is of importance as well on the removal efficiency of the membrane of NOM and disinfection by-product precursors (Bu et al., 2019). Addition of coagulant after adsorbent ensured the highest removal efficiencies (Bu et al., 2019). This was confirmed by Seckler et al. (2013) and (Sánchez López et al., 2021) who also found that dosing of PAC after coagulant ensures a higher OMP removal efficiency. Pre-coating of coagulant increased removal efficiency from 18%, 47%, 57% to 11%, 53% and 77% for poor, medium and good adsorbable OMP (Schwaller et al., 2021).

2.3 Water treatment mechanisms

In this section the water treatment mechanisms for membrane retention and adsorption are explained.

2.3.1 Membrane retention mechanisms for OMP

The solute transport mechanism in membranes, where the solute passes the membrane through pores from one side to the other, is driven by pressure in UF (Kim, Chu et al., 2018). Steric rejection and hydrophobic membrane surface adsorption are both rejection mechanisms for different OMP in UF (Kim, Chu et al., 2018; Yoon et al., 2006). Steric rejection is size exclusion; where the molecular size of the particle is larger than the pore size. Hydrophobic membrane surface adsorption is the attachment of compounds in liquid onto the membrane surface (Zhu, 2014). This attachment is driven by the minimalization of interfacial energy. The bonding process of adsorption can be both physical adsorption and chemical adsorption (Zhu, 2014). Physical adsorption is attributed to non-covalent interactions (van der Waals force, electrostatic attraction etc.). Chemical adsorption consists of a covalent bonding with adsorbate and adsorbent (Zhu, 2014). It is suggested that for strong hydrophobic compounds (log $K_{OW} > 3.0$), hydrophobic membrane adsorption is the main mechanism (Yoon et al., 2004, 2006). Competition for these adsorption sites comes from NOM and pore blockage (Yoon et al., 2004). In this same study of Yoon et al. (2004) the dominance of surface membrane adsorption was investigated for less hydrophobic compounds. Their results suggested that for less hydrophobic compounds the main retention mechanism was electrostatic exclusion.

2.3.2 Adsorption mechanisms for OMP

Adsorption of OMP onto PAC is mainly governed by hydrophobic interactions (Snyder et al., 2003). Therefore most non-polar organic compounds (log $K_{OW} > 2$) are efficiently removed by AC (Snyder et al., 2003). Affinity of polar OMP for AC depends on their functional groups (Ebrahimzadeh et al., 2022). For polar and hydrophobic OMP both hydrophobic and polar interactions are responsible for removal (Ebrahimzadeh et al., 2022). Removal of hydrophilic OMP is mainly governed by π-π interactions and hydrogen bonds (Ebrahimzadeh et al., 2022). Charged OMP removal is influenced by electrostatic attraction and repulsion. For PAC Norit (negative at pH 8) anionic OMP removal is influenced negatively and cationic OMP removal is influenced positively (Ebrahimzadeh et al., 2022).

2.4 Fouling of UF membranes

This section explains the fouling mechanisms of a membrane and the importance of fouling for OMP retention and operational stability. The main limitation of UF is fouling of the membrane which reduces membrane life and increases TMP (Schwaller et al., 2021; Siegers et al., 2021). Fouling is important for the operational stability of UF, however fouling influences the rejection of different OMP as well. Retention was found to be higher for fouled membranes than clean membranes, fouling reduced the pore size and as such enhanced retention through size exclusion (Devitt et al., 1998; Hu et al., 2014; Sutzkover-Gutman et al., 2010). Furthermore, tight bonds with endocrine disrupting chemicals, with strong electropositivity, and humic particles were formed which were then co-rejected (Devitt et al., 1998). Another important finding of the influence of fouling on retention was the influence of cake layer forming on retention (Hu et al., 2014). Cake layers formed under different pressures showed different effects on endocrine disrupting chemicals retention of which cake layers formed under 50kPA showed the best effect (Hu et al., 2014).

For an efficient use of membranes it is important to control the irreversible fouling of a membrane (Kimura et al., 2004). Irreversible fouling is defined as fouling which requires chemical cleaning to be mitigated or which can not be removed (Heijman et al., 2005; Kimura et al., 2004). Reversible fouling is fouling which can be removed by flushing and hydraulic backwashing Heijman et al., 2005; Huang et al., 2021). There are four theoretical kinetic models for fouling processes and mechanisms: complete blocking, intermediate blocking, standard filtration and cake filtration (Prfidanos et al., 1996). However these models only take homogeneous fouling into account while heterogeneous fouling is also present in UF membranes (Arkhangelsky et al., 2011; Heijman et al., 2005, 2007). Heterogeneous fouling is fouling such as capillary blocking, patches of fouling on the membrane, and settling of formed flocs (Arkhangelsky et al., 2011; Heijman et al., 2005, 2007). In order to reduce fouling of the membrane, coagulant addition is an effective technique (Bu et al., 2019; C. Schwaller et al., 2021). However, coagulation also influences heterogeneous fouling. Ferro-hydroxy-organic flocs are transported through the capillary by hydrodynamic bulk flow. They are dragging and rolling along the membrane wall towards the dead-end side of the membrane (Arkhangelsky et al., 2011). Therefore, a capillary can be divided into an active side and a backyard side where formed flocs settle (Arkhangelsky et al., 2011). Capillary blocking is a relatively unknown fouling problem of UF. Research on capillary blocking is scarce. A few studies mention capillary blocking due to coagulant flocs (Arkhangelsky et al., 2011; Heijman et al., 2005, 2007). The potting of the membrane at the top and bottom, where capillaries are glued together, is most susceptible to blocking (Heijman et al., 2007). Blocking at the potting is due to a less efficient hydraulic backwash and chemical enhanced backwash at the potting (Heijman et al., 2007).

3 Materials and methods

In this chapter the materials which are used are given and explained. The experimental set-up is described and relevant material characteristics of the membrane, coagulant, PAC and OMP are given. Additionally, the methods used for experiments on fouling, OMP removal, analytical, and cleaning methods are explained.

3.1 Experimental set-up

In this section the materials used are described. The specifics of the UF are given, along with the water, coagulant, adsorbent, and OMP characteristics.

The ultrafiltration unit was connected to the incoming water from the Afgedamde Maas at Bergambacht, of which approximately 9 m^3h^{-1} was available. During the pilot-scale experiments one pressure vessel was used with an active membrane area of 60 m^2. Five dosing units were installed, one for the coagulant, three for the chemical enhanced backwash (CEB) and one dosing unit with stirrer was included for the adsorbent. On several points a pressure transmitter was present, at both feed sides and at the permeate side (Figure 1). A pressure transmitter was also present after the pump. The flux was kept constant at 60 l/m/h2 and the flow at 3.6 m3/u. A filtration cycle consisted of a forward flush of 60 seconds, filtration mode of 30 minutes, a forward flush of 15 seconds and a backwash of 60 seconds. Every ten seconds data was logged. The filtration direction switches every cycle from top to bottom, which diminishes fouling. Filtration and backwash alternate between top and bottom as influent point. The UF was operated in dead-end configuration. The different filtration steps are presented in Figure 2.

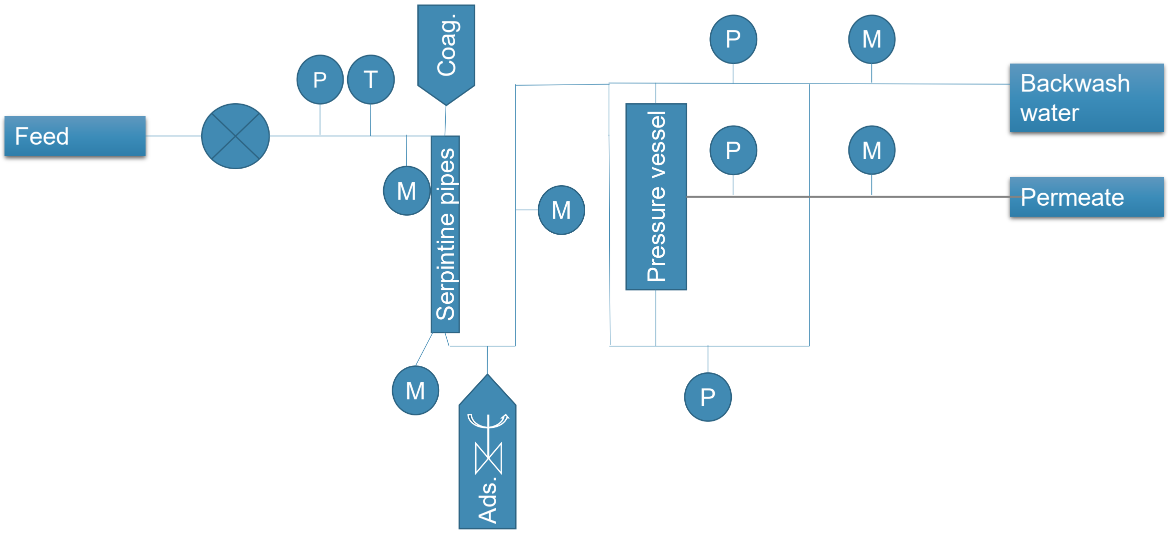

Figure 1 Schematic of the inline UF with the placement of transmitters and sample points

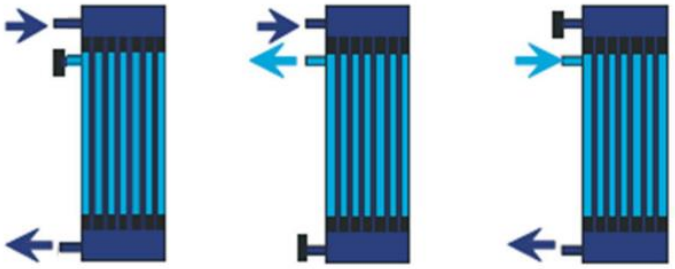

Figure 2 Different filtration modes used for the UF with inline dosing. From left to right: forward flush top, backwash top, filtration top. filtration modes shown for top are the same for bottom except for top being bottom (Logisticon, n.d.)[2]

3.1.1 Membrane module

The membrane module used was a Multibore©[3] membrane from Inge Dupont. The hollow fibre membrane was operated in dead-end mode with regular backwash intervals. It has a capillary diameter of 0.9 mm and a pore size of approximately 20 nm(*Multibore ® Membrane d*, 2020). The membrane was composed of a special modified polyethersulfone material (PESm) (*Product Portfolio Expertise in Ultrafiltration a DuPont brand*, n.d.). The membrane is negatively charged with a molecular weight cut off of around 100,000 DA (Dillmann et al., 2020). The flux range for filtration is 60-180 L/(m2.h) (*Multibore ® Membrane d*, 2020). It has around 17087 capillaries and a clean membrane pressure of 0.06 bar.

3.1.2 Water damed Maas

The water used in this study was water from the Afgedamde Maas. This water was taken in at Brakel and flowed through microsieves. The, it was transported to pumping station Bergambacht where the pilot scale study was conducted. Water from the Afgedamde Maas is surface water which has been dosed with ferrous sulphate (Fe(II)(SO4)3). The Afgedamde Maas is surface water which is regulated. Small variations in influent quality occur with the seasons of the year. Since the water was treated with ferrous sulphate and had a long settling time (6 weeks) the turbidity and SS content were low. The average concentrations of organic micropollutants with the highest concentrations are given in Table 1. These average concentrations are over the months February, March and April. Concentrations of different measured PFAS in influent water were all in the range of nanograms per litre.

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[2] Logisticon. (n.d.). FUNCTIONELE OMSCHRIJVING (FO). Retrieved from www.Logisticon.com

[3] Multibore ® Membrane d. (2020). Retrieved from www.dupontwatersolutions.com

Table 1 Concentration organic micropollutants present in Maaswater in the Afgedamde Maas. The average concentrations are over the months February, March and April

Organic micropollutants	*Average (µg/L)*		
1,4 dioxane	0.12	Iopromide	0.14
Acesulfame	0.44	Melamine	0.95
Sucralose	0.78	trifluoroacetic acid	0.92
aminomethylphosphonic acid	0.56	urotropine (hexamethylenetetramine)	0.65
desphenyl chloridazon	0.15	Cyanuric acid	0.63
N-carboxymethyliminobis (ethylenenitrilo)tetra(acetic acid) (DTPA)	2.59	Perchlorate	0.22
guanidine carboxamide	0.34	Caffeine	0.15
valsartan acid	0.13	4-methylbenzotriazole	0.22
Iomeprol	0.20	Benzotriazole	0.38
		Metformine	0.46

3.1.3 Coagulant and PAC dosing

Analysing data of influent water has been added per filtration mode including the measured PAC and coagulant concentrations in influent water. Dosing of coagulant and PAC was theoretically set at 1, 3 and 5, 15 respectively. PAC dosing was in the same range of other studies done with PAC-UF 8-30 mg/l, where 30 mg/l was used for wastewater effluent (Löwenberg et al., 2014; Margot et al., 2013; Schwaller et al., 2021). Another study with pre-treated Dunea water studied the removal of PAC with rapid sand filtration, this study used 2 mg/l (Ebrahimzadeh et al., 2022). Therefore a low PAC dose of 5 mg/l was used and a higher PAC dose of 15 mg/l, the same as for the study of Siegers et al. (2021). Coagulant dose was in the range of 3 to 15 mg/l (Löwenberg et al., 2014; Margot et al., 2013; Schwaller et al., 2021; Viegas et al., 2021). However, different studies used wastewater effluent instead of surface water except for Viegas et al. (2021) who used surface water and a coagulant dose of 3 mg/l. In studies with only inline coagulant dosing of Tang et al. (2019) and Peleato et al. (2017) results suggest an optimum dose of coagulant lower than 1 mg/l for surface waters. Therefore a low PAC dose of 1 mg/l is used and a higher dose of 3 mg/l..

The PAC dose was measured using suspended solid analysis and checked by measuring the level of the dosing tank. This showed that PAC dosing was unreliable due to sometimes large variations of more than 8 mg/l which caused high standard deviations for PAC dosing (Table 2). Iron dosing, determined with suspended solid analysis and the TPTZ method (HACH), is more constant with a deviation of 0.15 mg/l, although dosing was not accurate as it was always higher than the theoretical dose (Table 2).

Table 2 Influent water measured parameters

Mode Theoretical dose	*PAC (mg/l)*	*5*	*5*	*5*	*15*	*15*	*15*	*15*	*15*	*15*
Theoretical dose	*Fe (mg/l)*	1	1	3	1	3	1	1	1	1
Parameter	*Experiment Unit*	2	2	3	4	5	7 & 11	8	9	10
PAC dose	*mg/l*	4	10	9	15	13	15	12	14	10
PAC st.dev. (n>4)	*mg/l*	1	1	1	4	3	2	1	2	3
Iron dose (±0.15) (n=2)	*mg/l*	1.18	1.23	3.26	1.21	3.23	1.27	1.18	1.21	1.14
Iron raw water (±0.02) (n=2)	*mg/l*	0.12	0.10	0.15	0.25	0.17	0.02	0.01	0.03	0.00
Turbidity (daily mean)	*NTU*	2.28	3.74	3.74	3.18	3.18	2.24	1.98	2.08	1.79
UVT (±0.5) (n=2)	*-*	72.6	74.4	72.8	72.8	72.8	77.5	78.2	78.4	77.4
Conductivity (± 3) (n=2)	*µs/cm*	524	497	503	494	496	515	513	514	520
pH (±0.1) (n=2)	*-*	7.9	8.1	8.1	8.1	8.1	8.0	8.1	8.1	8.0
SS (±0.1) (n>4)	*mg/l*	2.9	3.0	4.4	2.8	2.6	1.5	2.3	1.9	4.2

3.1.3 Coagulant characteristics

As a coagulant Iron Chloride ($FeCl_3$) was used, which shows a higher settling velocity than $FeClSO_4$ and $NasAl_2O_4$ (Sher et al., 2021). $FeCl_3$ was dosed with a solution of 40% from Brenntag. It was kept in a tank of 100 l and dosed through a dosing hose with a diameter of 5 mm and 15 meters long. The pump used was a DDA 7.5 by Grundfos.

3.1.4 PAC characteristics

The PAC used was PAC Norit SA Super (Table 3). This fine powder was used due to its faster adsorption kinetics compared to larger PAC. It is a high mesoporous and hydrophobic PAC. It is also dosed at the rapid sand filtration of Dunea at Scheveningen, which enabled a comparison of removal between the UF-PAC system and the rapid sand filtration.

Table 3 Adsorbant characteristics of PAC dosed in the inline UF

PAC Norit SA Super		***Unit***
iodine number	950	-
Methylene blue adsorption	22	g/100 g
Phenol adsorption	5	g/100 g
Total surface area	1150	m2/g
Apparent density	250	kg/m2
Particle size > 150um	3	mass-%
Particle size D50	5	um
Ash content	10	mass-%
Phenol adsorption	alkaline	-
Moisture (as packed)	5	mass-%

3.1.5 OMP

In this study natural occurring concentrations in the influent water were used. The removal of PFAS is important due to its health risks and slow degradation (Pancras et al., 2018). Therefore the removal of 26 PFAS was measured (Appendix A.1). In order to obtain a broader insight in the removal efficiency of the treatment used in this study, the removal of another 20 OMP was measured (Appendix A.1). Not all PFAS and other OMP measured were present in Maaswater. In total 18 OMP, of which 9 were PFAS, were present in influent water during the experiments (Table 4). The OMP are classified based on charge and hydrophobicity. In order to describe the hydrophobicity the pH dependent octanol water distribution coefficient (Log D_{OW}) was used. Log D_{OW} was calculated with ChemAxon software. On general the log D_{OW} is a good indicator for the adsorption of an OMP (Ebrahimzadeh et al., 2022). However, for PFAS the log D_{OW} is less reliable due to the difficulty of measuring the log D_{OW}. The measuring of log Dow is influenced by water and lipid repelling properties which makes PFAS accumulate on the interface of water-octanol instead of being present in the fluids (Hodges et al., 2019). Therefore the molecular weight is used to classify PFAS.

Table 4 Physical chemical properties of measured OMP, calculated with ChemAxon software.

Compound	*Class*	*MW (Da)*	*Charge (pH=8)*	*Log D (pH=8)*
Perfluorobutanoic acid (PFBA)	PFAS	213.97	Negative	-1.22
Perfluorobutanesulfonic acid (PFBS)	PFAS	298.94	Negative	0.25
Perfluorooctanoic acid (PFOA)	PFAS	413.97	Negative	1.58
Perfluoroctanesulfonic acid (PFOS)	PFAS	499.94	Negative	3.05
6:2 fluorotelomer sulfonic acid (6:2 FTS)	PFAS	427.96	Negative	1.54
Perfluorheptanoic acid (PFHpA)	PFAS	363.98	Negative	0.88
Perfluorohexane sulfonic acid (PFHxS)	PFAS	399.94	Negative	1.65
Perfluorohexanoic acid (PFHxA)	PFAS	314.05	Negative	0.18
Perfluoropentanoic acid (PFPeA)	PFAS	263.98	Negative	-0.52
1H-Benzotriazole	ICP	119.05	Neutral	1.21
4,5-Methylbenzotriazole	ICP	133.06	Neutral	1.76
Caffeine	ICP	194.08	Neutral	-0.55
Carbamazepine	PHAR	236.09	Neutral	2.77
Clarithromycin	PHAR	747.48	Positive	2.20
Gabapentin	PHAR	171.13	Neutral	-1.28
Metformin	PHAR	129.10	Positive	-5.37
Sotalol	PHAR	272.12	Positive	-1.56
Theophylline	PHAR	180.06	Negative	-1.11

3.2 Method to measure the effect of different concentrations of PAC and coagulant on the fouling of UF with inline dosing

The method to determine what effect continuous and simultaneous dosing of coagulant and adsorbent had on fouling of UF is explained in this section. Secondly, the method for analysis of the results of membrane fouling is described.

3.2.1 UF fouling experiment

The pressure over at least 24 hours was measured at different points in the installation (Figure 1). Different operation modes were used in order to test the effect of PAC and coagulant on fouling of UF (Table 5). In order to minimize the amount of operations and achieve enough sets to evaluate the effect of PAC and coagulant separately only a high and low concentration of PAC and coagulant is used. The purpose of this research is to measure the effect of each and not to find an optimum operation mode. The influence of increasing filtration time was also taken into account to investigate the effect of higher loading of PAC and coagulant on fouling of the membrane. PAC doses were in the same range as for other research done with PAC-UF systems with PAC dosing of 8-30 mg/l (Löwenberg et al., 2017; Margot et al., 2013; Schwaller et al., 2021; Viegas et al., 2021). Different modes were compared to the reference mode which was UF dosed with coagulant (Table 5). Experiment modes with PAC and a higher iron dosing had a higher iron reference mode in order to measure the effect of PAC only.

Table 5 Different operation modes used in order to measure the effect of PAC and coagulant on UF fouling. Experiment modes are in concordance with experiment modes for retention which is why experiment 9 follows on experiment 6

Experiment mode	*FeCl3 [mg/l]*	*PAC [mg/l]*	*PAC dosing*
Reference	1	-	Continuous
Reference exp. 3 and 5	3	-	Continuous
1	-	-	Continuous
2	1	5	Continuous
3	3	5	Continuous
4	1	15	Continuous
5	3	15	Continuous
6	-	15	Continuous
9	1	15	Continuous filtration time

For all experiments one membrane is available. In order to minimize the effect of one experiment on the next the UF operation mode is started with a CEB. When an operation mode is tested, a reference mode with the desired coagulant dose is started after a CEB. In the case of no coagulant and adsorbent and only adsorbent, the reference with a low dose was used. This reference mode lasts for at least 10 cycles or until the cycles are stable in time.

At the end of the pilot the membrane was visually inspected at the top and bottom potting. Additionally, the membrane was cut vertically which gave a cross-section of the inside of the membrane. The membrane was emptied but not preserved and only opened after three week which might have influenced the results of the visual inspection.

All experiments were executed in duplicate except for only PAC addition (experiment 6) and increase of filtration time (experiment 9).

3.2.2 Membrane fouling analysis

In order to assess the fouling of the membrane the permeability was measured over time and the difference in forward flush pressure over the membrane (FFMP) was measured. The FFMP measures the blocking of capillaries while permeability does not show capillary blocking (Heijman et al., 2007). The reversible and irreversible fouling was then calculated by using the TMP pressure increase over time. The backwash water from the experiments was visually inspected. In order to correct for temperature differences permeability was used as a measure for operational stability instead of TMP. Permeability was calculated according to Equation 1 and TMP was calculated according to Equation 2.

$$Permeability = \frac{Q}{TMP \times A} \times TCF$$

Equation 1

$$TMP = \frac{P_{top} + P_{Bottom}}{2 \times P_{Permeate}}$$

Equation 2

Where Q is the flow through the membrane (l/h), TMP is in bar and A is the membrane surface in m^2. Where P_{top} is the pressure measured at the top of the membrane (bar), P_{bottom} is the pressure measured at the bottom of the membrane (Pa) and $P_{permeate}$ is the pressure measured at the permeate side of the membrane. TCF is the temperature correction factor and expressed as follows:

$$TCF = e^{-0.0019 \times (T-20)}$$

Equation 3

The fouling or resistance was determined by a difference in TMP and calculated by Darcy's law (Huang et al., 2021). The total fouling resistance (R) was acquired through measuring the fouling membrane flux (J) and TMP (ΔP) at the end of a cycle:

$$R = \frac{\Delta P}{\mu J}$$

Equation 4

where R is the total fouling resistance (m^{-1}), ΔP is the TMP, μ is the dynamic viscosity (Pa·s) and J is the flux ($l/h/m^2$). The total fouling resistance (R) over a filtration cycle at the end of filtration consists of the membrane filtration resistance (R_m), reversible fouling resistance (R_r) and the irreversible fouling (R_i). A resistance-in-series model was used, which is often used in fouling studies (Huang et al., 2021; Peleato et al., 2017). The model calculates R according to the following equation:

$$R = R_m + R_r + R_i$$

Equation 5

R_m was obtained by measuring the module flux (J_0) and TMP (ΔP_0) at the start of an experiment (Eq. 2). Which means R_m partly consists of the original membrane resistance of a virgin membrane and irreversible membrane resistance of previous experiments. R_m was obtained this way in order to prevent irreversible fouling from experiments done earlier being taken into account in irreversible fouling of the next experiment.

$$R_m = \frac{\Delta P_0}{\mu J_0}$$

Equation 6

The fouled membrane was flushed and backwashed after each cycle and at the end of an experiment, after which the water flux (J_1) and TMP (ΔP_1) were measured again in order to obtain the backwashed membrane resistance (R_b) (Eq. 3).

$$R_b = \frac{\Delta P_1}{\mu J_1}$$

Equation 7

In order to obtain the irreversible fouling over one experiment and as such one operation mode. The irreversible fouling was then calculated by subtracting the membrane filtration resistance at the start of an experiment (R_m) from the flushed filtration resistance at the end of the experiment ($R_{b\text{-end}}$) (Eq. 5).

$$R_i = R_{b-end} - R_m$$

Equation 8

For each cycle the TMP was measured of which the mean reversible fouling per experiment was then calculated (Eq. 6). Filtration and backwash changed for top and bottom every cycle. A difference between top and bottom was visible in TMP, thus the resistance for top and bottom were calculated separately.

$$R_r = \frac{\sum(R - R_{b-end})}{n}$$

Equation 9

Where n is the number of cycles per experiment. The forward flush pressure difference over the membrane was measured during a forward flush which lasted a minute and consisted of five data points. The following equation was used for the FFMP:

$$FFMP = \left|P_{top} - P_{Bottom}\right|$$

Equation 10

With photos of the visual inspection of the membrane an estimate was done for the total capillary blocking at the end. Blocked capillaries were estimated by adding a grid on the photos and colouring this grid. With the help of the following empirical relationship between pressure and closed capillaries an estimate of closed capillaries was made for all experiments. This empirical relationship was also used by Heijman et al. (2007) to estimate closed capillaries.

$$\Delta P_{membrane} = A + B \times \frac{1}{17087 \times N}$$

Equation 11

Where $\Delta P_{membrane}$ is the pressure difference between top and bottom of the membrane, N is the percentage of capillaries which are open and A and B are constants, A and B are included in the results.

3.2.3 Analytical methods

In order to check the dosing concentration of PAC and coagulant different measurements were done over different cycles. The turbidity, SS, pH, conductivity, UVT and iron were measured. The turbidity mean from the day of the experiment was taken from data from Dunea at Bergambacht. SS were measured by taking samples from the influent, influent with coagulant added and influent with PAC and coagulant added. The samples were taken over two minutes time halfway through a filtration cycle of 30 minutes. In order to measure the SS, samples were filtered through a filter of 20 µm. Iron was measured with the TPTZ method (HACH) and through SS method. The pH and conductivity were measured with multimeter HQ40d (HACH). The UVT was measured with an UV portable p meter (Van Remmen Real tech). The PAC dosing was also checked by measuring the level of PAC in the stirring tank.

3.3 Method to measure the retention of OMP including PFAS with different concentrations of PAC and coagulant in an integrated UF system

In this paragraph the method to measure the effect of varying concentrations of PAC and coagulant on OMP removal are described. Furthermore, the method to measure the effect of varying PAC dosing modes on OMP removal is explained.

3.3.1 UF experiment removal OMP including PFAS

Different operation modes were used in order to test the effect of PAC and coagulant the removal of OMP including PFAS (Table 6). In order to minimize the amount of operations and achieve enough sets to evaluate the effect and difference of PAC and coagulant separately only a high and low concentration of PAC and coagulant were used. The purpose of this research is to measure the effect of and the difference between each, not to find an optimum operation mode for the removal of OMP including PFAS.

Different experiments were done to measure the effect of varying PAC modes on the retention of OMP in this set-up of inline dosing in an UF (experiment 4,7,8 and 9 Table 6). The variables measured were dosing method, contact time, and duration of filtration during a cycle. The contact time differed between 25 and 200 seconds. The dosing method consisted of a pre-coating and continuous dosing of

PAC while coagulant was dosed continuously. At last the duration of one filtration cycle was changed from 30 to 60 minutes.

Furthermore, a time series over 30 minutes was done for PAC dosing continuous and pre-coating, experiment 10 and 11 respectively. These time series gave insight in OMP removal development during a cycle.

Table 6 Different operation modes for the retention of OMP including PFAS.

Experiment	*FeCl3 [mg/l]*	*PAC [mg/l]*	*PAC dosing*
1	-	-	Continuous
2	1	5	Continuous
3	3	5	Continuous
4	1	15	Continuous
5	3	15	Continuous
6	-	15	Continuous
7	1	15	Pre-coating
8	1	15	Contact time
9	1	15	Filtration time
10	1	15	Continuous time series
11	1	15	Pre-coating time series

The influent and effluent samples analysed were an average over one cycle. Sampling was executed by taking a sample during one minute every six minutes. Six samples are then obtained in total, of each 200 ml is mixed after shaking the samples gently. This combined sample is then analysed in order to obtain the average concentrations of PFAS and selected OMP over a cycle. The samples for OMP will be taken in duplicate over a cycle and PFAS single over one cycle. All experiments were replicated.

For all experiments one membrane is available. In order to minimize the effect of one experiment on the next the UF operation mode with the same reference cycle is started. The experiment is started when the PAC dosing and coagulant were continuous through a cycle.

The retention of different OMP including PFAS are measured over 1 cycle. The relative OMP removal efficiency was calculated according to the following equation:

$$relative\ removal\ [\%] = \frac{C_{Inlfuent-}C_{Permeate}}{C_{Influent}} \times 100$$

Equation 12

Where $C_{Influent}$ is the influent concentration in ng/l for PFAS and µg/l for other OMP. $C_{Permeate}$ is the permeate concentration in ng/l for PFAS and mg/l for other OMP.

3.3.2 Analytical methods removal OMP including PFAS

Analysis of PFAS was conducted via liquid chromatography tandem mass spectrometry (LC-MS/MS) with the SCIEX 7500 Triple Quad LC-MS. The sample was prepared according to 'method PFAS 3.0' by Het Water Laboratorium (HWL). At the laboratory the sample was prepared with a conservation fluid containing acetonitrile, methanol and formic acid. An internal standard was added after which it was filtered over a Spartan filter, 0,45 µm. After filtration 100 µl was added to the LC-MS/MS. In this method only linear PFAS are taken into account. The average limit of quantification can be found in Appendix C.1. The average measurement uncertainty per compound can be found in Appendix C.2. It differs from approximately 10 to 40 percent.

The sample was in some cases analysed after more than a week. Due to this longer period some PFAS were not detectable anymore or lower concentrations are measured according to the laboratory who analysed PFAS samples. The following PFAS are expected to be influenced by this: PFUdA, PFDA, PFOS, PFDoA, PFTrDA, PFNS, PFDS, PFUdS, PFDoS and PFTrDS.

Analysis of OMP except PFAS was conducted via liquid chromatography mass spectrometry (LC-MS) with the Xevo TQ-S micro. The sample was filtered over 0.45 µm, after which 495 µl was added to the LC-MS with 5 µl internal standard.

In order to check the dosing concentration of PAC and coagulant different measurements are done over different cycles. During the cycle in which PFAS and OMP samples are taken turbidity, SS, pH, conductivity, UVT and iron are measured. The daily mean for turbidity of influent water at Bergambacht was used for turbidity. SS are measured by taking samples from influent water, influent with coagulant added and influent with PAC and coagulant added. The samples for SS are taken at the start for one minute, at 15 minutes for one minute and at 29 minutes for one minute. These samples are filtered through a filter of 20 µm. After filtering the sample the filter is dried for two hours at 110 °C. The pH and conductivity are measured with multimeter HQ40d (HACH). The UVT is measured with an UVT and UV portable p meter (Van Remmen, Real tech) .

3.4 Chemical membrane cleaning

The membrane was cleaned with a CEB. The membrane was cleaned with citric acid (40%) by Brenntag. At the start of a CEB the membrane was emptied of water through an air drain. It was then dosed 60 seconds from the top and 60 seconds from the bottom with citric acid 40%. Which resulted in a dosing of 0,25 l of citric acid. Soaking lasted 30 minutes and was followed by an air drain again. Thereafter there was a backwash from the top and the bottom of 60 seconds. The CEB ended with a permeate dump of five minutes. Another CEB was executed with sodium hypochlorite solution (12.5% chlorine). The same procedure as for citric acid was followed except a lower dosing rate was used which resulted in 33.33 ml of sodium hypochlorite solution dosed.

4 Results and discussion

In this chapter the results for three sub-questions are given and discussed. In the first subsection the results on the influence of PAC and coagulant on fouling experiments are presented and discussed. Irreversible and reversible fouling is discussed and special attention was given to capillary fouling. The second subsection contains the retention experiments, where both PAC and coagulant results were given and discussed.

4.1 Effect of adsorbent and coagulant on fouling of UF

This section includes the effect of coagulant and adsorbent addition on the fouling of the UF. Results from permeability and capillary blocking are given and discussed. Results shown in in this paragraph are single and duplicates are presented in Appendix B. The duplicates in the appendix are graphs from the data screen UF-unit, due to logging problems they could not be transferred to Excel. However, these results show similar results as the graphs presented in paragraph 4.1. Unfortunately, experiment three with 3 mg Fe/l and 5 mg PAC/l could not be processed due to one failed experiment and logging failure of the duplicate, no graphs are shown of this experiment except in Appendix B.

4.1.1 Effect of coagulant dosing on irreversible fouling

As expected from other research, when adding coagulant permeability is constant, over 24 hours there is no visible permeability decrease as all reference modes and different experiments show (Figure 3, 5 and 6). However, some variation can be seen during the reference modes in the hours after a CEB (Figure 3 top). Sometimes a slight dip is visible after which the permeability increases again (Figure 3 top, 7. At the same time FFMP increases as well which suggests capillary blocking. This phenomenon will be discussed in paragraph 4.1.4 Capillary blocking. This dip in permeability is not seen in Figure 3 bottom. This absence can be explained due to a much longer reference time of two days instead of twelve hours as for most experiments. During these two days this dip was indeed visible in the first ten hours. However, after 12 hours permeability became very stable as can be seen in Figure 3 the bottom graph. A difference between top filtration and bottom filtration is also visible which suggests different build-up of fouling for top and bottom (Figure 3). A possible explanation for this might be capillary blocking which causes a backwash to be less efficient (Heijman et al., 2007). Different blockages may create a different backwash efficiency for top and bottom. It can be seen that this difference between top and bottom changes over time. After a CEB this difference between top and bottom is highest after which it decreases over time (Figure 3 and 5).

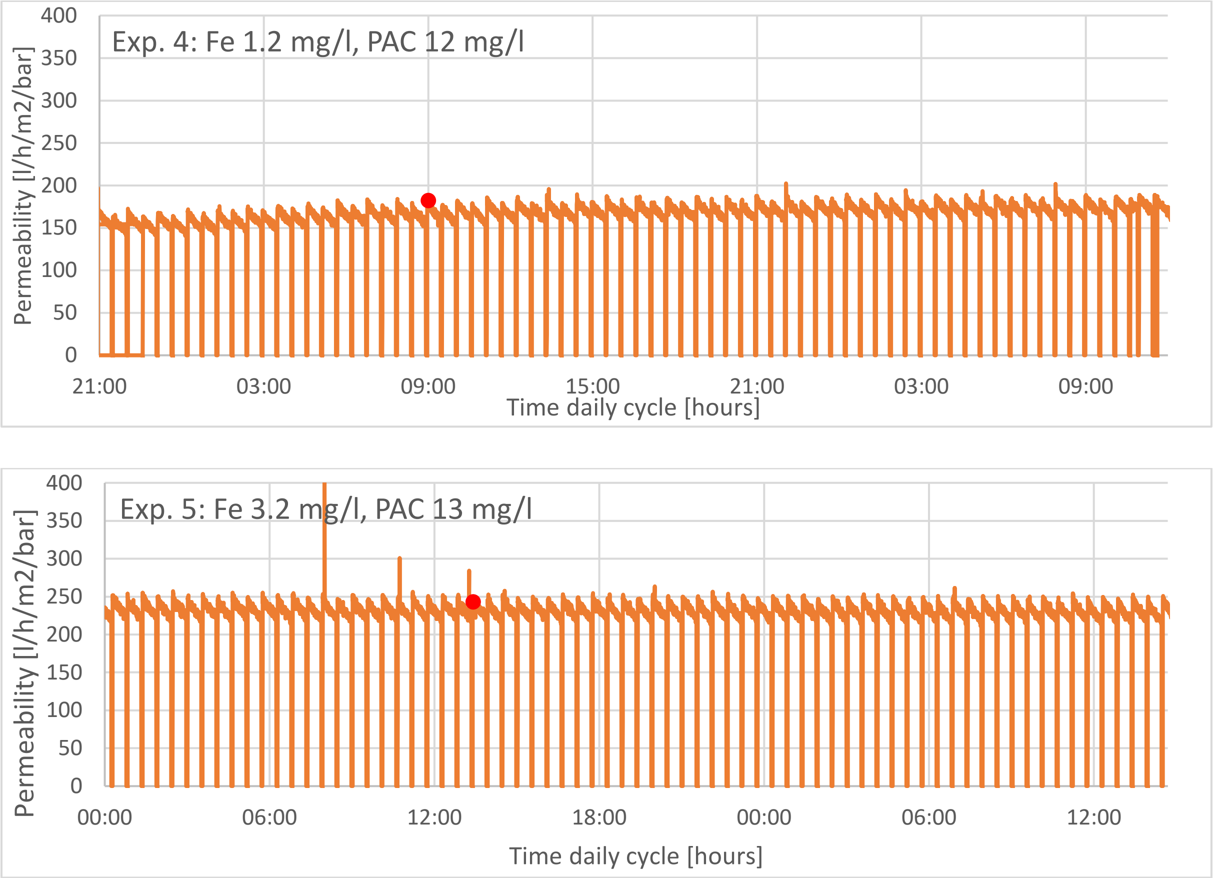

Figure 3 Top: Experiment 4 permeability with 1.2 mg Fe/l and 12 mg PAC/l, reference 1.2 mg Fe/l (May). Bottom: Experiment 5 permeability with coagulant dose of 3.2 mg/l and PAC 13 mg/l, reference 3.2 mg Fe/l

Irreversible fouling is small when coagulant is added, which is clear from Figure 4. The irreversible fouling resistance is small in the order of 10^9 $m^{-1}h^{-1}$. Experiment 1 and Experiment 6 are the only cases where coagulant was not added and irreversible fouling is in the order of 10^{10} $m^{-1}h^{-1}$. Negative fouling resistance in experiment four (Figure 4) is due to an unstable reference where permeability was still increasing after a CEB after which high FFMP was measured. Relatively high irreversible fouling at the reference in experiment 6 (Figure 4) is also during high FFMP increase (Figure 6). Change in PAC dose from 7 to 12 does not influence the positive effect coagulant dosing has. Likewise increase in coagulant dose does not affect the positive effect coagulant doing has. When filtration time is increased from 30 to 60 minutes the fouling resistance is in the same order of magnitude as for a filtration time of 30 minutes. UF with inline dosing of coagulant ensures an efficient hydraulic backwash, where irreversible fouling does not increase in 24 hours. The UF in combination with inline coagulant addition is operationally stable as expected from other research (Bu et al., 2019; Schwaller et al., 2021). Increasing coagulant dosing with 2 mg Fe/l does not change irreversible fouling resistance compared to 1 mg/l (Figure 3).

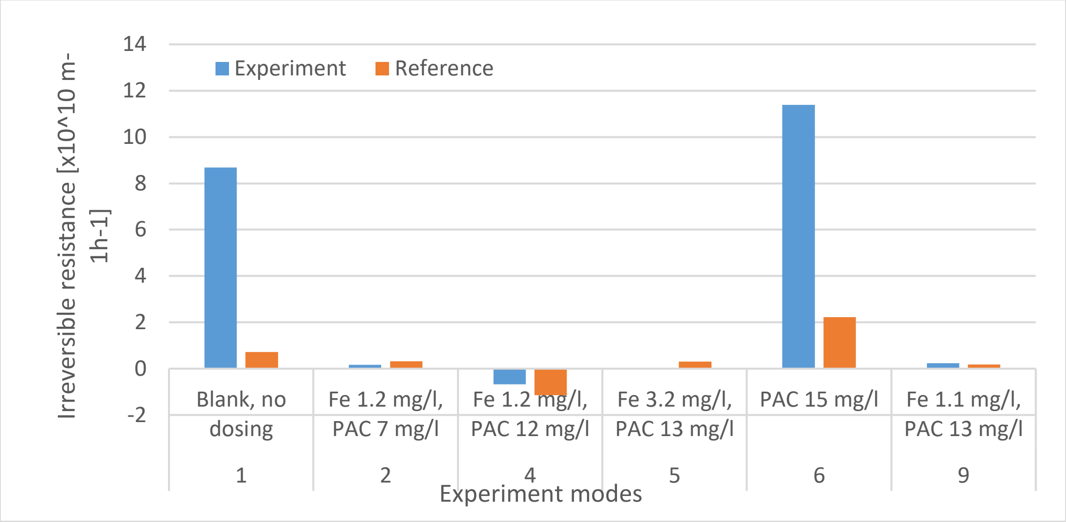

Figure 4 irreversible fouling resistance per hour measured over 24 hours for each experiment mode and 12 hours for each reference mode

No addition of coagulant (experiment 1) during spring created a permeability decrease of 210 to 120 l/h/m2/bar over 24 hours (Figure 5). Decrease in permeability due to membrane fouling continued until a CEB was initiated. Halfway through December and in February this decrease in permeability and as such membrane fouling was also visible with a filtration time of 60 minutes (Appendix D). The hydraulic backwash was not enough to clean the membrane efficiently since the permeability kept decreasing after every cycle. This corresponds with other research where the addition of coagulant reduces irreversible fouling and increases performance of the UF (Bu et al., 2019; Schwaller et al., 2021; Tang et al., 2019). After a CEB with acid permeability increased however, it did not reverse to the level before the start of the experiment (Figure 5). A CEB with chlorine only increased permeability temporarily for a few hours (Figure 5). Fouling caused through a blank filtration with no coagulant and adsorbent is not effectively reversed by CEB used in this study and causes permanent decrease in permeability.

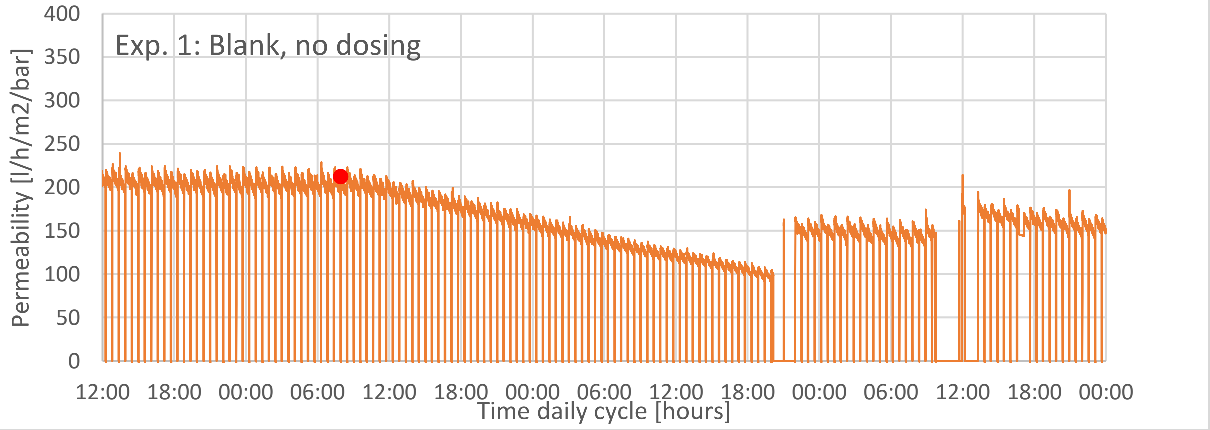

Figure 5 Reference until 10:00, Fe 1.2 mg/l. From 10:00 (red dot) experiment 1: blank filtration no coagulant and no PAC dosing. First gap CEB acid, second two gaps CEB chlorine. (May)

Inline dosing of coagulant in UF has a positive effect to prevent irreversible fouling. During dosing of coagulant permeability remains steady and there is only a small increase in irreversible fouling over 24 hours. Changing coagulant dose does not influence the positive effect coagulant has on irreversible fouling. A dose of 1.2 mg/l and 3.2 mg/l or a filtration time increase of 30 minutes all have irreversible fouling resistance in the same range (Figure 4). Absence of coagulant dosing causes irreversible fouling to increase by a factor ten and cannot be easily reversed with a CEB.

4.1.2 Effect of PAC dosing on irreversible fouling

When only PAC is dosed the permeability decreases from 175 to 95 l/h/m2/bar in 24 hours (Figure 6). Permeability continued to decrease until a CEB was initiated, the hydraulic backwash was not efficient to prevent irreversible fouling in 24 hours. A negative effect of only dosing PAC is also measured by other research done (Bu et al., 2019; K. Li et al., 2020; Schwaller et al., 2021). Irreversible fouling is worse compared to the blank filtration where no coagulant or PAC was dosed (Figure 4). Which means that addition of PAC increases irreversible fouling. Decreasing permeability during reference mode was simultaneously with an increase in FFMP. At the start of the experiment the FFMP was not stable yet (Section 4.1.4).

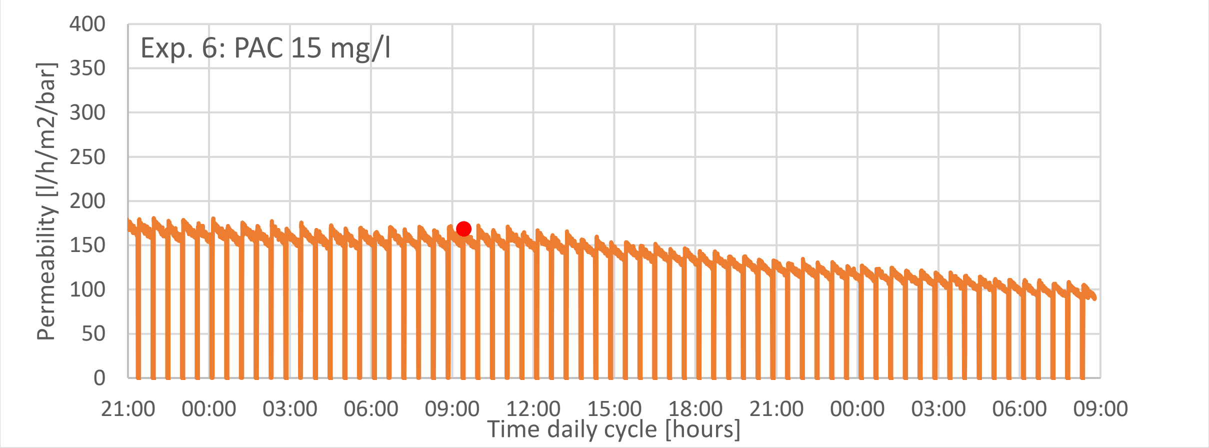

Figure 6 Permeability experiment 6. Reference mode 1.2 mg Fe/l, start experiment 6 at red dot, Pac dosing 15 mg/l

The addition of continuous dosing of 1.2 mg Fe/l is enough to overcome this negative effect of PAC on the permeability and ensures a steady permeability for at least 24 hours (Figure 7). This accounts for both dosing concentrations of PAC 7 and 12 mg/l (Figure 3 and 7). Schwaller et al. (2021) found the same results where PAC and coagulant (3 mg/l) dosing ensured a constant and steady permeability. Again this dip in permeability is visible after a CEB (12:00) with an increase in the FFMP (Figure 7). The result in Appendix B corresponding with figure 7 confirms that for that mode the TMP, corresponding with permeability, did not change compared to the reference. Using no coagulation and only PAC caused permeability decrease over 24 hours and as such higher irreversible fouling of the membrane than simultaneously dosing PAC and coagulant. Simultaneously dosing PAC and a small dose of 1 mg

Fe/l ensures a steady, constant permeability over 24 hours and a good hydraulic backwash efficiency (Figure 7).

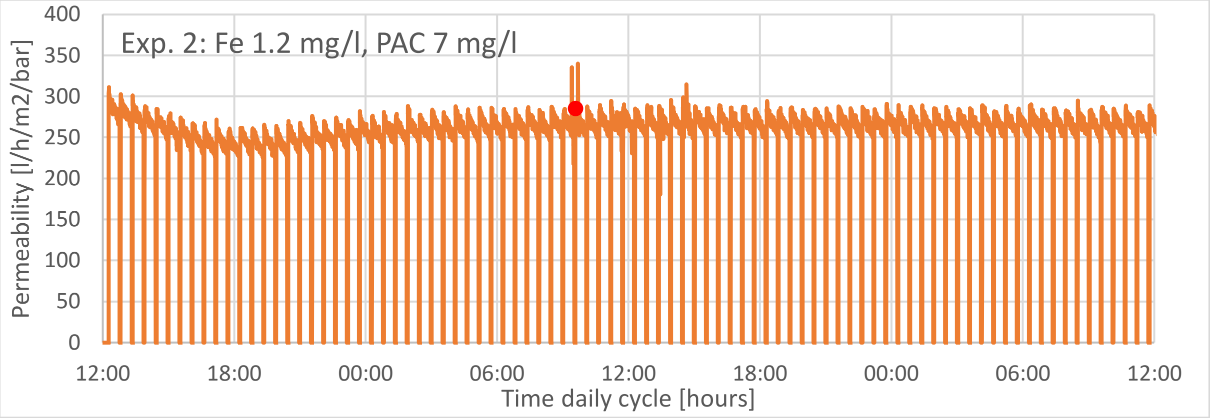

Figure 7 Experiment 2: Permeability with 1.2 mg Fe/l and 7 mg PAC/l. Start at experiment at red dot. Gap around 12:00 at first day is CEB.

When increasing the filtration time from 30 to 60 minutes (PAC 15 mg/l and 1 mg Fe/l) permeability remains steady (Figure 8). Therefore hydraulic backwash efficiency is good even when the cake layer formed by PAC and coagulant was doubled. This is promising since the removal efficiency increases with a longer filtration time, which is described in paragraph 4.2.1. Irreversible fouling is $2.4*10^9$ $m^{-1}h^{-1}$ for the experiment and $1.9*10^9$ $m^{-1}h^{-1}$ for the reference (Figure 4). Which is in line with irreversible fouling for a filtration of 30 minutes (Figure 4).

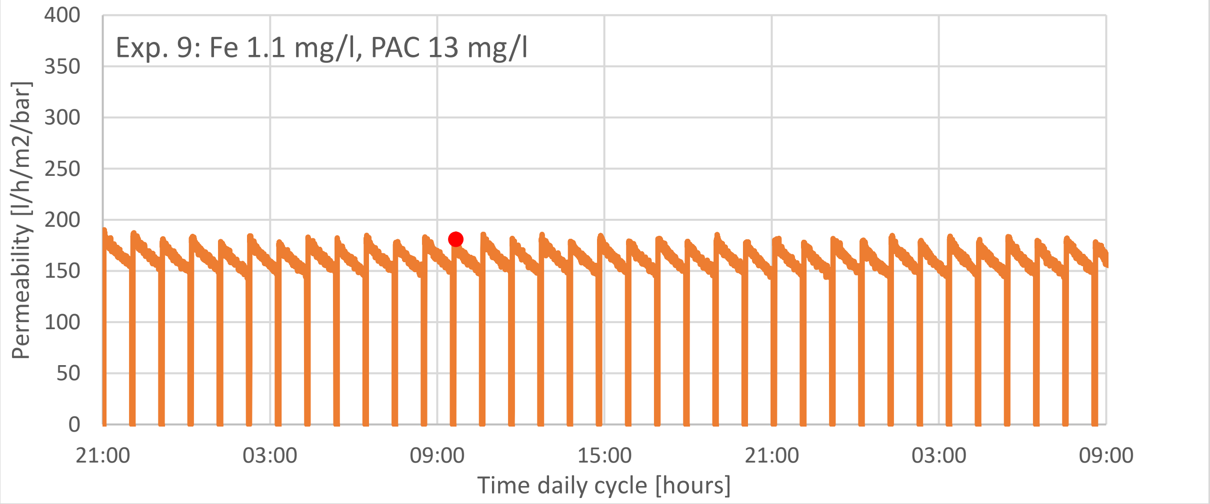

Figure 8 Experiment 9: permeability 21:00 – 09:34 reference (1.1 mg/l), 09:34 (red dot)-09:22 Experiment 9: PAC 13 mg/l and Fe 1.1 mg/l with a filtration time of 60 minutes

Inline dosing of PAC alone has a negative effect on permeability and increases irreversible fouling over 24 hours compared to only coagulant dosing. Inline dosing of both PAC and 1.2 mg Fe/l ensures a steady and constant permeability, irreversible fouling resistance is a factor 100 smaller when coagulant is dosed simultaneously. When increasing filtration time from 30 to 60 minutes, irreversible fouling resistance is in the same range as a filtration time of 30 minutes. Increasing PAC dose or increasing filtration time does not influence the positive effect of coagulant dosing.

4.1.3 Effect of PAC and coagulant dosing on reversible fouling

The average fouling resistance per experiment and reference mode is included in Figure 9. No dosing, experiment 1, has almost the same average reversible fouling as the reference mode with inline dosing of coagulant, 25.5*10^{10} $m^{-1}h^{-1}$ and 24.0*10^{10} $m^{-1}h^{-1}$ respectively. Standard deviation during no dosing is high, this is due to lower reversible fouling at the start of the experiment which increases over 24 hours. A possible explanation for this might be remaining coagulant, which was also found by Siegers et al. (2021). Remaining coagulant in the membrane may be due to an inefficient backwash because of capillary blocking (Heijman et al., 2007, Siegers et al., 2021). A decrease in reversible fouling resistance with coagulant addition is in concordance with other research done (Siegers et al., 2021). This is probably due to an increased cake porosity through coagulant dosing (Doyen et al., 2003; Siegers et al., 2021).

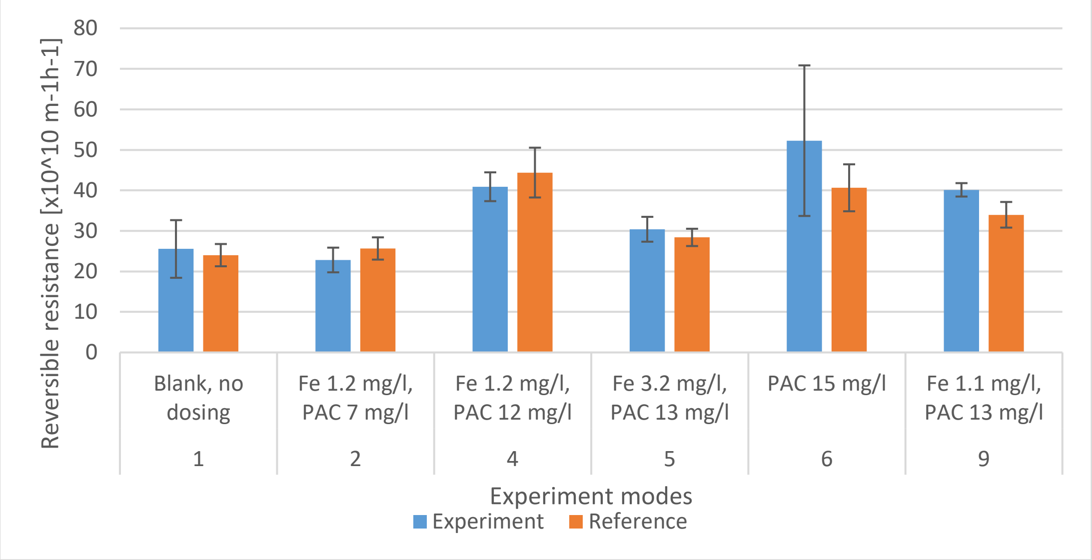

Figure 9 Reversible fouling resistance per hour for top and bottom of each experiment and reference, experiment 9 increase in filtration time 30 to 60 minutes.

There are differences visible in reversible fouling resistance of the references between experiments. A possible explanation is the increase peaks of FFMP, which were especially high for experiment 4 and 6. Therefore it is less reliable to look at differences between experiments and only differences between experiment and reference are compared. Reversible fouling resistance of experiment 2,4 and 5 and their references are all close and no clear increase in reversible fouling resistance is visible (Figure 9). Suggesting, addition of PAC does not change reversible fouling compared to the reference mode with only coagulant dosing. Meaning that even though the load on the membrane increases with 7 to 13 mg/l PAC this does not affect reversible fouling resistance. Increase in filtration time from 30 to 60 minutes (experiment 9) shows an increase for PAC addition from $33.0*10^{10}$ $m^{-1}h^{-1}$ to $40.1*10^{10}$ $m^{-1}h^{-1}$ (Figure 9).

Addition of PAC without coagulant dosing shows an increase in reversible fouling from $40.6*10^{10}$ $m^{-1}h^{-1}$ to $52.3*10^{10}$ $m^{-1}h^{-1}$ (Figure 6). This is not in line with other research done by Siegers et al. (2021). This can be explained by the longer experiment period. Reversible fouling resistance is not linear for both studies and increases over time starting with a lower reversible fouling resistance than the reference mode (Figure 6). This study has a twice as long experiment as Siegers et al. (2021) which results in a higher average fouling resistance and as such only then showing an effect of PAC dosing. This is the highest increase in reversible fouling resistance of all experiments. Only PAC dosing therefore induces the highest reversible fouling resistance.

Coagulant addition reduces reversible membrane fouling compared to no dosing. Dosing of PAC and coagulant shows no clear increase or decrease in reversible fouling resistance except when a longer filtration time was applied compared to only coagulant dosing. Only PAC dosing had a negative influence on reversible fouling resistance compared to coagulant dosing.

4.1.4 Capillary blocking

This paragraph gives the results for capillary blocking, a heterogeneous fouling mechanism. In Figure 10 and 11 the results of experiment 2 and 5 of at least 24 hours of PAC and coagulant dosing are shown. FFMP remains steady and no change over 24 hours is visible. Therefore, addition of PAC when coagulant is dosed does not influence FFMP and as such blocking of capillaries. Backwash is sufficient to prevent capillary blocking with low and higher PAC and coagulant dosing. Outlier points are due to a measurement at the start of FFMP when flow was still adjusting. A CEB for the experiment in Figure 11 was done two days before the start of the experiment. This extra time showed that even though the permeability was stable in a few hours the FFMP stabilization needed around 12 hours. This longer stabilization period was measured several times. This longer reference period is responsible for a more stable FFMP as can be seen in Figure 11 compared to the FFMP in other experiments. In alle experiments except for the one with the longer stabilization period, a difference between top and bottom FFMP is seen. This suggests an uneven blocking of capillaries at the top and bottom potting.

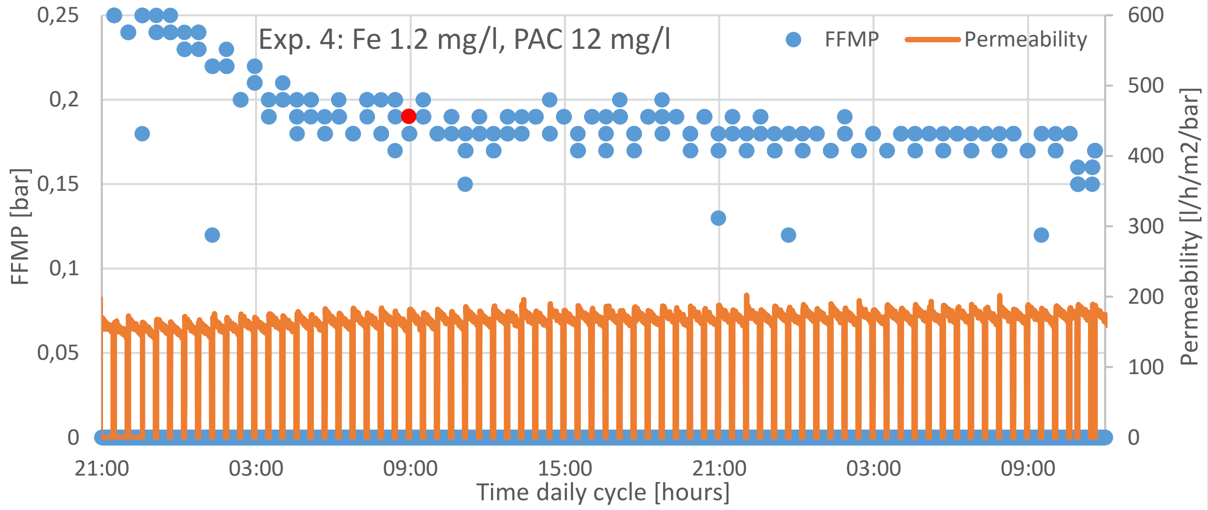

Figure 10 FFMP of experiment 4 UF with dosing of 1.2 mg Fe/l and 12 mg PAC/l. Reference (up to red dot) 1.2 mg Fe/l, red dot is start PAC dosing. (May)

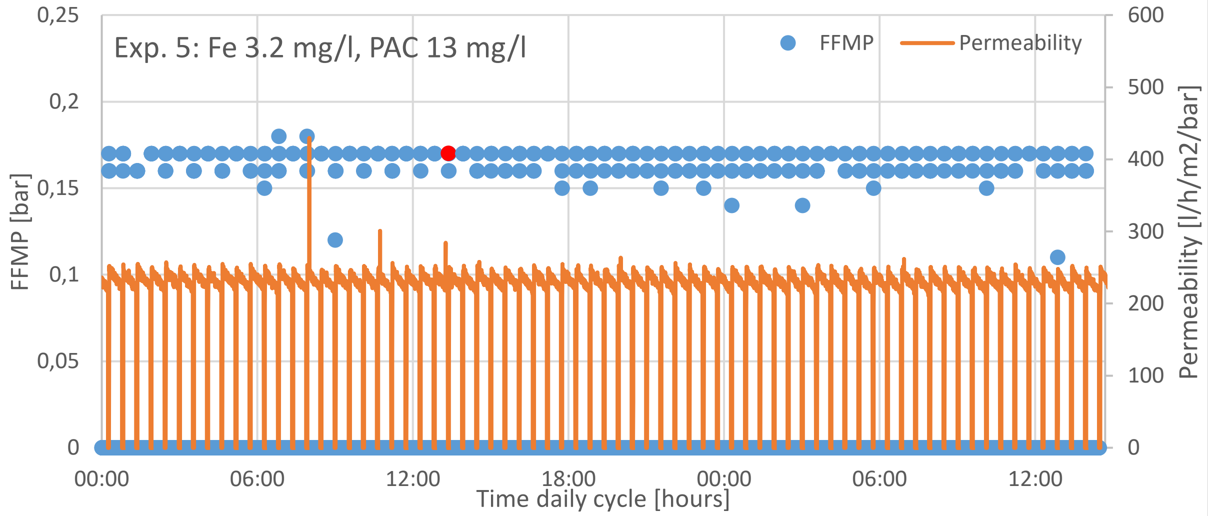

Figure 11 FFMP of UF with dosing of 3.2 mg Fe/l and 13 mg/l PAC. Reference up to red dot, red dot is start PAC dosing experiment 5. (April)

The experiment where no coagulant or adsorbent was dosed shows no additional increase in FFMP during the experiment (Figure 12). The FFMP is even lower compared to all other experiments and references where coagulant is being dosed, 0.12-0.14 compared to 0.17-0.18. This means that coagulant addition is responsible for a part of the capillary blocking. Capillaries blocked by coagulation is partly reversed immediately when coagulation stops (where blank filtration starts, Figure 12).

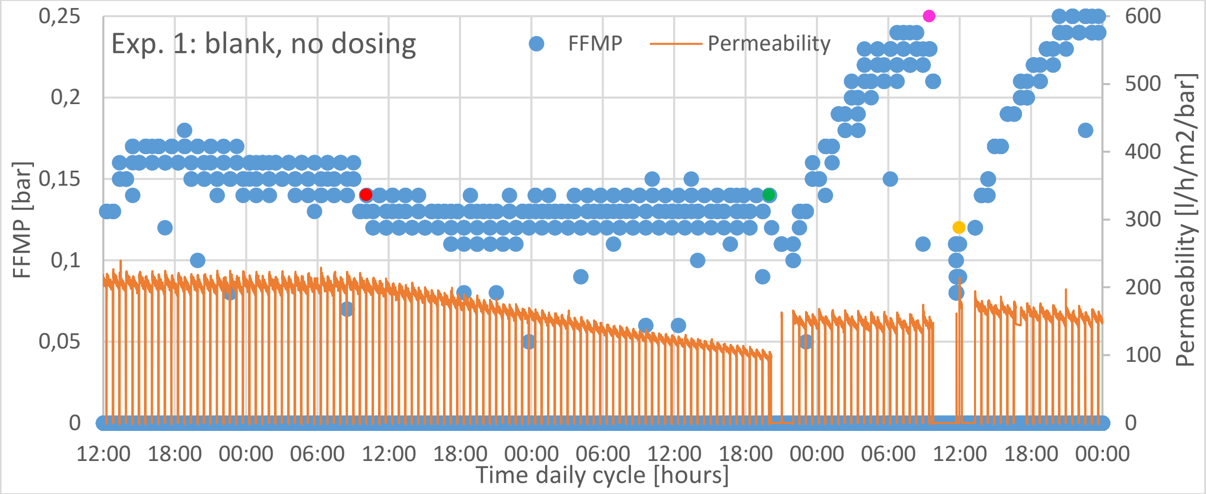

Figure 12 FFMP of experiment 1, UF with blank filtration, no dosing. Reference (up to red dot) 1.2 mg Fe/l, red dot is start PAC dosing, Green acid CEB, Pink and Yellow CEB chlorine. (May)

In addition to a negative effect of coagulant dosing, a negative effect of CEB on capillary blocking is seen before and afterwards of experiment 1 (Figure 10) and other experiments as well. An increase of FFMP is visible after different CEB, both acid and chlorine have this effect. This effect can also be seen in Figure 10, 13 and 14, where the increase and decrease in the reference period are due to a CEB before the reference. Before all these CEB the FFMP was constant. Hence, capillary blocking increases after a CEB. The increase in FFMP differs substantially per CEB. Highest increase of FFMP is seen by a CEB directly after an experiment with no dosing of coagulant and PAC (Figure 12). This suggests that fouling without the addition of coagulant and a CEB afterwards creates a situation where capillary blocking increases. Over time the FFMP does recover from this increase, since the FFMP goes back to 0.17-0.18. A possibility for this phenomenon is an inefficient CEB where fouling is not flushed properly from the membrane. An inefficient backwash and CEB are caused or at least worsened by capillary blocking (Heijman et al., 2007) .This loose fouling agglomerates in the membrane blocking pores, which are slowly unblocked during every backwash afterwards.

During these peaks of FFMP it can be seen that permeability decreases slightly (Figure 10 and 13). A possible explanation is complete blocking of capillaries which increases permeability due to the way permeability is calculated where the surface membrane area is assumed to be constant. When capillaries are blocked active surface membrane area decreases and pressure increases. However, in the formula of permeability only pressure is taken into account and as such a decrease in permeability is visible.

Increase in filtration time does not show an increase in FFMP (Figure 13 compared to figure 14). Therefore no more additional capillaries are being blocked during filtration. Accordingly, the hydraulic backwash is efficient with a filtration time of 60 minutes to prevent capillary blocking.

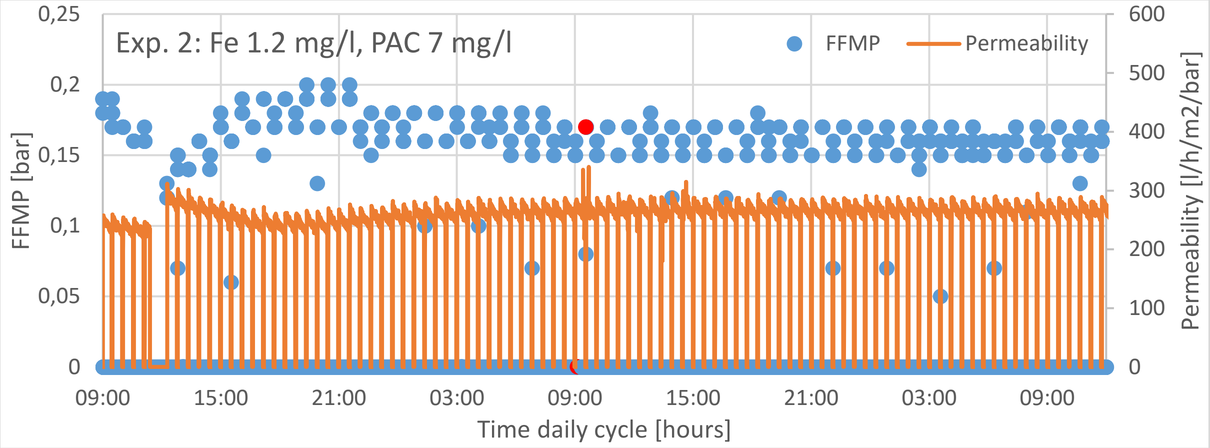

Figure 13 FFMP of UF with dosing of coagulant and PAC. Gap at 11:30 is CEB. Reference up to red dot, red dot is start PAC dosing of experiment 2. (March)

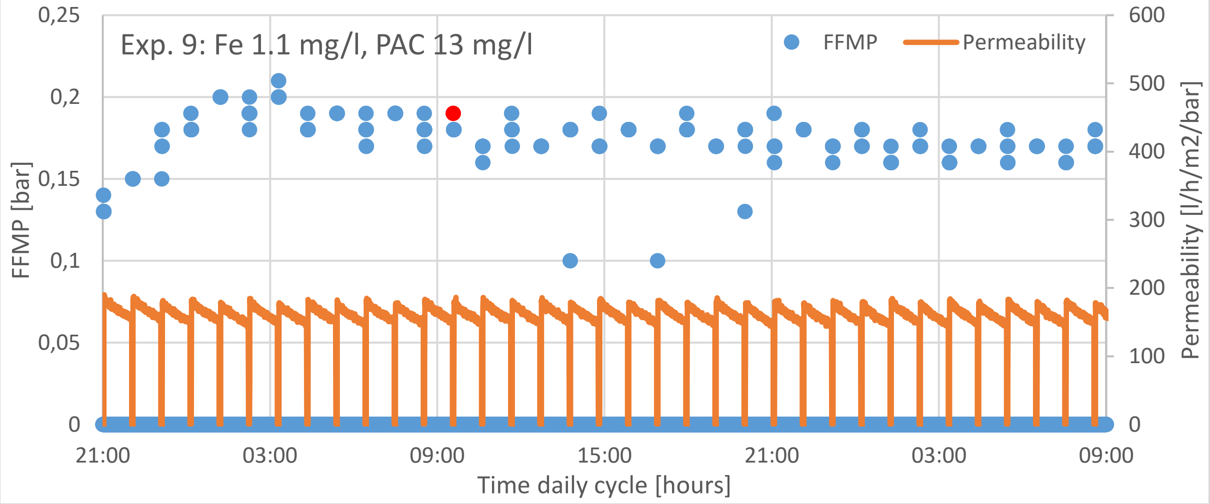

Figure 14 FFMP of experiment 9 UF with dosing of 1.1 mg Fe/l and 13 mg PAC/l with a filtration time of 60 min. Reference (up to red dot) 1.1 mg Fe/l, red dot is start PAC dosing. (May)

After the CEB, during the reference mode, the FFMP increased, just as seen before other experiments (Figure 15). Due to the CEB the FFMP was not completely stable at the beginning of the experiment even though permeability was. The reason for the larger increase in FFMP compared to other experiments after a CEB is not clear. When only PAC is being dosed it can be seen that the average FFMP is lower than for all experiments and references where coagulant is being dosed. The FFMP stabilizes at 0.12-0.14 (Figure 15) compared to 0.17-0.18 with coagulant and PAC dosing (Figure 10, 11, 13 and 14). The FFMP is the same for blank filtration and is stable, which indicates that PAC is not responsible for blocking of capillaries.

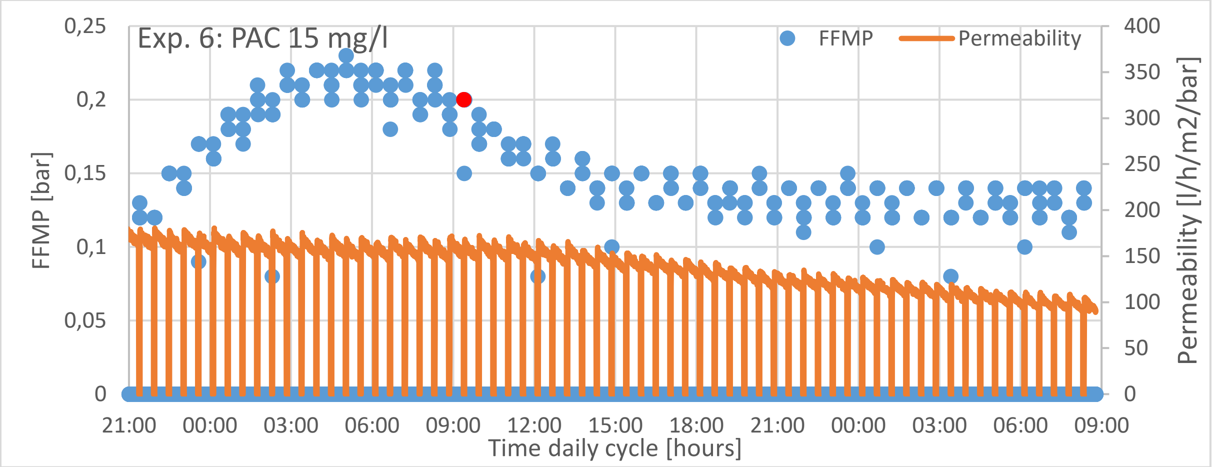

Figure 15 FFMP of experiment 6, UF with dosing of 15 mg/l PAC. Reference up to red dot (Fe 1.2 mg/l), red dot is start PAC dosing and stop iron dosing (May)

Visual inspection

In order to translate the FFMP to the number of capillaries blocked the membrane was visually inspected at the end of all experiments. After all experiments, a backwash of several minutes was executed to clean the membrane. The membrane was visually inspected at the bottom and top side of the membrane and at 1/3 of the membrane a cross-section (Figure 16). The top and bottom of the membrane give an indication of around 70-75% blocked capillaries. However, the cross-section gives an indication of 72-79% blocked capillaries. The membrane was only opened after a few weeks, which is why this indication of blocked capillaries is an estimate. The membrane was fouled with PAC and coagulant, therefore it was difficult to see is capillaries were blocked or only foul. As rough estimate around 25% of capillaries are still open at the end of all experiments for both sides. Assuming these 25% open capillaries are different capillaries for both sides than 50% is completely blocked from both sides and possibly even more. The cross-section shows fouled capillaries at the permeate side of the membrane. These fouled capillaries suggest complete blockage of capillaries from both sides as backwash was not possible through these capillaries. Heijman et al. (2007) who also investigated blocking of capillaries, found 95% of capillaries blocked. However, their filtration was only one way and did not switch from top to bottom. Furthermore, dosing of iron was higher with 60 mg Fe/l. Even so it does give indication that a substantial amount of capillaries can be blocked during UF inline dosing of coagulant.

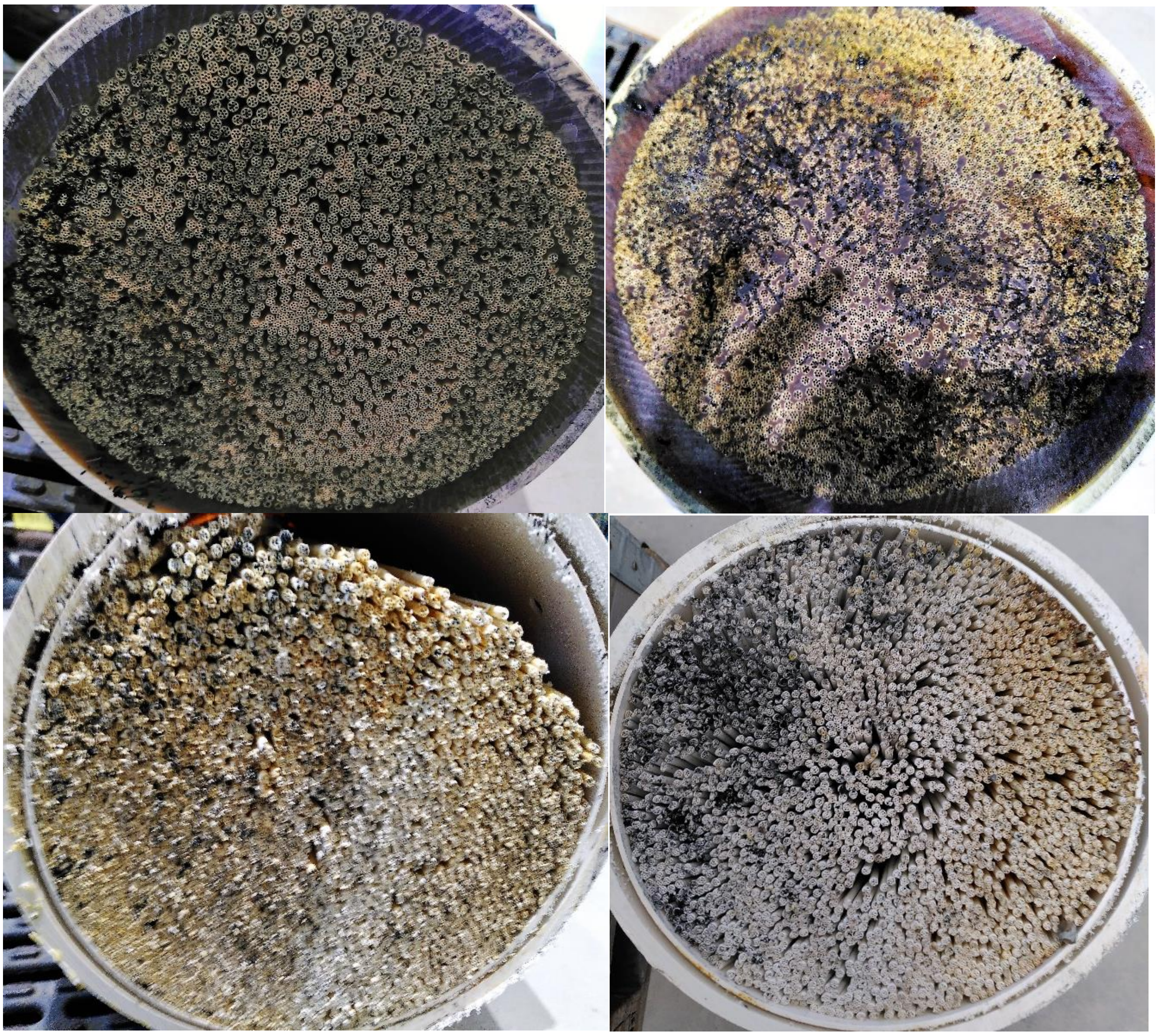

Figure 16 Inside of the membrane after seven months of use with coagulant and PAC. Clockwise starting left top: Bottom, top, bottom half cross-section (wet), top half cross-section (dried).

With an FFMP of 0.18 bar measured at the end an indication of closed capillaries was obtained with the empirical relation between pressure and closed capillaries estimated through visual inspection (Eq. 13). Starting values were 0.06 bar with all capillaries open. Where A in this case is 68348000 and B is 2000. With this empirical relation an estimate of closed capillaries could be made for all experiments. An overview of closed capillaries per experiment is given in Table 7. Before the start of the experiments the membrane was already in use and coagulant was already dosed. An irreversible increase in FFMP which could not be reversed with a CEB was caused due to a high iron dose pre-coating of 18 mg Fe/l, caused the FFMP to increase with 0.05 bar. The FFMP from that moment already was around 0.11 bar. Another increase was seen at the 31 of January, the reason for this increase is not clear. Dosing was 3 mg Fe/l and PAC 6 mg/l and did not change during the day even though the FFMP increase was 0.05 bar in a few hours. Influent water or inconsistent dosing of PAC could be the reason the FFMP increased however, no hourly data on influent composition was available.

Table 7 Closed capillaries during the experiments and two incidents. Note values closed capillaries are an estimate (±10%), differences between closed capillaries are from FFMP and based on the estimate of blocked capillaries in total (±1.5%). Data presented in chronological order. Reference shows first number average blocking and higher number is peak value (Figure 10, 12-15). a: no average, only peak value

Exp.	Pac dosing [mg/l]	Iron dosing [mg/l]	Closed capillaries [%] Ref. (Iron dose only of exp.)	Exp.	Increase	Comments
	-	3	-	-	33 -> 33	Pre-coating 10 min (14 Dec)
	-	18	-	-	33 -> 56	Pre-coating 10 min (15 Dec)
	6	3.3	56	75	64 -> 75	31 Jan. Inconsistent PAC
2	7	1.2	71-78	71		
5	13	3.2	73	73		
1	-	-	71-75	67	CEB 83	
4	12	1.2	78-83	75		
9	13	1.1	76-79	73-76		Filtration 60 min
6	15	-	81[a]	60-67		

Coagulation has a negative effect on capillary blocking with an increase of 4-8% compared to no coagulant or adsorbent. Interestingly, a CEB followed by coagulation shows an increase in capillary blocking, with a highest increase of 16%, which resulted in 83% of capillaries blocked. Irreversible increase of blocked capillaries was caused by high doses of coagulant due to pre-coating. Another irreversible increase could not be explained. Dosing of only PAC showed the same decrease in blocked capillaries as no dosing compared to inline dosing of coagulant, 4-8% respectively. A longer filtration time from 30 to 60 minutes did not show any additional pore blocking.

4.2 Retention of organic micro pollutants including PFAS by inline dosing of coagulant and adsorbent in UF

In this section the retention of organic micropollutants is given for the experiments with inline dosing of coagulant and PAC. The effect of varying modes of adsorbent dose and coagulant dose is given and discussed. Standard deviations were high due to low concentrations present in influent water, especially for Metformin, Gabapentin and Caffeine because their removal was low (Appendix C.3). Standard deviations in relative removal were sometimes more than 100% which is why these are presented in Appendix C.3 in ng/l. It should be taken into consideration that especially for low removable OMP these high standard deviations make these outcomes less reliable. For this reason removal is not assessed per OMP but in high and low adsorbable OMP groups and in total.

4.2.1 Influence of varying PAC modes on removal efficiency

The removal efficiency varies from 10 to 63% for continuous inline dosing of 16 mg/l PAC and coagulant in UF (Figure 17). OMP with higher affinity for PAC reach removal efficiencies of 47-63%, while OMP with lower affinity (Caffeine, Gabapentin and Metformin) reach removal efficiencies of 10-13%. Removal efficiency results are in line with results from Schwaller et al. 2021 with 18%, 47% and 57% for continuous dosing of PAC (15 mg/l) and coagulant. Increasing the continuous dosing of PAC from 4 to 15 mg/l increases the removal efficiency a few percent up to 24% (Figure 17). Lower removal of Metformin, Gabapentin and Caffeine are in line with other research done on the removal of OMP with AC (Ebrahimzadeh et al., 2022; Nam et al., 2014). An explanation for low removal of metformin is given by Ebrahimzadeh et al. (2022) who suggests a rapid breakthrough because of non-cyclic structures of Metformin. However, in Figure 20 it can be seen that Metformin does not have high adsorption already from the first few minutes. OMP with a higher adsorption such as 1H-benzotriazole, 4,5-methylbenzotriazole, Carbamazepine, and Sotalol corresponds with other research as well (Ebrahimzadeh et al., 2022; Nam et al., 2014).

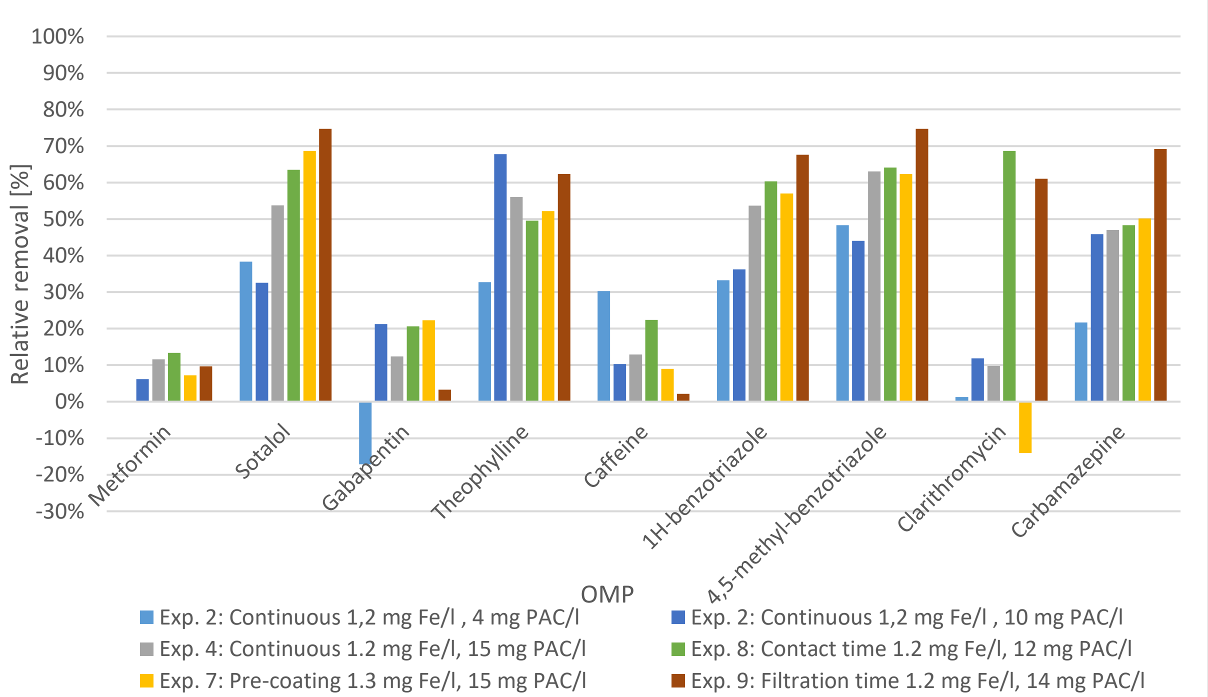

Figure 17 Removal OMP with varying modes of PAC dosing. There are two experiments two due to a large difference in PAC dosing n=2 (4 mg PAC/l) for all others n=4 except for exp. 4 where n=6, standard deviations included in appendix C.3 .

Extending filtration from 30 to 60 minutes ensures highest removal efficiency, up to 74%, with the same dosing concentration of PAC (Figure 17). Pre-coating PAC increases removal efficiency with a few percent compared to continuous dosing of PAC. Research from Schwaller et al. (2021) showed a higher increase of 20% for good adsorbable OMP with pre-coating. Probably due to shorter filtration time of 30 minutes, increasing filtration time is expected to give better results due to a bigger PAC cake layer and reducing the percentage of time needed for coating per filtration cycle (Figure 18). Theophylline shows a negative effect for pre-coating and contact time. A possible explanation might be that Theophylline is more sensitive for the exact PAC dosing concentration than different modes of dosing used since it follows the order from highest PAC dose to lowest PAC dose, except for PAC 12 and 14 mg/l, however this difference is within the standard deviation of both. Continuous dosing of PAC needs around 12 minutes to reach removal efficiencies of around 60 percent for good adsorbable OMP (Figure 18). With a filtration time of 30 minutes more than one third of that time is needed to create a large enough PAC layer to reach removal efficiencies higher than 60%, making 30 minutes of contact time an inefficient set-up. Increasing contact time of PAC with water before the membrane from 25 to 200 seconds increases efficiency with a few percent up to 9% in contrast to continuous dosing of PAC, even though PAC dosing was 3 mg/l lower. However, this increase is within the uncertainty interval and is therefore less reliable. Increasing the PAC cake layer inside the membrane has a bigger influence on removal than increasing the residence time of PAC in the water before the membrane and pre-coating of PAC.

A time series of pre-coating and continuous dosing of PAC shows the removal increase and decrease over time (Figure 18). Pre-coating the membrane takes 6 minutes, which is a fifth of the total concentration time. Samples were taken at the start and every 6 minutes which means that the actual build-up of removal efficiency in those first six minutes is not visible. As a consequence, the removal efficiency might reach as much as 80% before minute six. The line followed by continuous dosing of PAC in Figure 17 is representative for the first six minutes of the pre-coating PAC mode. A slightly lower removal efficiency is observed from 18 minutes and onwards for pre-coating. It does not qualify as a breakthrough however, it does show that a dosing of 15 mg/l is necessary for this influent water. This high dose of PAC (+10 mg/l) compared to PAC dosing on the rapid sand filtration at the same treatment plant may be due to different influent composition due to other pre-treatment.

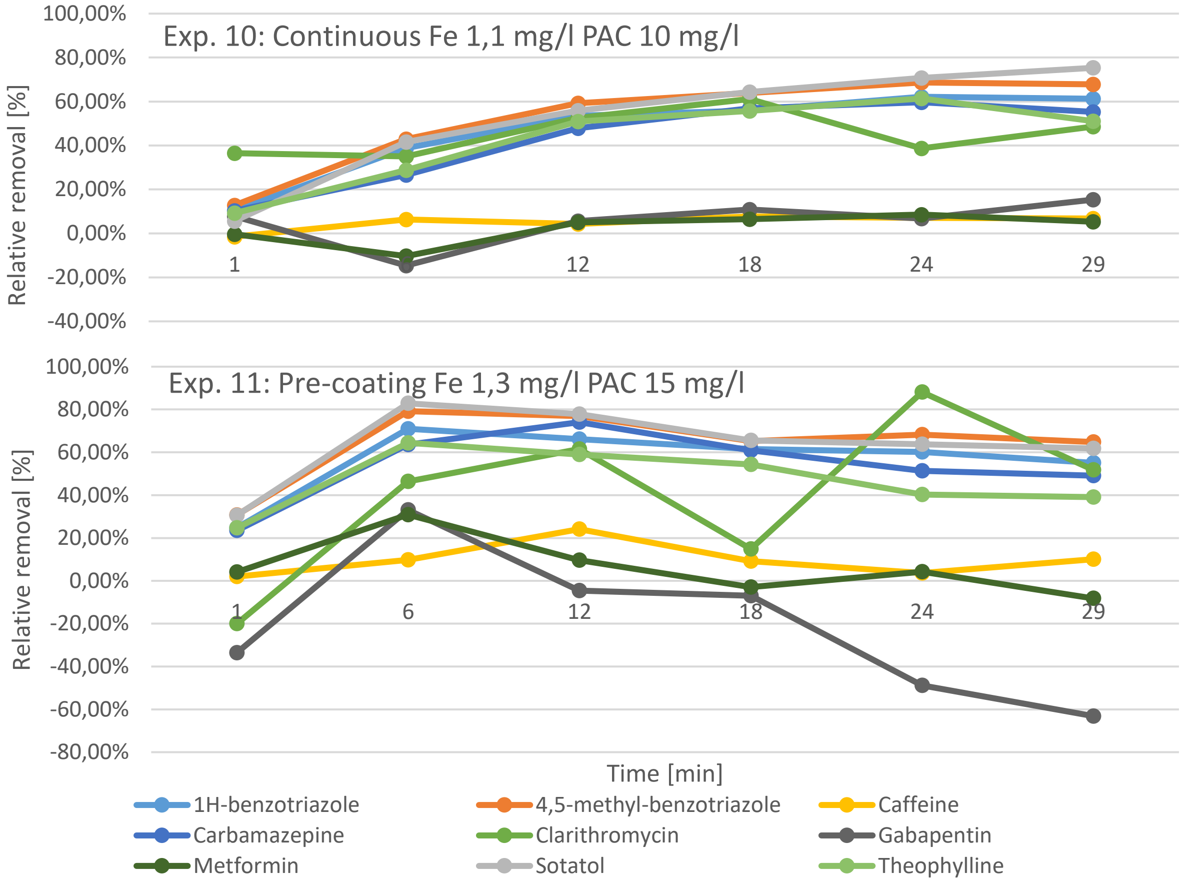

Figure 18 top: Removal efficiency in time with continuous PAC dosing and a filtration time of 30 min (experiment 10), Bottom: PAC pre-coating removal efficiencies in time during filtration cycle of 30 min (experiment 11)

Removal efficiencies reached with continuous dosing of PAC (15 mg/l) and coagulant (1.2 mg Fe/l) are lower than the efficiencies reached when PAC is dosed in the rapid sand filters of the drinking water treatment plant (Ebrahimzadeh et al., 2022). A possible explanation might be different influent water composition since rapid sand filtration received several additional treatment steps. DOC was around twice as low than influent water for this research. DOC influences adsorption of OMP negatively (Q. Wang et al., 2022). However different research report higher OMP removal with lower and higher DOC efficiencies (Kennedy et al., 2021; Löwenberg et al., 2014; Margot et al., 2013; Viegas et al., 2021). Except for Kennedy et al. (2021) (50 mg/l) PAC dosing was in the range of 5 to 15 mg/l for these studies. It is therefore unlikely that DOC concentration is the cause of the low OMP removal. Schwaller et al. (2021) showed removal efficiencies of lower than 60% with continuous dosing of coagulant which increased when coagulant was dosed as a pre-coating (Schwaller et al., 2021). In this study and the research of Schwaller et al. (2021) the hydraulic retention time of PAC is short in the order of seconds to a maximum of a few minutes (Schwaller et al., 2021). On the contrary, the hydraulic retention time in Margot et al. (2013) and Löwenberg et al. (2014) is between 40 minutes and more than 2 hours, a contact tank before UF was used to achieve this (Löwenberg et al., 2014; Margot et al., 2013).

PFAS

The removal efficiencies measured of PFAS are between a few percent and 37% for continuous inline dosing of 15 mg/l PAC and 1.2 mg/l coagulant in UF (Figure 19). However, the average measurement uncertainty for PFAS in surface water is around ten percent for most PFAS, with 20 and 40% for 6:2 FTS and PFOA respectively (Appendix C.2). The high measurement uncertainty for PFOA is due to higher background noise compared to other PFAS. Increasing the PAC dosing with 11 mg/l increases the removal of PFAS from almost no removal to a few percent up to 37% (Figure 19). Dosing PAC as a pre-coating instead of continuous does not increase the removal efficiency for PFAS. Increasing the contact time suggests a small increase in removal efficiency. However, this increase is within the measurement uncertainty. These removal efficiencies are a few percent lower than the removal efficiencies reached by Ebrahimzadeh et al. (2022). The difference might be explained due to different pre-treatment. However, dosing concentrations of PAC were 2 mg/l compared to 15 mg/l in this study. In another study of Snyder et al. (2009) removal efficiencies of 17 up to 50% were found. Inline of PAC-UF has a low removal efficiency for PFAS compared to other treatments with PAC.

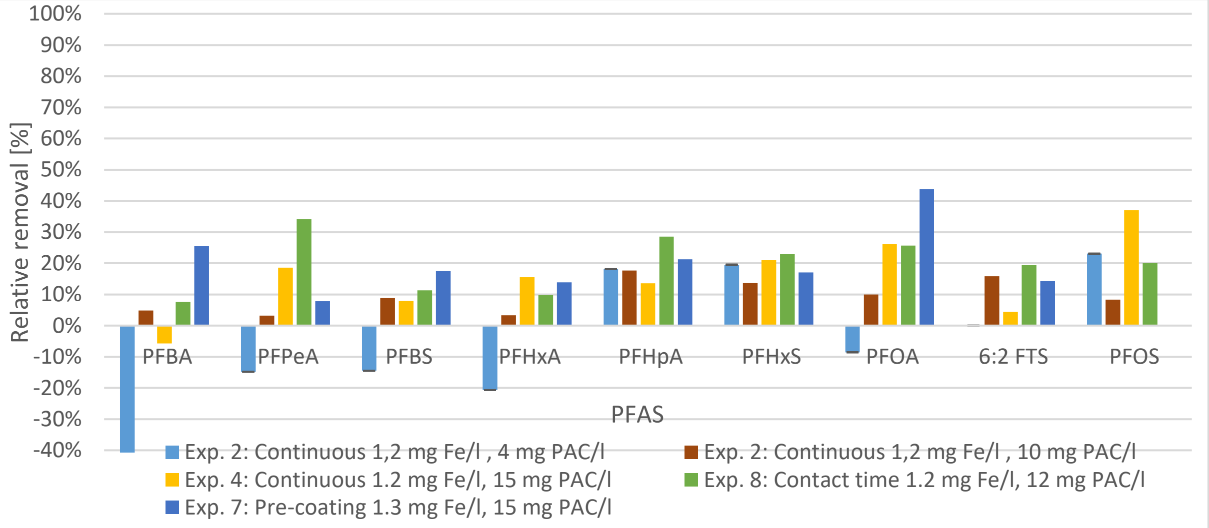

Figure 19 Removal PFAS with varying modes of PAC dosing. There are two experiments two due to a large difference in PAC dosing for these n=1 for all others n=2, standard deviations included in appendix C.3

The actual removal for most PFAS is below 0.5 ng/l, with some exceptions reaching at most 1 ng/l (Appendix C.3). The average total removal of PFAS for continuous dosing of 15 mg PAC/l and 1.2 mg Fe/l is 3.4 ng/l, 14% percent of the total PFAS concentration in the influent water. The total PFAS removal is 4.67 ng/l, 20% when the contact time is increased from 25 to 200 seconds. When PAC is dosed as a pre-coating the removal is 3.83 ng/l, 16% of total PFAS measured in influent water is removed. Removal of individual PFAS are between a few percent and 37%. Affinity of PFAS for PAC is known to be low. However, the adsorption was lower than other studies using surface water and PAC treatment. Furthermore the maximum advised threshold by the RIVM of 4.4 ng/l for drinking water is not reached. Even with adjustments of set-up such as increased filtration time or pre-coating of PAC it would not be certain that removal of PFAS would be enough to reach levels set by the RIVM. PFAS removal with PAC is not recommended when high removal efficiencies need to be reached.

Removal efficiencies of poor and good adsorbable OMP are in line with other research done on inline dosing of PAC and coagulant. Removal efficiencies reached with continuous dosing of PAC and coagulant are lower compared to other PAC-UF set-ups. PFAS reaches removal efficiencies of only 37%. Inline dosing of PAC with coagulant shows potential for direct treatment of surface water when using longer filtration times (60 minutes). Removal efficiencies of 74% are reached however, if the aim is to achieve removal efficiencies of more than 90%, the PAC dosing should be increased or the hydraulic retention time should be increased.

4.2.2 Influence of varying coagulant modes on removal efficiency

OMP results experienced high standard deviations, for some even more than 100% when looking at relative removal. These high standard deviations are caused due to low influent concentrations and worsened when removal is low. In order to make the graphs readable standard deviations are added in Appendix C.3 in ng/l. It should be taken into account that especially for low removable OMP these high standard deviations make these outcomes less reliable. For this reason removal is not assessed per OMP but in high and low adsorbable OMP groups and in total.

When simultaneously and continuously dosing coagulant and PAC, coagulant dose has a negative influence on the removal of OMP with a dosing concentration of 10 mg/l PAC (Figure 20). This is consistent with other literature where the influence of adding coagulant on removal efficiency showed a negative effect (Schwaller et al., 2021; Seckler et al., 2013). However, Altmann et al (2015) does not experience a negative influence of coagulant dosing on OMP removal. In the study of Altmann et al (2015) batch tests with different dosing sequences were done with a contact time of ten minutes. Suggesting dosing method, in this case inline continuous and simultaneous in UF, influences coagulant impact. When increasing dosing concentration with 2 mg Fe/l with a low PAC dose (9-10 mg/l), decrease in removal efficiency is a few percent up to more than 40% depending on which OMP. However, when increasing PAC dosing concentration from 10 to 15 mg/l this negative effect of coagulant dosing is not seen (Figure 20). Hindrance of adsorption by coagulation is dependent upon the ratio of PAC and coagulant dosing. A possible explanation for reduced removal efficiencies is by continuously dosing PAC and coagulant, causes the PAC to be incorporated in the iron hydroxide flocs which are being formed (Altmann et al., 2015; Sánchez López et al., 2021). As could be seen by visual inspection and confirmed by the study of Heijman et al. (2007) iron hydroxide flocs are not spread homogeneously over the membrane. Particles larger than a certain diameter are transported to the dead-end of the capillary (Arkhangelsky et al., 2011). Accordingly, PAC particles will not be spread homogeneous over the membrane reducing the effectiveness of the PAC layer on the membrane (Schwaller et al., 2021). Visual inspection from backwash water shows by eye separate iron flocs and PAC. However, seen from under a microscope PAC is indeed incorporated in iron flocs.

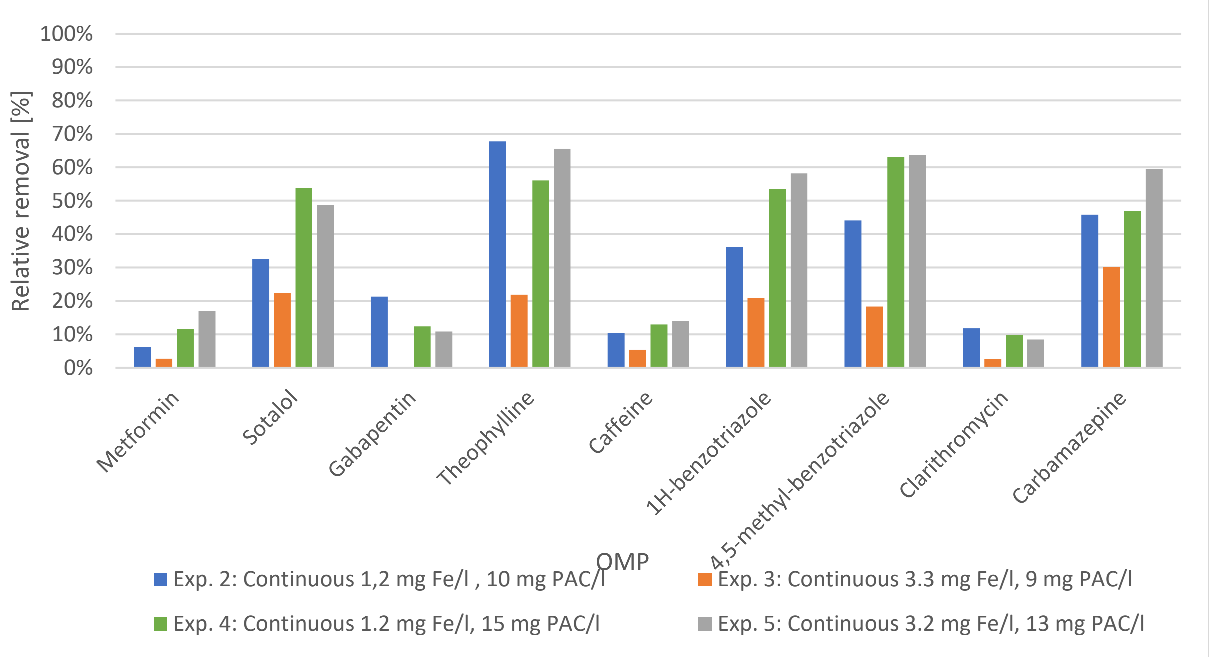

Figure 20 Removal OMP with high and low coagulant doses with inline dosing of PAC and coagulant in UF (n=4). Standard deviations included in Appendix C.3

Likewise a negative effect on removal efficiencies when increasing coagulant dosing with 2 mg Fe/l can be seen for PFAS removal with a PAC dosing of 10 mg/l (Figure 21). Even though the removal of PFAS is low and even negative all removal efficiencies with lower coagulant dosing are higher for every PFAS measured except for PFOA (Figure 20). PFOA has a high standard deviation and is therefore less reliable (Appendix C.3). As for the other OMP, this negative influence of iron dosing on PFAS removal is not visible with a higher PAC dosing of 15 mg/l (Figure 21). This suggests a PAC dosing of 15 mg/l is high enough to overcome the negative influence of iron dosing on PAC adsorption.

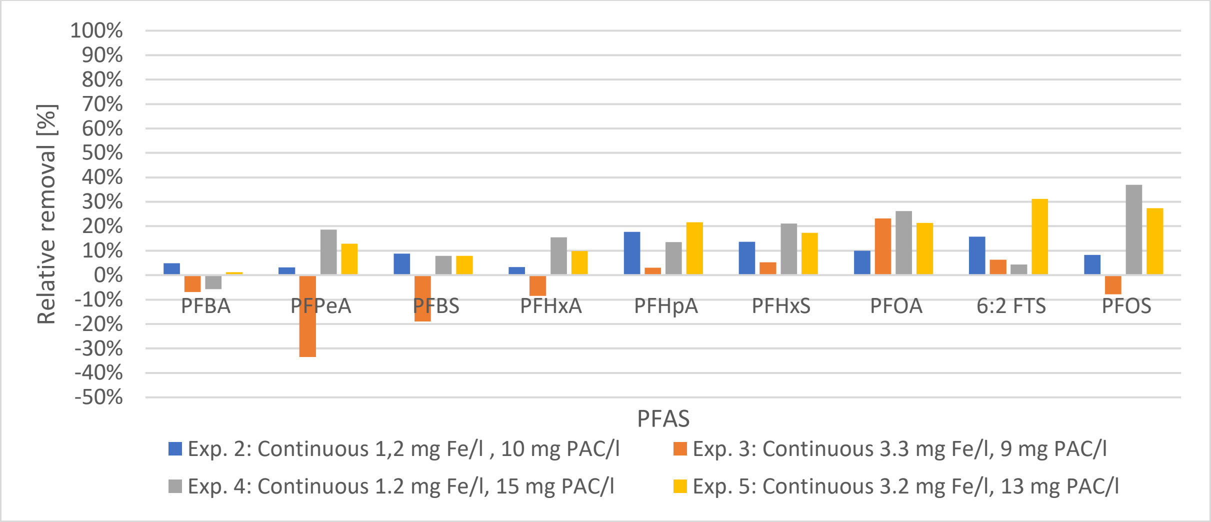

Figure 21 Top: Removal efficiencies PFAS with different coagulant dosing concentrations with inline dosing of PAC and coagulant in UF (n=2). Standard deviations included in Appendix C.3

Continuous dosing of coagulant has a negative impact on OMP adsorption. This negative effect is possibly caused by incorporation of PAC in hydroxide flocs which blocs adsorption sites for OMP and reduces homogeneous PAC layer forming. In order to overcome this negative effect higher doses of PAC are needed to reach the same removal efficiencies as for no coagulant addition.

5 Conclusion and recommendations

This chapter contains the conclusions and recommendations for the effect of inline dosing of coagulant and adsorbent in UF on fouling and retention of organic micropollutants including PFAS for direct surface water treatment.

5.1 Conclusion

Due to water stress on drinking water resources including water quality, and increasing awareness of OMP health risks, OMP removal in drinking water is important. In this study, hybrid membrane treatment with inline dosing of PAC and coagulant on UF was assessed. The objective was to investigate the fouling of UF membrane including capillary blocking and removal of different OMP including PFAS. Which was answered by looking at the effect of different concentrations of PAC and coagulant on fouling, looking at effect of different concentrations of PAC and coagulant on OMP removal and effect on varying PAC dosing modes on fouling and OMP removal.

Inline dosing of coagulant in UF has a positive effect to prevent irreversible fouling. During dosing of coagulant permeability remains steady and there is only a small increase in irreversible fouling over 24 hours, in the order of 0.2-0.7*10^9 $m^{-1}h^{-1}$. Changing coagulant dose does not influence the positive effect coagulant has on irreversible fouling. A dose of 1.2 mg/l and 3.2 mg/l or a filtration time increase of 30 minutes all have irreversible fouling resistance in the same order of magnitude. Absence of coagulant dosing causes irreversible fouling to increase to 8.7*10^{10} $m^{-1}h^{-1}$ and cannot be easily reversed with a CEB.

On the other hand inline dosing of PAC alone has a negative effect on permeability and with an irreversible fouling resistance of 11.4*10^{10} $m^{-1}h^{-1}$ over 24 hours compared to only coagulant dosing. Inline dosing of both PAC and 1.2 mg Fe/l ensures a steady and constant permeability, irreversible fouling resistance is between 0.17-0.24*10^{10} $m^{-1}h^{-1}$ when coagulant is dosed simultaneously. When increasing filtration time from 30 to 60 minutes, irreversible fouling resistance is in the same order of magnitude as a filtration time of 30 minutes. Increasing PAC dose or increasing filtration time does not influence the positive effect of coagulant dosing.

Coagulant addition reduces reversible membrane fouling compared to no dosing, starting with low reversible fouling resistance increasing over 24 hours. Therefore, average reversible fouling resistance was almost the same, 24.0*10^{10} $m^{-1}h^{-1}$ (coagulant) and 25.5*10^{10} $m^{-1}h^{-1}$ (No coagulant). Dosing of PAC and coagulant shows no clear increase or decrease in reversible fouling resistance except when a longer filtration time was applied compared to only coagulant dosing, 33.0*10^{10} $m^{-1}h^{-1}$ to 40.1*10^{10} $m^{-1}h^{-1}$. Only PAC dosing had a negative influence on reversible fouling resistance compared to coagulant dosing of 40.6*10^{10} $m^{-1}h^{-1}$ to 52.3*10^{10} $m^{-1}h^{-1}$.

Coagulation has a negative effect on capillary blocking with an increase of 4-8% compared to no coagulant or adsorbent. Interestingly, a CEB followed by coagulation shows an increase in capillary blocking, with a highest increase of 16%. In 24 hours, this increase of blocked capillaries was reversed. During this increase a small dip in permeability was also visible, possibly caused by complete blocking of capillaries. PAC did not influence pore blocking, inline dosing of PAC and no dosing caused the same amount of capillaries being blocked. Increasing the load of PAC and coagulant by increasing the filtration time did not influence pore blocking.

The second aim of this study was to assess the removal efficiencies of different OMP including PFAS. Varying modes of PAC dosing were assessed, increase in contact time of PAC before the membrane, increase in filtration time and continuous and pre-coating. Increasing filtration time (30 to 60 minutes) showed the highest removal efficiency of 75% for Sotalol and 5-Methyl-1H-Benzotriazole, both good adsorbable OMP. Less adsorbable OMP showed removal efficiencies of a few percent up to ten percent, however these removal efficiencies are less reliable due to high standard deviations. Removal of PFAS are between a few percent and 37%. Increasing contact time of PAC with water before the membrane did not affect removal efficiency as did pre-coating of PAC. Furthermore continuous dosing of coagulant has a negative impact on OMP adsorption including PFAS. With a higher PAC dose (15 mg/l) this negative effect was overcome.

5.2 Recommendations

Based on this research several questions were answered while new questions arose which are unanswered. The recommendations for the future are given in this paragraph.

1. Lower retention of OMP by PAC-UF compared to other PAC-UF systems with a different set-up such as longer hydraulic retention time and different dosing sequence. Suggests a different set-up enhances OMP removal efficiency. However, research at this point is scarce and more research is needed to find the optimal set-up for PAC-UF systems.

2. Capillary blocking is mainly influenced by coagulant addition, however CEB gave an increase in capillary blocking. Furthermore, there were several occasions where capillary blocking increase could not be attributed to a change in dosing of PAC or coagulant. Further research could investigate the effect influent water composition has on capillary blocking.

3. With complete blocking of capillaries on both sides, the active membrane surface area changes. This should be taken into account when calculating permeability. Furthermore, capillary blocking should be monitored frequently with daily use of UF since it influences backwash efficiency and even permeability.

4. In this study varying modes of PAC were investigated. Varying modes of coagulant addition in combination with PAC dosing should be investigated in order to assess the effect of coagulant addition on OMP removal.

5. In this study influence of changing influent composition during seasons was not an objective. Especially for fouling but also for removal of OMP, seasonal changes in influent water should be investigated further on pilot scale.

6. Natural surface water concentrations of OMP were used to assess the removal efficiency of different OMP including PFAS. Concentrations were low, especially for PFAS only a few nanograms per litre. In order to increase reliability of PFAS removal efficiencies spike experiments should be executed.

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Appendix

The appendices give background information on OMP and PFAS analysed for this study. Secondly, duplicate experiments of fouling of the membrane are included. Thirdly, background information on limit of quantification and measurement uncertainty on PFAS are given. Lastly, additional results which were uncovered outside of the experiments are explained.

A. Background information on micro pollutants analysed in this research

This appendix gives information on the OMP analysed and measured in this study.

A.1 List of analysed OMP

Table 8 OMP analysed for this study, in bolt OMP measured in this study.

OMP analysed	
benzotriazole	*Metoprolol*
Metformin	***Sotalol***
4,5-methylbenzotriazole	*Trimethoprim*
Gabapentin	*Diclofenac*
Theophylline	*Sulfadimethoxine*
caffeine	***Clarithromycine***
Carbamazepine	*Clofobric acid*
Sulfmethoxazole	*Hydrochlorothiazide*
Ketoprofen	*Acetaminophen*
	Propranolol
PFAS analysed	
11Cl-PF3OUdS	*Perfluorododecanoic acid (PFDoA)*
6:2 fluorotelomersulfonic acid	*Perfluorododecane sulfonic acid (PFDoS)*
9Cl-PF3ONS	*Perfluoroheptane sulfonic acid (PFHpS)*
DONA	***Perfluoroheptanoic acid (PFHpA)***
EtFOSAA	***Perfluorohexane sulfonic acid (PFHxS)***
HFPO-DA	***Perfluorohexanoic acid (PFHxA)***
Perfluorobutane sulfonic acid (PFBS)	*Perfluorononoic acid (PFNA)*
Perfluorobutanoic acid (PFBA)	*Perfluorononane sulfonic acid (PFNS)*
Perfluorodecane sulfonic acid (PFDS)	***Perfluorooctane sulfonic acid (PFOS)***
Perfluorodecanoic acid (PFDA)	***Perfluorooctanoic acid (PFOA)***
Perfluorotridecanesulfonic acid (PFTrDS)	***Perfluoropentanoic acid (PFPeA)***
Perfluorotridecanoic acid (PFTrDA)	*Perfluoropentane sulfonic acid (PFPeS)*
Perfluoroundecane sulfonic acid (PFUdS)	*Perfluoroundecanoic acid (PFUdA)*

A.2 Structures measured OMP

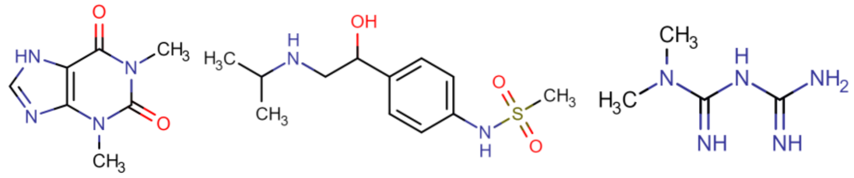

Figure 22 From left to right structures of: theophyllin, sotalol and metformin

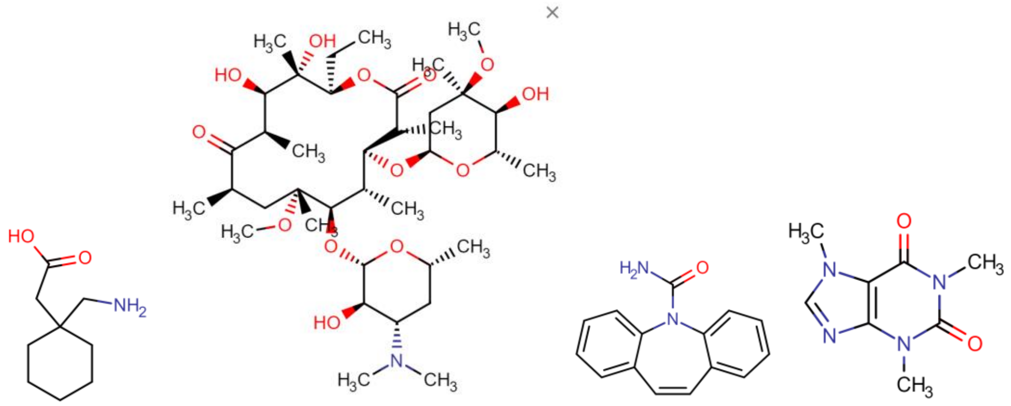

Figure 23 From left to right structures of: gabapentin, clarithromycin, carbamazepine, caffeine

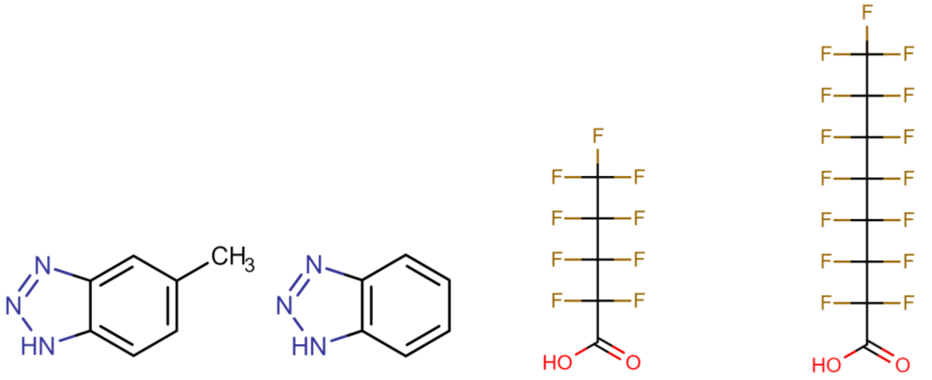

Figure 24 From left to right structures of: 5-methylbenzotriazole, 1H-benzotriazole, Perfluoropentanoic acid, Perfluorooctanoic acid

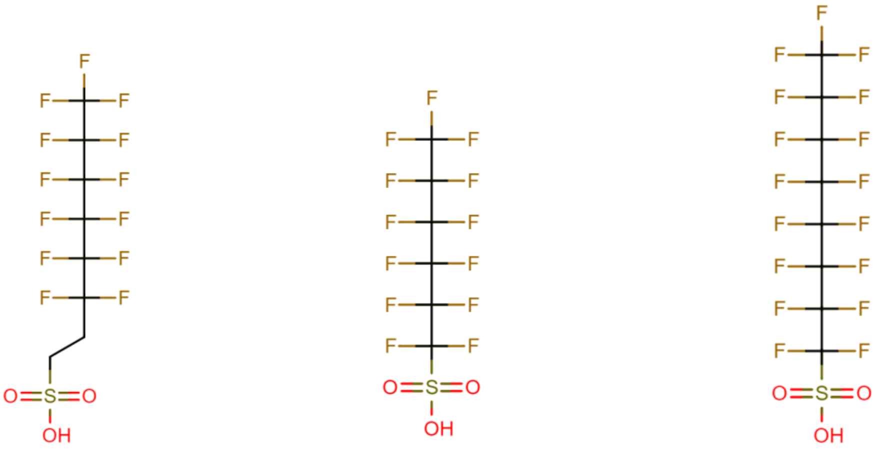

Figure 25 From left to right structures of: 6:2 Fluorotelomersulfonic acid, perfluorohexanesulfonic acid, and perfluorooctanesulfonic acid

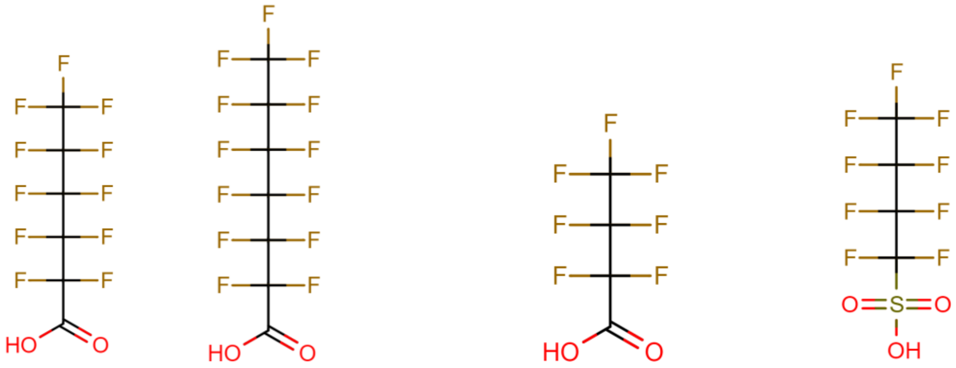

Figure 26 From left to right structures of: perfluorohexanoic acid, perfluoroheptanoic acid, perfluorobutanoic acid, perfluorobutanesulfonic acid

B. Duplicate results of fouling experiments

In this section the results of the duplicate experiments for fouling of the membrane are presented.

Due to problems they could not be transferred to Excel. Below are graphs from the UF data-screen.

Experiment 2:

Reference of this experiment was not logged.

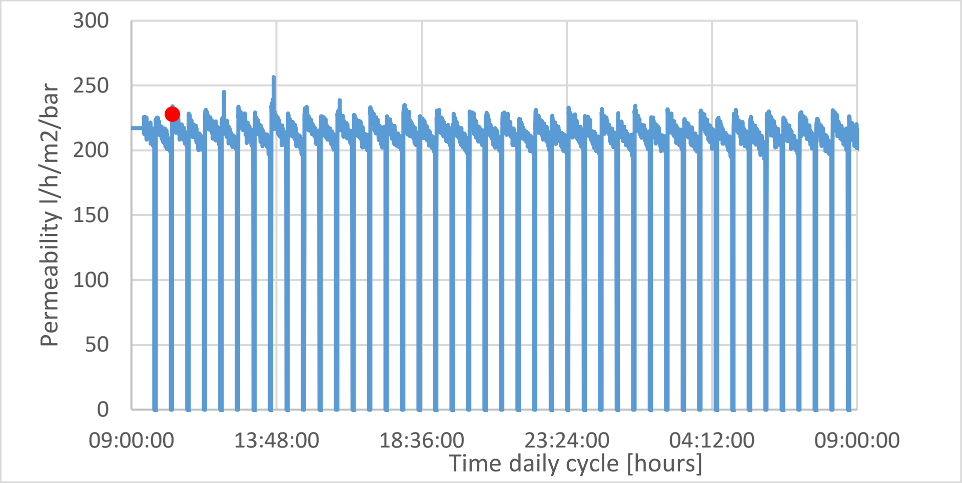

Figure 27 Duplicate experiment 2 fouling (Fe 1.2 mg/l, PAC 6 mg/l). Start experiment at red dot, no reference logged

Experiment 6:

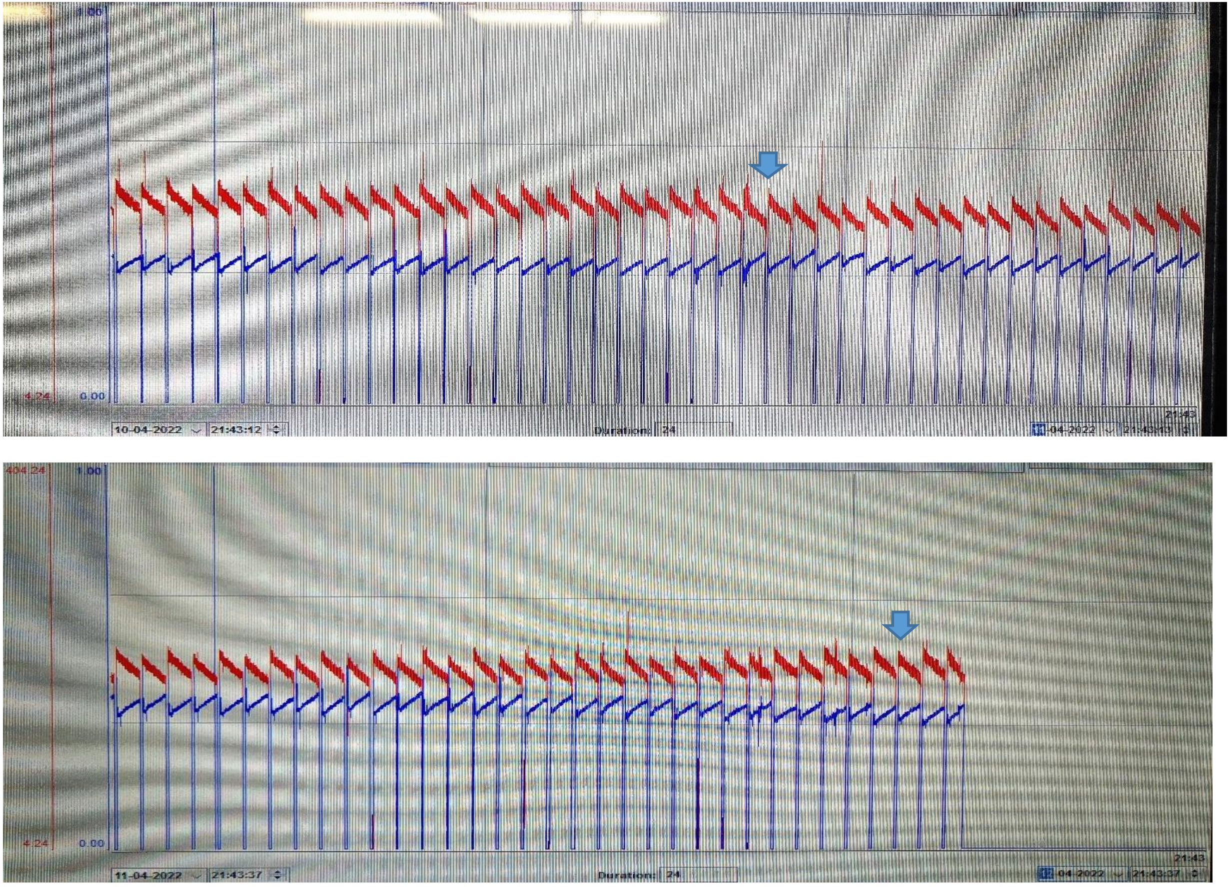

Figure 28 Duplicate experiment 6 fouling (Fe 3.2 mg/l, PAC 13 mg/l). Top: start experiment at blue arrow, before that reference. Bottom: continuation experiment 6, stop at blue arrow. Blue is TMP, red is permeability. Scale TMP 0-1 bar, scale permeability 4.24-404.24 l/h/m2/bar

Experiment 4:

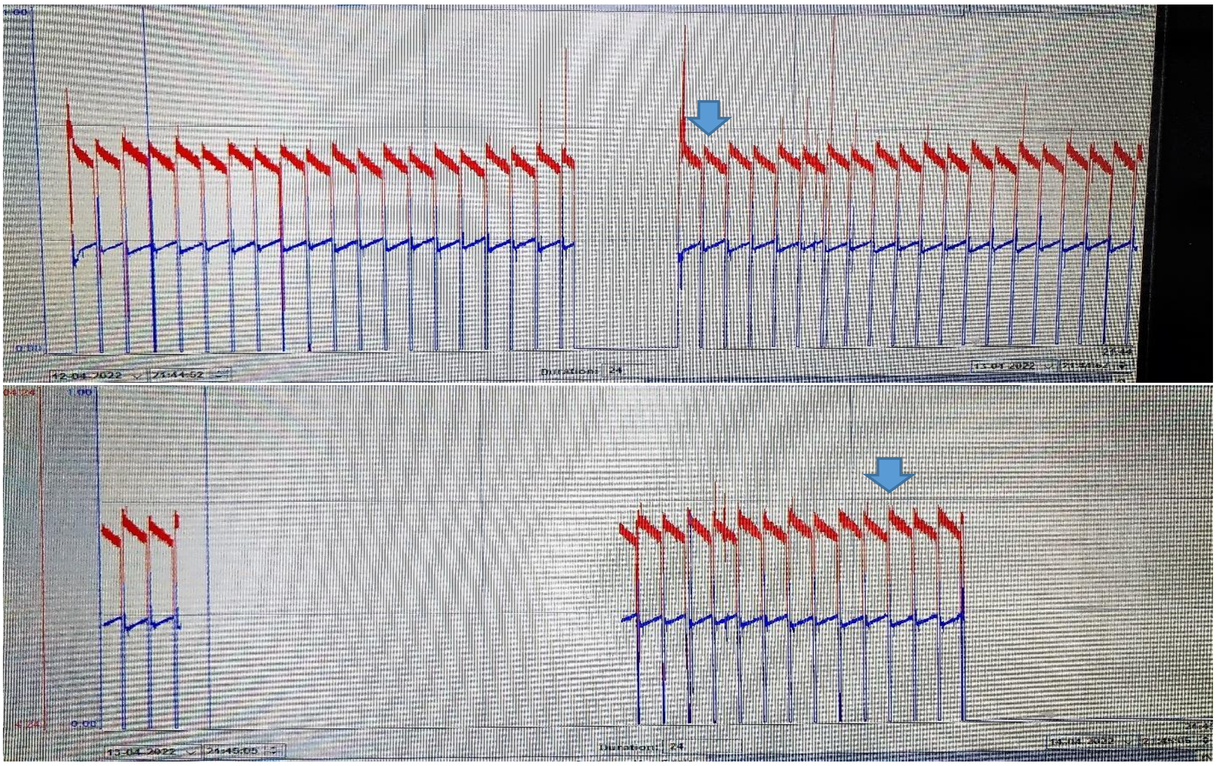

Figure 29 Duplicate experiment 4 fouling (Fe 1.1 mg/l, PAC 7 mg/l). Top: start experiment at blue arrow, before that reference. Gap is due to stop influent water. Bottom: continuation experiment 4, stop at blue arrow. Gap: screen stopped working, UF continued working, no data logged. Blue is TMP, red is permeability. Scale TMP 0-1 bar, scale permeability 4.24-404.24 l/h/m2/bar

Experiment 5:

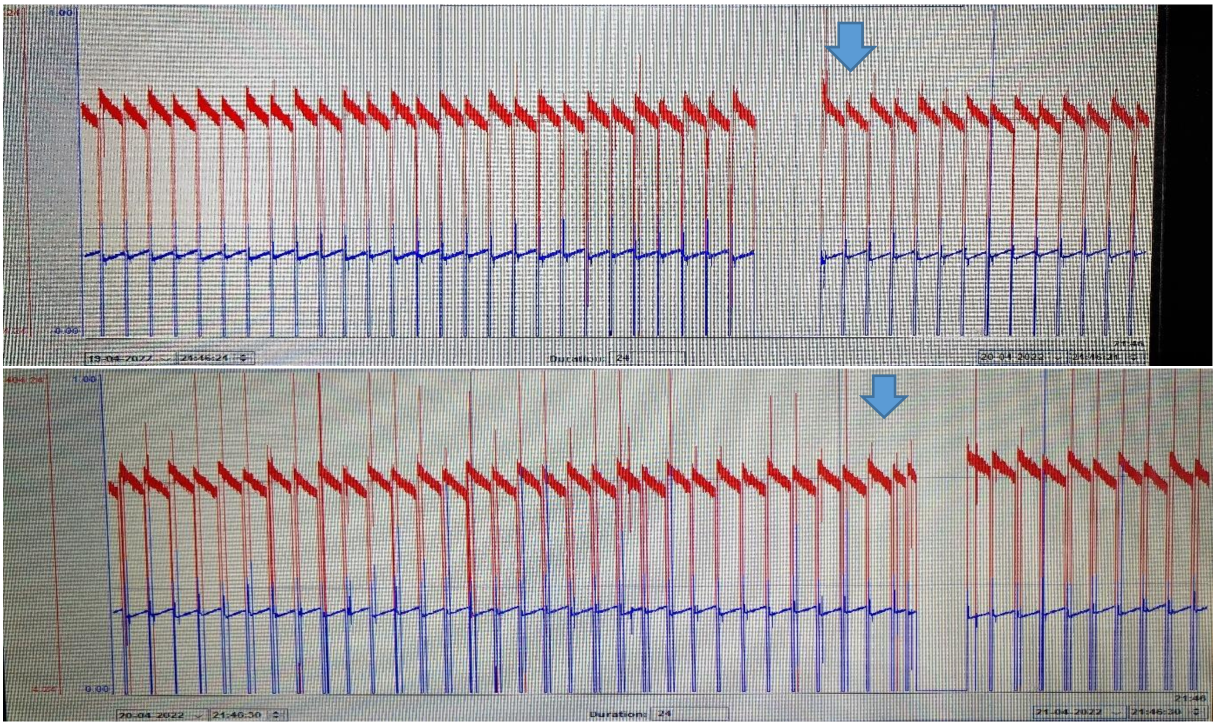

Figure 30 Duplicate experiment 5 fouling (Fe 1.2 mg/l, PAC 15 mg/l). Top: start experiment at blue arrow, before that reference. Gap is due to stop influent water. Bottom: continuation experiment 5, stop at blue arrow. Gap: CEB. Blue is TMP, red is permeability. Scale TMP 0-1 bar, scale permeability 4.24-404.24 l/h/m2/bar

Experiment 1:

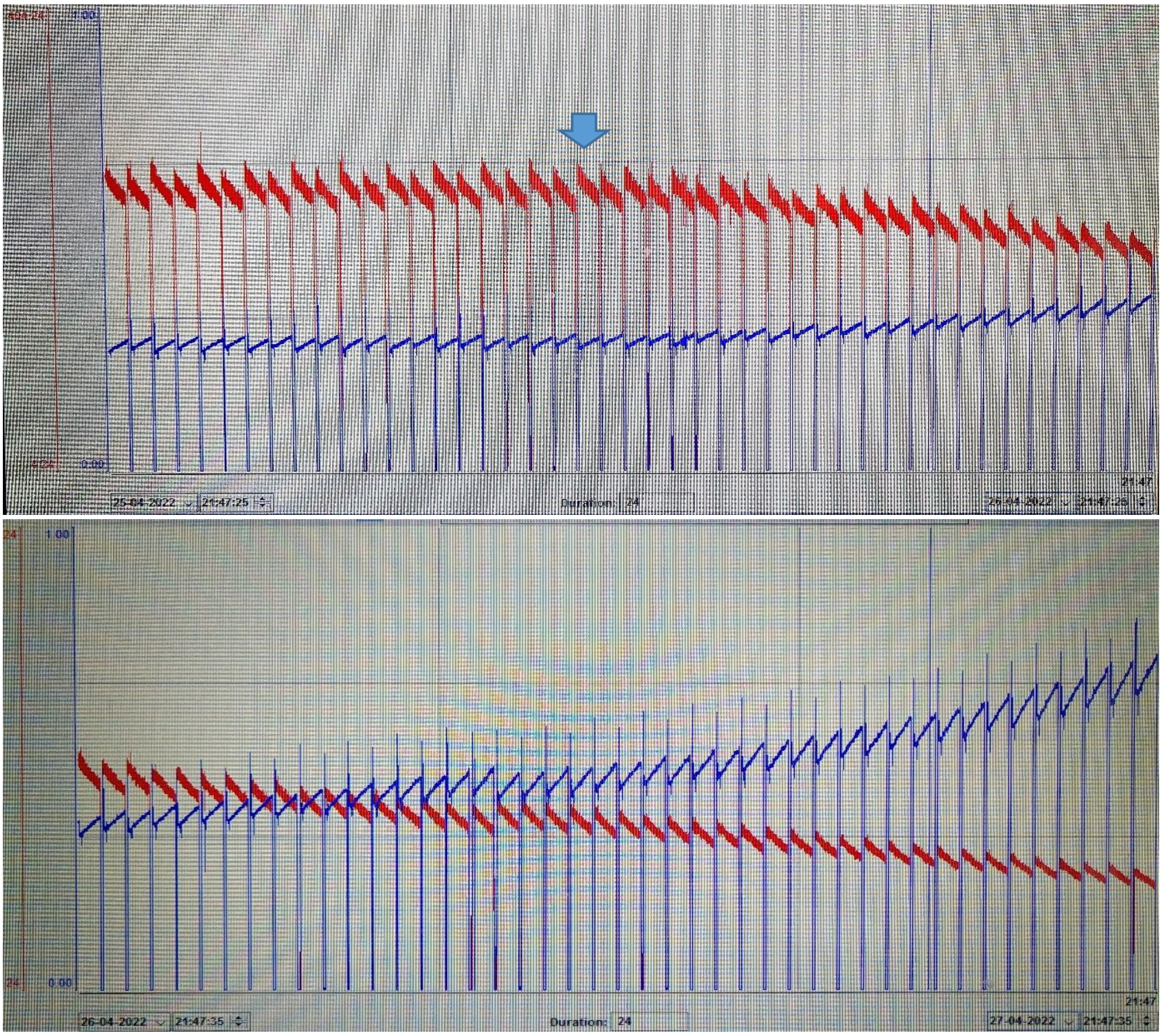

Figure 31 Duplicate experiment 1 fouling (no dosing). Top: start experiment at blue arrow, before that reference (1.2 mg/l) Bottom: continuation experiment 1. Blue is TMP, red is permeability. Scale TMP 0-1 bar, scale permeability 4.24-404.24 l/h/m2/bar

C. Measurement uncertainties and standard deviations experiments OMP including PFAS

This section includes the average limit of quantification, average measurement uncertainty and measurement uncertainty of this experiment for PFAS analysed and measured.

C.1 Limit of quantification PFAS

Table 9 Limit of quantification PFAS 3.0 method (HWL)

Component	***Limit of quantification (ng/L)***
PFHxS	*0.2*
PFNA	*0.5*
PFOS	*0.2*
PFOA	*0.5*
PFBA	*0.2*
PFPeA	*0.2*
PFHxA	*0.2*
PFHpA	*0.2*
PFDA	*0.5*
PFUdA	*0.5*
PFDoA	*0.5*
PFTrDA	*1*
PFBS	*0.2*
PFPeS	*0.2*
PFHpS	*0.2*
PFNS	*0.2*
PFDS	*0.2*
PFUdS	*0.2*
PFDoS	*0.2*
PFTrDS	*2*
HFPO-DA	*0.2*
DONA	*0.2*
6:2 FTS	*0.5*
EtFOSAA	*0.2*
9Cl-PF3ONS	*0.2*
11Cl-PF3OUdS	*1*

C.2 Average measurement uncertainty PFAS

Table 10 Measurement uncertainty PFAS 3.0 method (HWL)

Component	*Measurement uncertainty*
	Surface water
PFHxS	10.0 ng/l ± 11.7%
PFNA	10.0 ng/l ± 18.9%
PFOS	10.0 ng/l ± 7.90%
PFOA	10.0 ng/l ± 40.4%
PFBA	10.0 ng/l ± 7.10%
PFPeA	10.0 ng/l ± 10.5%
PFHxA	10.0 ng/l ± 9.40%
PFHpA	10.0 ng/l ± 11.3%
PFDA	10.0 ng/l ± 18.4%
PFUnA	10.0 ng/l ± 24.1%
PFDoA	10.0 ng/l ± 24.1%
PFTrDA	10.0 ng/l ± 32.2%
PFBS	10.0 ng/l ± 6.50%
PFPeS	9.4 ng/l ± 8.20%
PFHpS	10.0 ng/l ± 10.0%
PFNS	9.62 ng/l ± 9.10%
PFDS	10.0 ng/l ± 8.10%
PFUdS	9.68 ng/l ± 16.4%
PFDoS	9.70 ng/l ± 58.3%
PFTrDS	9.72 ng/l ± 84.2%
HFPO-DA	10.0 ng/l ± 11.5%
DONA	9.44 ng/l ± 8.40%
6:2 FTS	9.52 ng/l ± 19.5%
EtFOSAA	10.0 ng/l ± 14.0%
9Cl-PF3ONS	9.34 ng/l ± 7.10%
11Cl-PF3OUdS	9.44 ng/l ± 16.3%

C.3 Standard deviation experiment PFAS and OMP

Figures are available on request at Dunea

Figure 32 Influence PAC on removal OMP in ug/l with standard deviation (n=4)

Figure 33 Influence PAC on removal PFAS in ug/l with standard deviation (n=2)

Figure 34 Influence coagulant on removal OMP in ug/l with standard deviation (n=4)

Figure 35 Influence coagulant on removal PFAS in ug/l with standard deviation (n=2)

D. Additional results outside of experiments

Build-up of TMP is not constant at different moments through the season, when no coagulant or adsorbent was dosed (Figure 5). This may be due to the influence of specific fouling in the membrane due to a change in influent water composition. On the 20th of December in the morning a CEB with acid was executed which did not influence the TMP. On the 21st of December a CEB with chlorine was executed which did show effect. This suggests a change in influent water since a week before a CEB with acid was still effective. However, fouling might also be influenced due to coagulation which started in December.

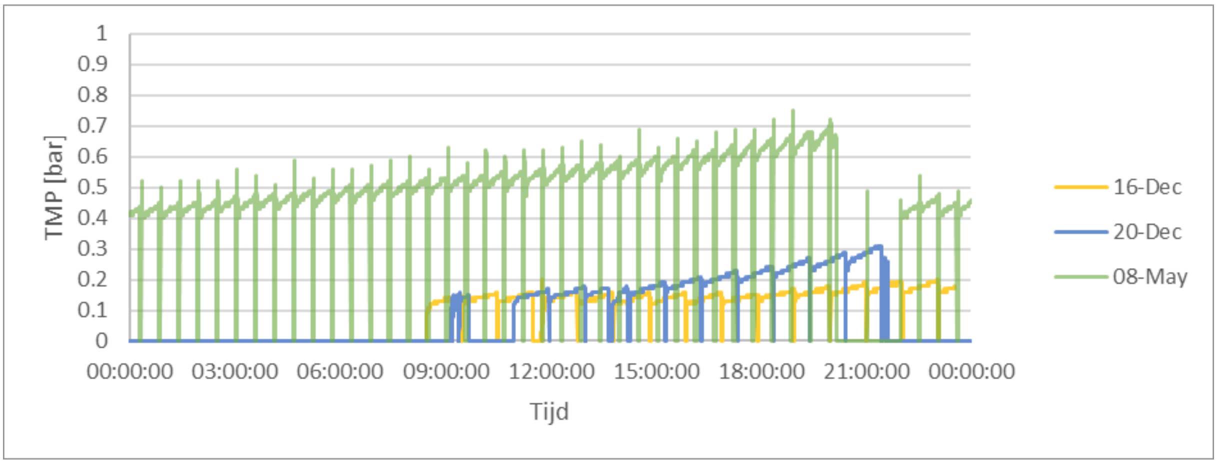

Figure 36. 16 and 20 December filtration time 60 minutes with no addition of coagulant or adsorbant. 8 May filtration time 30 minutes with no addition of PAC or coagulant. Increase in TMP visible

During the start-up in November the membrane ran for a few days without the addition of coagulant. In December the membrane even run with no coagulant and a filtration cycle of 60 minutes (Figure 6). Both modes showed a steady and constant TMP which did not change or increase. The operating hours of the membrane may have been of influence here as the membrane had less operating hours at November and December. There were no significant changes in influent water from the 8th of December onwards such as turbidity increase and algae growth does not start in December. Therefore, data shows a possible relation between coagulant addition and TMP increase when coagulant is stopped. Coagulant may initiate a change in fouling of the membrane. Other studies only found a positive influence on coagulant addition even though they used one membrane for more experiments as well, during their blank filtration experiments TMP only increased (C. Schwaller et al., 2021)(C. Schwaller et al., 2021). However, before their blank filtration the membrane already received a few cycles with coagulant dosing.

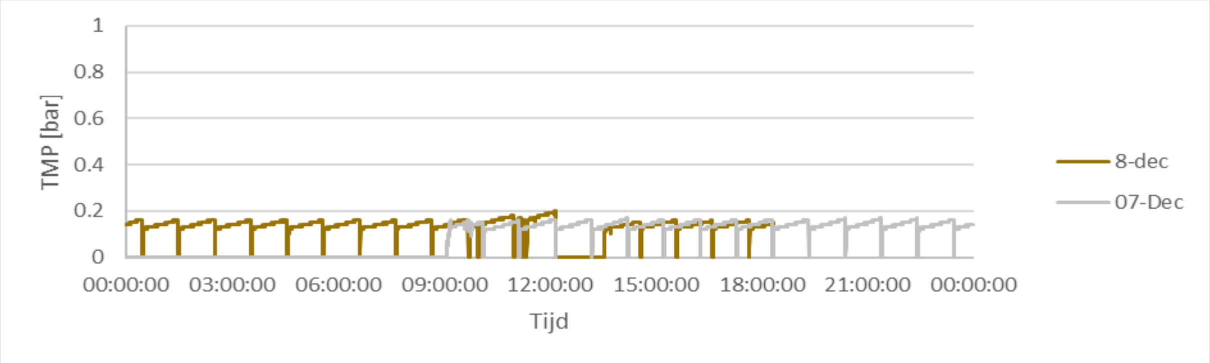

Figure 37 7-8 Dec (until 12:00) December, Filtration time 60 minutes no coagulant no adsorbent, no increase in TMP visible. One day continues at start into the next day.

The initial start value of the TMP increased from 0.11 at the start in October up to 0.37 at the end in May. This difference is due to an irreversible increase in TMP and as such fouling. During both experiments where coagulant was turned off, it became clear that when coagulant was turned off the build-up of TMP was not completely reversible even with a CEB with acid and chlorine (3.4 Chemical membrane cleaning). The TMP increase which was not reversible was 0.04 bar.

Two instances were reported where the turbidity of the influent water increased to more than 60 NTU. In both cases the TMP increased to more than 0.6 and 0.7 bar respectively. Without the addition of coagulant the TMP increased to more than 0.6 bar and became stable from that point even though turbidity was still high (Figure 7). The days after, the TMP remained high even though turbidity was low again and only a CEB with acid twice, brought he TMP back to 0.3 bar. During the second occasion the TMP increased to more than 0.6 after which a CEB with acid was initiated and afterwards coagulant was dosed. With the addition of coagulant the TMP remained constant and steady at 0.4-0.5 bar. With high turbidity's of more than 60 NTU addition of coagulant is able to stop the build-up of TMP over more filtration cycles. Addition of 1 mg Fe/l ensures a good backwash removal efficiency and therefore lowers irreversible fouling. This high turbidity was caused by water from the polders which mainly holds clay colloids.

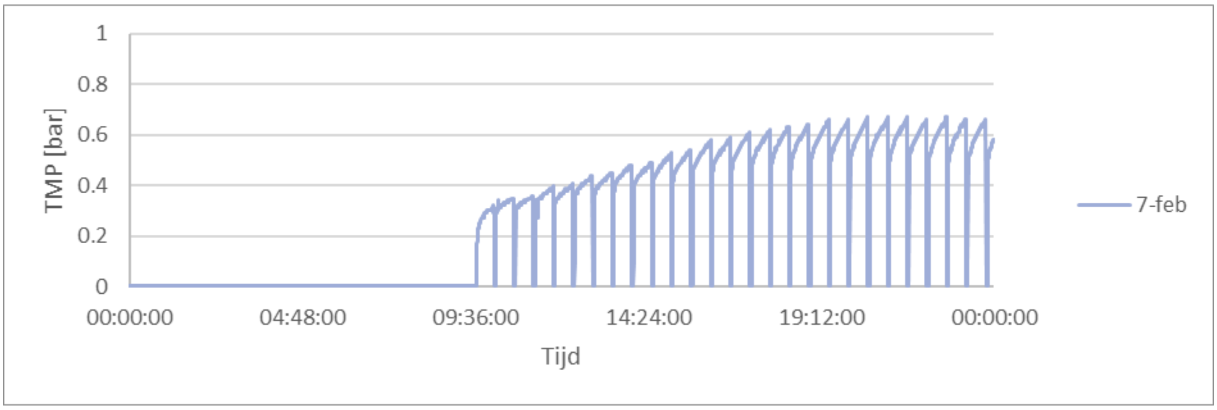

Figure 38 TMP build-up with high turbidity >60 NTU, no addition of coagulant or PAC