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Evaluation of the efficiency of treatment techniques in removing perfluoroalkyl substances from water

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Abstract

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Perfluoroalkylated substances (PFASs) are a group of synthetic compounds that have gained growing attention due to their environmental persistence, toxicity and their potential to bioaccumulate. Even though PFASs are not occurring naturally in our environment, they are globally distributed and can be found ubiquitously in air, water, soil, wildlife as well as in humans. PFASs have primarily been used, due to their unique properties of being both hydrophilic and hydrophobic, as surfactants in numerous products such as firefighting foams, paint, leather and textile coating. The occurrence of PFASs in drinking water as well as in wastewater makes it important to develop effective techniques to remove these compounds from drinking water sources and wastewater. To be able to effectively remove PFASs from drinking water and wastewater it is important to understand which treatment process is most efficient and how the removal efficiency is affected by the physicochemical properties of PFASs and characteristics of water.

In this study, the removal efficiency of PFASs was investigated using six different water types with varying dissolved organic carbon (DOC) character. Four different treatment techniques were evaluated including anion exchange using MIEX$^{®}$ resins, coagulation with iron (III) chloride ($FeCl_3$), adsorption using powdered activated carbon (PAC) and nanofiltration (NF) membrane. The batch experiments were performed in laboratory-scale for 14 individual PFASs including C_{3-11}, C_{13} perfluoroalkyl carboxylic acids (PFCAs), C_4, C_6, C_8 perfluoroalkyl sulfonic acids (PFSAs) and perfluorooctane sulfonamide (FOSA). The results showed that the removal efficiency of PFASs was dependent on both perfluorocarbon chain length as well as functional group, with an increase in removal efficiency with increased perfluorocarbon chain length. Short-chained PFASs ($C \leq 6$) were removed in less extent than the long chained PFASs for all treatment techniques. Amongst the four treatment techniques investigated, NF membrane exhibited the best removal efficiency for both short- and long chained PFASs (on average, 51%). Lower removal efficiencies for PFASs were observed for MIEX (33%) < $FeCl_3$ (16%) < PAC (14%). However, all tested treatment techniques used in this study exhibited generally low removal efficiency (< 78%), in particular for the short-chained PFASs ($C \leq 6$, < 41%) Results using three different doses of PAC (i.e. 20, 50, 100 mg L^{-1}) showed an increase in removal (i.e. 2.2-41%, 8.0-78% and 12-92% respectively) with increasing dose. No significant trends were found between PFAS removal and DOC removal for any of the treatments ($p<0.05$, student t-test). However, the removal efficiency was different of the six different water types, which indicates that the DOC characteristics (i.e. Freshness, humification index, pH and absorbance) have an influence on the removal efficiency of PFASs in water.

Keywords: PFAS, removal efficiency, MIEX$^{®}$, iron (III) chloride, Powdered activated carbon, nanofiltration membrane, dissolved organic carbon

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Referat

Utvärdering av behandlingstekniker för att rena vatten från perfluoralkylerade ämnen.

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Perfluoroalkylerade ämnen (PFAS) är en grupp syntetiska ämnen som har fått allt större uppmärksamhet den senaste tiden då de har visat sig vara persistenta, toxiska och bioackumulerande. Även om PFAS inte förekommer naturligt i vår miljö är de globalt fördelade och kan återfinnas i luft, vatten, mark, djur och hos människor. PFAS har främst använts, på grund av sina unika egenskaper att vara både hydrofila och hydrofoba, som tensider i många produkter såsom brandsläckningsskum, färg, läder och textil. Förekomsten av PFAS i dricksvattentäkter och i många reningsverk gör det viktigt att utveckla effektiva metoder för att ta bort dessa föreningar i vattenreningsverk. För att effektivt kunna avlägsna PFAS från dricks- och avloppsvatten är det viktigt att ha kunskap om vilken behandlingsmetod som är effektivast och hur reningseffektiviteten påverkas av ämnenas fysikalisk-kemiska egenskaper och vattnets karaktär.

Syftet med denna studie var att undersökta reningseffektiviteten för PFAS i sex olika vatten innehållande olika typer av löst organiskt kol (DOC). Detta undersöktes för fyra olika behandlingsteknikert; jonbyte med MIEX®, koagulering med järnklorid ($FeCl_3$), adsorption med hjälp av pulveriserat aktivt kol (PAC) och nanofiltrering. Försöken gjordes små skaligt i laboratorie och 14 olika PFAS undersöktes; $C_{3-11,13}$ perfluoralkyl karboxylsyror (PFCA), C_4, C_6, C_8, perfluoralkyl sulfonsyror (PFSA) och perfluoroktan sulfonamid (FOSA). Resultaten visar att reningseffektiviteten för PFAS var beroende av både den perfluorerade kolkedjans längd och funktionell grupp, med en ökning av reningseffektivitet med längre perfluorerad kolkedja. PFAS med kort perfluorerad kolkedja ($C \leq 6$) renades i mindre utsträckning än PFAS med lång perfluorerad kolkedjade; detta gällde för alla behandlingstekniker. Bland de fyra behandlingstekniker som undersöktes uppvisade nanofiltreringen den bästa reningseffektiviteten för PFAS med både korta och långa kolkedjor (i genomsnitt, 51%.). Lägre reningseffektivitet för PFAS observerades för MIEX®(33%), < $FeCl_3$(16%) < PAC (14%). Totalt sett erhölls en relativt låg reningseffektivitet (<78%) för samtliga reningstekniker, speciellt för de kortkedjade PFAS ($C \leq 6$, < 41%). Resultat från försök med tre olika doser PAC (e.g. 20, 50, 100 mg L^{-1}) visade på en ökad reningseffektivitet (2,2-41%, 8,0-78% och 12-92%) med ökad dos PAC. Inga signifikanta trender kunde urskiljas vad gäller reningseffektivitet av PFASer och rening av DOC ($p<0.05$, student t-test), detta gällde för samtliga behandlingstekniker. Det fanns dock tydliga skillnader i reningseffektivitet mellan de sex olika vattentyperna vilket indikerar på att DOC egenskaperna (Freshnessindex, humifieringsindex, pH, absorbans) har en påverkan på reningseffektiviteten för PFASer i vatten.

Nyckelord: PFAS, reningseffektivitet, MIEX®, järnklorid, pulveriserat aktivt kol, nanofilter membran, löst organiskt kol

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Lutz Ahrens acted as supervisor and mentor, Sarah Josefsson was the subject reviewer, both at the Department of Aquatic Sciences and Assessment. Stephan Köhler, from the same department was the project owner. Fritjof Fagerlund at the Department of Earth Sciences at Uppsala University acted as the final examiner.

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Populärvetenskaplig sammanfattning

Utvärdering av behandlingstekniker för att rena vatten från perfluoralkylerade ämnen.

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Per- och polyfluoroalkylerade ämnen (PFASer) är en grupp av syntetiska, organiska ämnen som har fått allt större uppmärksamhet den senaste tiden då dessa ämnen har visat sig vara persistenta, toxiska och bioackumulerande. Detta innebär att de bryts ner väldigt långsamt och att de är giftiga och har en tendens att ansamlas i levande organismer. Även om PFASer inte förekommer naturligt i vår miljö är de globalt fördelade och kan återfinnas i djur, biota, vatten, mark, luft och hos människor. Kunskapen om hur dessa ämnen påverkar oss människor är fortfarande begränsad men ämnena misstänks bl.a. vara hormonstörande, ge upphov till cancer och ha toxisk påverkan på immunförsvaret.

PFASer har främst använts, på grund av sina unika egenskaper att stöta bort både vatten och fett, som tensider i många produkter såsom brandsläckningsskum, färg, läder och textiler. En av anledningarna till att PFASer är så allmänt förekommande i miljön tros bero på att PFASer är så svårnedbrytbara i reningsverk och i miljön. Idag är regelverket kring de flesta av dessa ämnen begränsade men det ämne som fått mest uppmärksamhet inom denna grupp, PFOS, inkluderades 2009 i Stockholmskonventionens lista över persistenta organiska föroreningar (POPs). Detta innebär att produktionen och användandet av PFOS begränsandes från och med införandet 2009. Förekomsten av PFASer i dricksvattentäkter och i många reningsverk gör det viktigt att utveckla effektiva metoder för att ta bort dessa föreningar i vattenreningsverk. För att effektivt kunna ta bort PFASer från dricks- och avloppsvatten är det också viktigt att förstå hur reningseffektiviteten påverkas av ämnenas fysikalisk-kemiska egenskaper och vattnets karaktär.

Få studier har gjorts gällande reningen av PFASer i vatten och hur reningen påverkas av hur mycket organiskt kol som vattnet innehåller. Syftet med denna studie var att undersöka reningseffektiviteten för PFASer i sex olika vatten innehållande olika typer av löst organiskt kol (DOC). Försöken gjordes små skaligt i laboratorie och 14 olika PFASer undersöktes; $C_{3\text{-}11,13}$ perfluoralkyl karboxylsyror (PFCAer), C_4, C_6, C_8, perfluoralkyl sulfonsyror (PFSAer) och perfluoroktan sulfonamid (FOSA).

Följande behandlingstekniker utvärderades, jonbyte med MIEX®, koagulering med järnklorid ($FeCl_3$), adsorption med hjälp av pulveriserat aktivt kol (PAC) och nanofiltrering. Jonbyte innebär att PFASer, som är negativt laddade, byter plats med ett annat ämne med samma laddning och på så sätt binds till en jonbytesmassa som sjunker och kan avlägsnas från vattnet. Koagulering är en teknik där, vid tillsats av en kemikalie (FeCl3), PFASer binder till varandra och bildar större molekyler som med hjälp av tyngdkraften sjunker och kan på detta vis avlägsnas. Pulveriserat aktivt kol fungerar ungefär på samma sätt som järnkloriden, där PFASer adsorberas till det aktiva kolet och kan avlägsnas när kolet antingen sjunker eller flyter upp till ytan. Tekniken med nanofiltrering fungerar som ett filter, där det förorenade vattnet pressas genom ett membran med porer i nanostorlek som hindrar de större molekylerna att tränga igenom.

Resultaten visar att reningseffektiviteten för PFASer var beroende av både kolkedjans längd samt vilken funktionell grupp som varje ämne hade, där en ökad kolkedja gav upphov till högre reningseffektivtet. PFASer med kort kolkedja ($C \leq 6$) renades i mindre utsträckning än de PFASer med lång kolkedja, detta gällde för alla behandlingstekniker.

Bland de fyra behandlingstekniker som undersöktes uppvisade nanofiltreringen den bästa reningseffektiviteten för PFASer med både korta och långa kolkedjor (i genomsnitt, 51 %.). MIEX® uppvisade en något lägre reningseffektivitet (33 %) jämfört med nanofiltrering och likaså järnklorid (16 %). PAC var den teknik som gav upphov till lägst reningseffektivitet (14 %). Totalt sett erhölls en relativt dålig reningseffektivitet (<78 %), för samtliga reningstekniker. Resultat från försök med tre olika doser PAC (e.g. 20, 50, 100 mg L^{-1}) visade på en ökad reningseffektivitet (2,2-41 %, 8,0-78 % och 12-92 %) med ökad dos PAC.

Det var svårt att urskilja några tydliga samband vad gäller reningseffektivitet av PFASer och reningen av organisk kol detta gällde för samtliga behandlingstekniker. Det fanns dock tydliga skillnader i reningseffektivitet mellan de sex olika vattnen och några signifikanta samband erhölls mellan reningseffektiviteten av PFASer och några av de olika egenskaperna som det lösta organiska kolet besatt, vilket indikerar på att DOC egenskaperna har en påverkan på reningseffektiviteten för PFASer i vatten.

Abbreviations

BV – Bed volume

Da – Dalton, standard unit, indicates mass on a molecular scale, equivalent to $g\ mol^{-1}$.

DOC - Dissolved organic carbon

$FeCl_3$ – Iron(III) chloride

FOSA – Perfluorooctane sulfonamide

Fr - Freshness

HIX - Humification Index

MIEX® - Magnetic Ion-Exchange resin

MF - Microfiltration

MWCO - Molecular weight cut-off

NF - Nanofiltration

PAC - Powdered activated carbon

PFAA – Perfluoroalkyl acid

PFAS – Per- and polyfluoroalkyl substance

PFBA – Perfluorobutanoate

PFBS – Perfluorobutane sulfonic acid

PFDA – Perfluorodecanoate

PFDoDA – Perfluorododecanoate

PFHpA – Perfluorohepanoate

PFHxA – Perfluorohexanoate

PFHxS – Perfluorohexane sulfonic acid

PFNA – Perfluorononanate

PFOA – Perfluorooctanoate

PFOS – Perfluorooctane sulfonic acid

PFPeA – Perfluoropentanote

PFTeDA – Perfluorotetradecanoate

PFUnDA – Perfluoroundecanoate

TMP – Transmembrane pressure, pressure difference between the feed and permeate.

TOC – Total organic carbon

UF - Ultrafiltration

WWTP - Wastewater treatment plant

Evaluation of the efficiency of treatment techniques in removing perfluoroalkyl substances from water

1. Introduction

During the last decades, per- and polyfluoroalkyl substances (PFASs) have gained growing attention due to their environmental persistence, toxicity and global distribution (Ahrens et al., 2011). PFASs is a large family of substances that are man-made and been widely used since the 1950s due to their unique properties of being both hydrophilic and hydrophobic (Naturvårdsverket, 2012). Even though PFASs are not compounds that occur naturally in our environment they are globally distributed and can be found ubiquitously in animals, biota, water, soil, air as well as in humans (Rahman et al., 2013; Zhao et al., 2012).

PFASs have primarily been used, due to their ability to lower surface tension and repel both water and grease, as surfactants in numerous products such as firefighting foams, paint, leather and textile coating, clothes and carpets. Among the many areas where PFASs can be found, firefighting foams and wastewater treatment plant (WWTP) effluents have been pointed out as major points sources (Rahman et al., 2013; Zhao et al., 2012; Naturvårdsverket, 2012). There are many compounds within the PFAS family and they all consist of a fluorinated carbon chain of different length and with different functional group. The two PFASs compounds that have received most attention and also the most studied of the PFASs are perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA). These two compounds have been detected most frequently in the environment, even in remote areas such as open oceans, the Arctic and Antarctic (Butt et al., 2010; Ahrens et al., 2010).

There are many pathways for PFASs to enter the aquatic environment, for example through surface runoff, rain, septic discharge and via wastewater effluent (Zhao et al., 2012; Guo, 2010). One of the reasons that PFASs are so ubiquitous in the environment is believed to be due to the persistence of PFASs in wastewater treatment plants (WWTPs) and the environment. Previous studies regarding PFOS and PFOA in WWTP shows that these compounds cannot be effectively removed by conventional treatment processes (Yu et al., 2013; Schröder et al., 2010; Guo et al., 2010).

PFOS and PFAS have been detected all around the world in both ground- and surface sources of drinking water as well as in finished drinking water. The occurrence of PFASs in drinking water sources as well as in many WWTPs makes it important to develop effective techniques to remove these compounds from water treatment plants (Yu et al., 2013). Many studies today regarding PFASs removal in water are performed in the absence of dissolved organic carbon (DOC) or in very low concentrations, although this is believed to be an important factor (Rahman et al., 2013). More studies are needed to improve our understanding how the removal efficiency is affected by the physicochemical properties of PFASs and the characteristics of water.

1.1 Objectives and hypotheses

The overall aim of this study was to investigate the removal efficiency of PFASs using four different treatment techniques and the interaction with DOC. The following treatment techniques were evaluated in this study, anion exchange using MIEX resins, coagulation with Iron(III) chloride ($FeCl_3$), adsorption using powdered activated carbon (PAC) and nanofiltration (NF) membrane. Each treatment was performed in six different waters with different DOC character that were spiked with selected PFASs. A literature study was performed in order to improve our understanding of PFASs and their properties as well as the used treatment techniques. The following three hypotheses were investigated:

- The removal efficiency for PFASs will differ depending on perfluorocarbon chain length and functional group.
- The presence of DOC in the water will decrease the removal efficiency for PFASs depending on the DOC character.
- The removal efficiency of PFASs for the examined treatment techniques will decrease in the following order: Powdered activated carbon > NF membrane > MIEX > $FeCl_3$.

1.2 Focus and delimitations

This study is not intended to optimize these four treatment techniques but instead using the state of the art design to identify trends for individual PFASs and different water types. Six different water types were examined and spiked with 14 PFASs at environmentally relevant concentrations (in $\mu g\ L^{-1}$ range). The PFASs were selected based on the detection frequency and concentration levels which is commonly detected in wastewater and drinking water (Xiao et al., 2013; Prevedouros et al., 2006). This study was performed in collaboration with two other master projects performed by Sarah Nilsson and Sofia Wängdahl (2014) and therefore some of the methods had to be adapted to suit both projects and to allow a comparison with results obtained by Sarah Nilsson and Sofia Wängdahl.

2. Background

2.1 Per- and polyfluoroalkylated substances (PFASs)

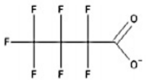
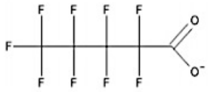
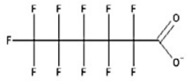
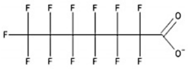
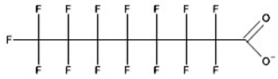
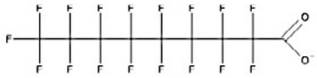
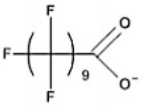
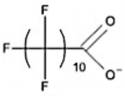
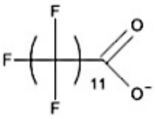
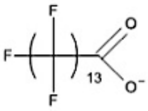
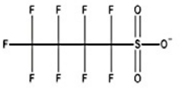
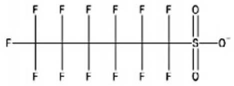
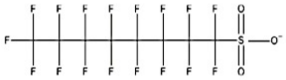
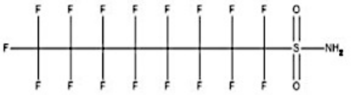
PFASs are a group of synthetic compounds with the same basic structure; they all contain a carbon chain of different length that is partly (poly) or fully (per) fluorinated, followed by a functional group. These compounds are written on the general formula C_nF_{2n+1}-R, where n refers to the number of carbon atoms and R is the functional group, which can consist of, for example, a sulfonic acid (-SO_3H, PFSAs) or a carboxylic acid (-COOH, PFCAs) (Rahman et al., 2013; Butt et al., 2011; Buck et al., 2011).

The fluorinated carbon chain is hydrophobic while the functional group is hydrophilic. One reason why the PFASs are so stable is the extremely strong and stable covalent bond between the carbon and fluorine atoms. The strong covalent bond makes the substances both chemically and thermally stabile (Buck et al., 2011; Naturvårdsverket. 2012; Ahrens, 2010). Besides PFOS and PFOA there are many compounds within the PFASs family that have been given less attention but which are still of concern. Some of the PFASs are so-called precursor substances with the ability to decompose to, for example, PFOA and PFOS in the environment (KEMI, 2006).

PFASs can be divided into several subfamilies with different properties depending on their structure (Buck et al., 2011). The subgroup that has gained most attention and occupies a substantial part of the literature on PFASs are perfluoroalkyl acids (PFAAs) (Buck et al., 2011; Butt et al., 2010). The following are an account of the substances relevant for this study, PFCAs, PFSAs and FOSA (Table 1).

Perfluoroalkyl carboxylic acids (*PFCAs*), amongst which PFOA is the most prominent substance, is a part of the PFAAs family. PFCAs are characterized by a carboxylic functional group (-COOH). Perfluoroalkane (-alkyl) sulfonic acids (*PFSAs*) are also included in the PFAAs family, with a sulfonic functional group (-SO_3H). In this group of compounds PFOS is the most studied substance amongst all PFASs and known for its persistent, bioaccumulative and toxic properties. Many PFCAs and PFSAs in the environment are products of abiotic and biotic degradation of certain precursor PFASs (Buck et al., 2011). Perfluorooctane sulfonamide (*FOSA*) is also part of the PFAAs family and one of the compounds examined in this study. FOSA is characterized by a sulfonamide functional group (-SO_2NH_2). FOSA belong to a subgroup of precursors to PFSAs, meaning FOSA has the potential to degrade into PFOS (Benskin et al., 2013). Mobility is affected by which chemical form the PFAAs has in the environment, the protonated or anionic form as well as which type of compound (Buck et al., 2011).

Table 1. List of PFASs compounds examined in this study as well as molecular weight (MW), octanol-water partition constant (log $K_{ow,\ dry}$) and water solubility (S_w) for PFASs relevant for this study. [a]Rayne and Forest (2009), [b]Wang et al (2011). Structure from Naturvårdsverket (2012).

Compound	Acronym	Structure	Chemical formula	MW	Log $K_{ow,\ dry}$	Log S_w (mg L^{-1})
PFCAs						
Perfluorobutanoate	PFBA		$C_3F_7CO_2H$	213.04	2.91^{a} 2.82^{b}	0.42^{b}
Perfluoropentanoate	PFPeA		$C_4F_9CO_2H$	263.05	3.69^{a} 3.43^{b}	-0.37^{b}
Perfluorohexanoate	PFHxA		$C_5F_{11}CO_2H$	313.06	4.50^{a} 4.06^{b}	-1.16^{b}
Perfluorohepanoate	PFHpA		$C_6F_{13}CO_2H$	363.07	5.36^{a} 4.67^{b}	-1.94^{b}
Perfluorooctanoate	PFOA		$C_7F_{15}CO_2H$	413.08	6.26^{a} 5.30^{b}	-2.73^{b}
Perfluorononanoate	PFNA		$C_8F_{17}CO_2H$	463.09	7.23^{a} 5.92^{b}	-3.55^{b}
Perfluorodecanoate	PFDA		$C_9F_{19}CO_2H$	513.10	6.50^{b}	-4.31^{b}
Perfluoroundecanoate	PFUnDA		$C_{10}F_{21}CO_2H$	563.11	7.15^{b}	-5.13^{b}
Perfluorododecanoate	PFDoDA		$C_{11}F_{23}CO_2H$	613.12	7.77^{b}	-5.94^{b}
Perfluorotetra decanoate	PFTeDA		$C_{13}F_{27}CO_2H$	713.14	8.90^{b}	-7.42^{b}
PFSAs						
Perfluorobutane sulfonic acid	PFBS		$C_4F_9SO_3H$	300.12	3.90^{b}	-1.00^{b}
Perfluorohexane sulfonic acid	PFHxS		$C_6F_{13}SO_3H$	400.14	5.17^{b}	-2.24^{b}
Perfluorooctane sulfonic acid	PFOS		$C_8F_{17}SO_3H$	500.16	4.67^{a} 6.43^{b}	-3.92^{b}
FOSAs						
Perfluorooctane sulfonamide	FOSA		$C_8F_{17}SO_2NH_2$	499.18	5.62^{b}	-5.05^{b}

2.1.1. Physicochemical properties of PFASs

Generally most PFASs have high water solubility (S_w) and low pKa values, which are reasons for which the aquatic environment is seen as an important transport pathway for PFASs. The partitioning of PFASs between different phases depends mainly on chain length and functional group. Short-chained PFCAs ($C<6$) have shown a higher tendency to occur in the dissolved phase whiles longer chained PFCAs and PFSAs bind more strongly to particles. This allows the shorter chained PFCAs to easterly be transported long distances via the aqueous environment (Ahrens, 2010; Du et al., 2014).

As mentioned above, both PFCAs and PFSAs are strong acids with low pKa values. At pH values encountered in the environment, they dissociate to their anionic form and will mostly be found bound to particles or dissolved in water. Due to this, both PFCAs and PFSAs generally have low volatility and high water solubility (Buck et al., 2011). For both PFCAs and PFSAs, the water solubility decreases with increased chain length (Table 1) (Rayne and Forest, 2009). The PFASs that are neutral, such as FOSA, are generally less water-soluble and volatilize more easily and has shown to bind very strongly to particles (Ahrens, 2010). The neutral compounds are less persistent than PFCAs and PFSAs due to the fact that their hydrophilic functional group is uncharged (Buck et al., 2011).

For many of the PFASs the pKa values are unknown and under review, but estimations has been made for the most commonly used compounds (Buck et al., 2011). Reported pKa values for 21 different PFCAs ranges from -0.2 and 4.2 (Goss, 2007). Values for PFSAs are estimated to be lower ($<< 0$), where PFOS values are expected to range from -3.27 to 0.14 (Zhou et al., 2009; Brooke et al., 2004; Steinle-Darling and Reinhard, 2008). The pKa value for PFOA ranges from -0.5 to 3.8 (Goss, 2007; Vierke et al., 2012; Prevedouros et al., 2006). The pKa values for neutral compounds, such as FOSA, are estimated to be higher and range from 6.2 to 6.5 (Benskin et al., 2012; Rayne and Forest, 2009).

The octanol-water partition coefficient (K_{ow}) is an indication of how hydrophobic a compound is (Rahman et al., 2013). The coefficient describes the partitioning between lipids and water where octanol is used as a lipophilic solvent. This means that the lower K_{ow} value a compound has the more hydrophilic the compound is. Since PFASs have a tendency to aggregate at the interface between octanol and water, the log K_{ow} values are difficult to determine and have mainly been estimated using different computational methods (Wang et al., 2011; Harrison et al., 2007). A study conducted by Wang et al., (2012) shows that the log K_{ow} value increases with increased chain length for both PFCAs and PFSAs. Moreover, the study showed that PFSAs had higher log K_{ow} values than PFCAs with the same chain length (Table 1).

2.1.2. Production

Emissions to the environment are due to both direct and indirect sources where direct sources originate from the use and manufacture of PFASs, whiles the dominating pathways for indirect release is due to precursor substances being either abiotically or biotically degraded to form a specific PFAS (Prevedouros et al., 2006; Butt et al., 2010; Buck et al., 2011).

The first large global producer of PFOS started producing PFOS and PFOS-related products in the 1950s until the phase-out started in 2000. Instead of using PFOS in the production, short-chained compounds are being used as these substances have shown less tendencies to bioaccumulate since they are rapidly eliminated in organisms. However, PFOS and its precursors are still being manufactured in large amounts in other parts of the world (Prevedouros et al., 2006; Butt et al., 2011; Buck et al., 2011).

2.1.3. Legislative action and regulation

In 2008 the use of PFOS and PFOS-related compounds in chemicals products and articles was prohibited within the EU (Naturvårdsverket, 2012). In May 2009, PFOS was acknowledge as a persistent organic pollutant (POPs) and included into Annex B of the Stockholm Convention, which has led to a restricted production and use of this compound within the countries that have signed the convention (Vierke et al., 2012; Ahrens, 2010). The same year PFOS and PFOS-related substances were also included in the Convention on Long-Range Transboundary Air Pollution (CLRTAP) and PFOS and PFOA can also be found in the OSPAR List of Chemicals for Priority Action (Flores et al., 2013; Naturvårdsverket, 2012).

In 2006, eight leading global companies and US Environmental Protection Agency (USEPA) agreed to work towards reducing the emission and product content of PFOA and other related compounds by 95% by 2010 and by 2015 the goal is that these chemicals are eliminated. Similar agreements have been set in Canada and by the European Union Marketing and Use Directive (Buck et al., 2011). The Swedish Environmental Protection Agency (EPA) has proposed limit values for PFOS in an attempt to protect human health. In drinking water the limit values has been set to 0.35 - 1µl L^{-1} (Naturvårdsverket, 2012).

2.1.4. Exposure and toxicity

The first reports on the occurrence of PFOS, in both wildlife and human blood, were published a decade ago and since then it has been a rapid increase in research concerning these compounds and their toxicity. PFASs are bioaccumulating and biomagnifying compounds and studies show that PFAS concentrations, in for example dolphins and other top-predators, are higher than the levels in animals further down in the food chain (Kannan et al., 2002). Studies on animals have also indicated that PFASs can have long-term toxic effect on the endocrine system, liver and the immune system (Stahl et al., 2011).

Pathways for humans to be exposed to PFASs are through, for example food, drinking water, breast milk, air and food-contact material (Buck et al., 2011). Even though studies show that PFASs have been detected in human blood and tissue worldwide, there is still limited knowledge on the toxicological effects on humans. Some studies suggest that there is a link between low birth weight and certain levels of PFASs in blood serum, associations has also been seen between contaminated drinking water leading to kidney and testicular cancer (Rahman et al., 2013).

2.1.5 Occurrence of PFASs in wastewater and drinking water

PFOS and PFOA have been detected globally in numerous of surface and ground water sources (Xian et al., 2013). In freshwater all around the world (i.e. Japan, U.S, Scandinavia) concentration of PFASs have been detected in the lower range of ng L^{-1}, whiles in WWTP effluents > 500 ng L^{-1} concentrations have been detected (Prevedouros et al., 2006; Post et al., 2012). In samples from drinking water there has repeatedly been levels of both PFOS and PFOA, when concentrations of PFOA reaches levels > 40 ng L^{-1} it is considered to be a danger to the general population (Xiao et al., 2013). Analyzed concentrations of PFOA in drinking water within levels in the lower range of ng L^{-1} has been found in many part of Europe (Vierke et al., 2012). Since PFAS contaminated water is both a growing and critical problem it is necessary to find treatment techniques with the ability to remove these compounds in an effective way.

2.1.6 DOC and interaction with PFASs

DOC is the general description for organic molecules of varying composition and origin. The organic material can be divided into two main groups, humic and non-humic. The proportion of the humic fractions in natural water can vary from 35% to 70% depending on the origin. The humic material is generally hydrophobic while the non-humic material is hydrophilic (Machenbach, 2007). Humification Index (HIX), freshness (Fr) and ultraviolet (UV) absorbance at 254 nm wavelength (UV_{254}) are used to characterize the DOC material. HIX is a measure on how humified a material is, and the higher HIX the more hydrophobic is the water (Zsolnay et al., 1999). Fr is the ratio between recently derived carbon and highly decomposed carbon, thus the higher the Fr value the higher is the amount of freshly produced carbon (i.e. hydrophilic) (Wilson and Xenopoulos, 2009). UV_{254} provides information on the hydrophilicity of the DOC and can also be used to better understand the DOC content. The DOC molecules that are being adsorbed at 254 nm wavelength are the hydrophilic material, meaning a low UV_{254} value indicates more hydrophilic DOC (Machenbach, 2007).

Knowledge regarding the interaction between PFASs and DOC in drinking water and wastewater are limited and whether or not the presence of DOC does influence the removal efficiency of PFASs in water. When looking at the sorption of PFASs to sediment the dominant parameter is considered to be the organic carbon content of the sediment, where hydrophobic interaction is believed to be the main force for sorption to organic matter (Chen et al., 2012; Jeon et al., 2011). The affinity for PFCAs to organic carbon increases with increased perfluorocarbon chain length (Appleman et al., 2013b).

2.2 Treatment techniques

2.2.1 Ion exchange with MIEX®

Treatment using ion exchange is a process that involves replacing ions (cations or anions) with other similarly charged ions on a solid charged surface. The process is reversible and today it is primarily used for softening, which means removing calcium and magnesium, but it is also used to remove other unwanted dissolved ionic compounds (EPA, 2014b).

Magnetic Ion-Exchange resin (MIEX®) is a type of anion exchange that is used in the removal of contaminants in water and wastewater. The MIEX®technology was developed jointly by Orica Watercare, Commonwealth Scientific Industrial Research Organisation and South Australian Water Corporation in the mid 1980s. The technique was specifically developed to remove dissolved organic carbon (DOC) from water, but can also be used to remove other contaminants such as nitrate, arsenic, sulfide and color (Orica Watercare, 2014).

The two main mechanisms for removal through ion exchange resins are electrostatic interactions and absorption via hydrophobic interactions (Rahman et al., 2013). Since the particles are positively charged they works as anion exchangers and compared to conventional ion exchange the particle size is 2-5 times smaller, around 150 µm, increasing the contact area per volume resin (Cook et al., 2001; Singer and Bilyk, 2002). Both hydrophilic and hydrophobic acids should be possible to remove from water using MIEX® resins, due to its anion exchange properties (Singer and Bilyk, 2002). The resins work as individual magnets, due to the fact that the resins contain a magnetized component (Orica Watercare, 2014). Compounds can also be reduced by diffusing into the internal pores in MIEX® particles. This applies, however, only to very small molecules, and it is a slow process (Slunjski et al., 2000).

When the MIEX® resins are mixed with raw water, the negatively charged anions in the water will exchange for chloride ions on the MIEX® resins. This process is referred to as adsorption. When the resins are loaded, a regeneration of the MIEX® resin is required. This is done by mixing the loaded resins with a saline solution (NaCl), so that the high concentration of chloride will exchange for the compounds adsorbed from the raw water (Figure 1) (Orica Watercare, 2014).

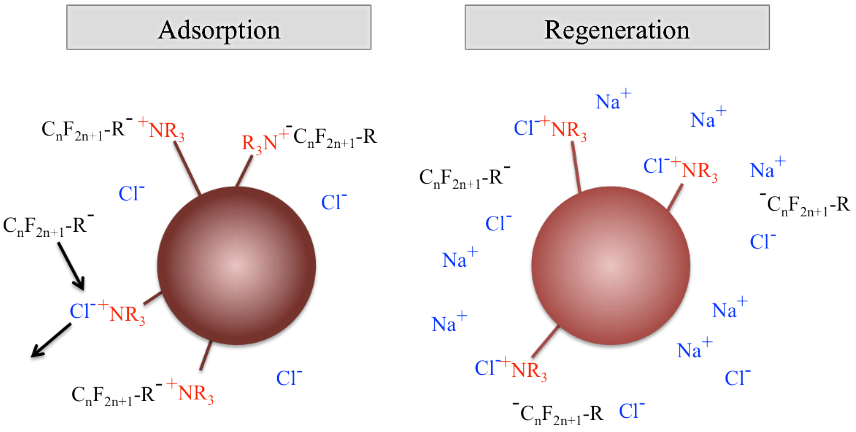


Figure 1. When raw water comes in contact with the MIEX® resins (left), adsorption of PFASs occurs. The resins are regenerated through adding a NaCl solution (right). The picture is modified from Orica Watercare (2014).

The amount of water that the resins has already treated, called bed volumes (BV), plays an important part in the efficiency of the resins. BV is defined as treated water volume divided by used volume MIEX®. The presence of other competing anions such as nitrate and sulfate also plays an important part in the efficiency of the resins (Orica Watercare, 2014).

Few studies has been performed on the efficiency of removing per- and polyfluoroalkyl substances with MIEX®, though other ion exchange techniques have proven to be efficient (Appleman et al., 2013b; Deng et al., 2010). Removal efficiency with ion exchange seems to be dependent on chain length. When using anion exchanger FerrIX A33 there was a wide spread in terms of removing efficiency, where longer chained PFCAs, such as PFHpA and PFOA, were removed in a range of 54% to 76%, though the resin failed to efficiently remove short chained PFCAs. Higher removal efficiency was obtained for PFSAs, around 80-98% (Appleman et al., 2013b).

Moreover, another study has shown that MIEX® does not remove small neutral organic compounds but is efficient in removing smaller anionic compounds that contain carboxylic groups (Mergen et al., 2007). Du et al.,, (2014) reports that previous studies have shown a tendency for smaller PFASs to adsorb faster to anion-exchange resins, due to faster diffusion into the resins than the larger PFASs. However, most studies with anion resins have been conducted in the absence of DOC and therefor studies including DOC are needed (Rahman et al.,, 2013).

2.2.2 Coagulation with $FeCl_3$

A conventional method that is commonly used for removing contaminants in wastewater treatment plants is coagulation processes using Iron(III) chloride ($FeCl_3$) as coagulation compound. The process is easily available, include low costs and easy to use. A typical coagulation process is composed of two stages, first a fast mixing followed by a slow mixing. The coagulation compound is rapidly distributed in the water during the fast mixing, while during the slow mixing the coagulant and the contaminants clump together into flocs. When flocs have formed they sink, float or are filtrated away (Xiao et al., 2012).

Two different mechanisms can occur during coagulation, charge neutralization and sweep flocs. When $FeCl_3$ is added to the water the iron-chloride bond breaks and the flocculation compound is transferred into its ionic form, Fe^{3+} (Matilainen et al., 2010). Charge neutralization appears when positively charged ions bind to negatively charged particles in the water, which reduces or neutralizes the negative charge of the particle. The electric repulsion between the particles are then reduced or eliminated and they can form colloids and fuse into flocs (Equation 1) (Svenskt Vatten, 2010a).

$$Fe^{3+} + B^{n-} \rightarrow FeB^0 \qquad (1)$$

Sweep flocks occurs when the flocculation compounds is added to the water, the iron-chloride bond breaks and the flocculation compound forms metal hydroxides (Svenskt Vatten, 2010a; Matilainen et al., 2010). These hydroxides can adsorb particles in the water and in this way remove them from the water (Equation 2) (Svenskt Vatten, 2010a).

$$2\,FeCl_3 + 6\ HCO_3^- \rightarrow 2\,Fe(OH)_3 + 6\,Cl^- + 7\,CO_2 \qquad (2)$$

For removal of contaminants with $FeCl_3$ it is important to achieve the optimal pH, since the charge of the dissolved flocculent compound and amount of flocs that are formed is a function of pH (AWWA staff, 2010). For coagulation with $FeCl_3$ studies have shown that the ideal pH level is between 5.0-5.1, where pH values between 4.9-5.2 are acceptable. At this pH levels there are low risks of traces of dissolved $FeCl_3$ in the water after treatment, this due to the fact that the flocculation compound has the lowest solubility around this pH interval (Svenskt Vatten, 2010a).

Conventional treatment techniques, such as coagulation, have proven not to be efficient in removing PFASs from drinking water. Few studies have been made on removal efficiency of PFAS with $FeCl_3$ as coagulant although a previous study show that basically no PFOS was removed when using a $FeCl_3$ dosage of 3-5 mg L^{-1} (Xian et al 2012; Appleman et al., 2013b).

2.2.3 Powdered activated carbon (PAC)

Adsorption has been used for a long time to remove contaminants from water. When using PAC, a substance accumulates at the interface between liquid and solid phases making the process both physical and chemical. Activated carbon (AC) can adsorb almost all type of organic compounds but to different degrees. In drinking water treatment, activated carbon is often used to adsorb taste, odor, natural organic compounds and synthetic compounds. The advantages of using active carbon is primarily that it is a highly porous material and that it provides a large surface area, up to 1000 m^2g^{-1} AC, where contaminates can adsorb (EPA, 2014a; Hansen et al., 2010; Chowdhury et al., 2012).

Active carbon is a product made out of different organic feedstock, for example wood, lignite, coconut shells and bituminous coal. The reason why activated carbon has been used for water treatment is mainly due to the internal pore structure. The activation of pore structure can be done in two ways, thermally or chemically. Depending on which activation method and raw material used, the surface area, surface chemistry and pore distribution may vary widely (Chowdhury et al, 2012).

Normally the surface of activated carbon contains different oxygen complexes that add a polar nature to the activated carbon. There are mainly two forces contributing to adsorption, solubility and affinity. Depending if a compound is hydrophilic or hydrophobic it has less or more tendencies to adsorb. A hydrophobic compound dislikes the water system and will rather adsorb than stay in the water (Cecen and Aktas, 2011). Active carbon has shown the ability to strongly sorb hydrophobic organic compounds and has therefore been used for the intention of removing PFASs from water (Hansen et al., 2010). The second force, affinity, means that an attraction occurs between the activated carbon and the compound. Due to van der Waals attractions or chemical interaction, adsorption can occur (Cecen and Aktas, 2011).

There are two types of active carbon used in water treatment; powdered activated carbon (PAC) and granular activated carbon (GAC) (EPA, 2014a). The use of PAC instead of GAC has shown significantly higher adsorption rate for both PFOS and PFOA (Yu et al., 2013; Du et al., 2014). A disadvantage with using GAC instead of PAC is also that the removal efficiency might be reduced by the presence of organic matter (Altmann et al., 2013) For this thesis; the focus was on the first type of active carbon, PAC.

The dosage of PAC depends on the type and concentration of the contaminant but normally ranges between 1 to 100 mg L^{-1} (EPA, 2014a). According to Chowdhury et al., (2012), to remove 80 % of a target compound that occurs in concentrations < 1 μg L^{-1} a PAC dose of 20 mg L^{-1} is sufficient.

A number of studies have shown that active carbon is efficient for removal of PFASs (Yu et al.,, 2014; Hansen et al., 2010; Qu et al., 2009). A study performed by Hansen et al (2010) show that, at a PAC dose of 25 mg L^{-1} and a contact time of 10 min, 60-90% of the PFASs (i.e. PFBS, PFHxS, PFOS, PFHxA, PFHpA, PFOA, PFNA) were removed, this when the initial concentrations of PFASs were within ng-μg L^{-1}. Water used in this study was natively PFAS contaminated water with a DOC concentration of 5.27 ng L^{-1}. In studies performed by Yu et al., (2014) experiments were done by combining PAC treatment with membrane where a dose of both 30, 80 and 100 mg L^{-}

^{1} PAC was used. The study was conducted on synthetic wastewater with PFASs concentrations of 0.2 mg L^{-1} and showed that for PFOS and PFOA, at the smallest PAC dose (30 mg L^{-1}), 68% and 77% were removed, while at the highest dose of 100 mg L^{-1} around 90% was removed for both compounds and that PAC accounted for a significant part of the removal. Du et al., (2014) reports that previous studies have shown a tendency for smaller PFASs to adsorb faster to activated carbon, as they seem to diffuse quicker into activated carbon than the longer PFASs.

Previous studies using GAC for removal of PFASs show that presence of DOM has a great effect on the removal efficiency and that removal efficiency is highest in low DOC water. It is believed that the organic matter competes for pore space or sorption sites, in this way preventing other compounds to sorb. The same tendencies have been seen for treatment of other organic compounds when treated with PAC and GAC, where the removal efficiency has been reduced due to the competition with DOM (Appleman et al., 2013a). It has also been shown that in order to achieve a 90 % removal of a target compound, the PAC dose has to increase with increased amount total organic carbon (TOC) in the water (Chowdhury et al., 2012).

2.2.4. Nanofilter (NF) membrane

Separation by use of membrane covers the entire size range of water components, from larger particles to dissolved organics and salts. Which type of membrane process is required varies depending on the required separation efficiency needed (Machenbach, 2007).

There are two types of pressure-driven membranes, micro- and ultrafiltration (MF and UF), that operates at pressure around 0.8-3 bar and nanofiltration (NF) that is a semipermeable membrane usually operating above 3 bar. Nanofiltration, which is used in this study, is a so-called high-pressure membrane with capabilities to remove dissolved compounds and normally has a pore size between 1 to 10 nm (Machenbach, 2007; Svenskt Vatten, 2010b). High-pressure membranes are often categorized by molecular weight cut-off (MWCO), which describes the separation ability of the membrane based on the molecular weight in the water. In NF membrane the MWCO often ranges from 200 to 2000 D. Other factors that affects the purification is also the surface charge of the membrane as well as whether the surface is hydrophilic or hydrophobic (Machenbach, 2007). The technique of using high-pressure membrane is on the rise due to the operating efficiency, low costs and the fact that most membranes can tackle a wide range of contaminants (Rahman et al., 2013).

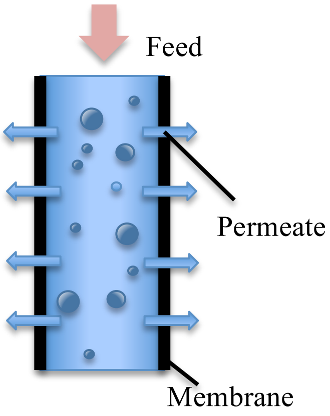


Figure 2. The flow through a cross-flow filter.

The process with pressure-driven membrane means that molecules, ions and similar compounds are filtered when applying an overpressure. There are different types of filter techniques, dead-end or cross-flow filtration. Dead-end filtration is primarily used for low-pressure membrane, where all water flows through the membrane and the water that comes out are purified. Treatment with NF membrane is usually performed under cross-flow conditions. This means that the water being filtrated circulates in the filter. The pressure will make a part of the water permeate through the filter while the other part will run back to the feedtank (Figure 2). This process increases the concentration in the water that is not permeated through the membrane. The water that circulates in the membrane module is called feed while the water filtrated through the membrane is called permeate (Svenskt Vatten, 2010b; Pentair (1), 2006).

The main disadvantage using membrane treatment is the risk of fouling. When this happens the pores of the membrane get clogged or compounds accumulate on the membrane surface. Increased pressure is required for the module to be able to permeate water through the membrane, which decreases the performance of the membrane. To reduce the risk of fouling the membrane can be cleaned, using chemicals as a cleaning solution or by backwash. Backwash means that water is being flushed backwards to remove particles or “filter cakes” that formed on the membrane (Machenbach, 2007).

The water flux (J) through a membrane where fouling has not occurred, depends on the transmembrane pressure (TMP), the viscosity of the water (μ) and the hydraulic membrane resistance (Rm) (Equation 3). The transmembrane pressure (TMP) is the pressure difference between the feed and permeate (Machenbach, 2007). The temperature affects the viscosity of the water, when the temperature decreases the viscosity increases, which in turn affects the performance of the membrane. Therefore it is important to maintain the same temperature during the entire treatment (Svenskt Vatten, 2010b).

$$J = \frac{TMP}{\mu \times R_m} \quad (3)$$

A study performed by Appleman et al. (2013a) showed that >93 % of the PFAAs in the experiment were removed by NF membrane when using both deionized water and artificial groundwater with PFAA levels of approximately 1 μg L^{-1}. Moreover, Tang et al., (2007) performed treatment with three different NF membranes and received a removal efficiency of PFOS that ranged from 90-99% with an initial PFOS concentration of 10 mg L^{-1}. For uncharged PFASs such as FOSA, the removal can be expected to vary and be significantly lower than for the charged compounds (Rahman et al., 2013; Steinle-Darling and Reinhard, 2008). Moreover, the removal of ionic PFASs is more efficient for compounds with a molecular weight of 300 D or greater (Steinle-Darling and Reinhard, 2008).

A study performed by Steinle-Darling and Reinhard (2008) shows that a membrane with high affinity leads to decreased removal efficiency. Moreover, sorption of PFASs compounds to the membrane causes high removal efficiency at a early stage of treatment while over time the membrane sorption capacity will decrease and so will the removal efficiency. The same study showed that this process could be just as important as MWCO when removing PFASs.

A study made on the removal efficiency by treating water with Electro-Microfiltration performed by Tsai et al (2010) shows that the removal efficiency of both PFOA and PFOS decreases in the presence of DOC. However, many bench-scale studies on NF membrane have been conducted in the absence of DOC. Therefore, further studies are needed to gain knowledge regarding the removal efficiency in the presence of DOC (Rahman et al., 2013).

3. Material and methods

3.1 Chemicals and material

In this study 14 PFASs were investigated including PFBA (purity 98%), PFPeA (97%), PFHxA (≥97%), PFHpA (99%), PFOA (96%), PFNA (97%), PFDA (98%), PFDoDA (95%), PFUnDA (95%), PFTeDA (97%), PFBS (98%), PFHxS (≥98%), PFOS (98%), FOSA (purity not available) and were purchased from Sigma-aldrich (Table 1).

The waters used for the treatment were spiked with 100 μL of a mix of the 14 PFASs ($c=480$ μg mL^{-1}) to each water container holding a volume of 9.6 L of water ($c=5$ μg L^{-1}). The waters were spiked with a high concentration of PFASs to be able to trace the compounds. These concentrations are in the upper range as has been detected in WWTP effluents (Prevedouros et al., 2006; Post et al., 2012).

Experiments were performed using 1000 mL glass beakers (Duran Schott, Germany) and all samples were collected in 100 mL PE-bottles. Tubes used for the NF membrane module were Masterflex platinum-cured silicone tubes and Tubclair® al tubes (07/19/CE, PVC).

Chemicals used throughout the laboratory work are as follows. Methanol (LiChrosolv, Germany, >99.9%) used for rinsing equipment, in solutions and experiments involving methanol. Millipore water (MilliPak, 0.22 μm filter) used for rinsing equipment, in solvents and experiments. Acetone (SupraSolv, Germany, >99,8%) used for rinsing equipment. Ammonium acetate (Fluka, Netherlands, >99 %) and Ammonium hydroxide solution (Sigma-aldrich, Spain, 28-30%) were used for the solid extraction. Sodium hydroxide (Emsure, Germany, 99%) and hydrochloric acid (Suprapur, Germany, 30%) were used when performing the experiments with $FeCl_3$. Sodium hypochloride (GPR. Rectapur, France, 17% active chloride) was used for cleaning the NF membrane.

Internal standards (ISs) were added to each sample after treatment and right before solid phase extraction to be able to correct for possible loses during the extraction. ISs used included $^{13}C_4$ PFBA, $^{13}C_2$ PFHxA,$^{13}C_4$ PFOA, $^{13}C_5$ PFNA, $^{13}C_2$ PFDA, $^{13}C_2$ PFUnDA, $^{13}C_2$ PFDoDA, $^{18}O_2$ PFHxS, $^{13}C_4$ PFOS, M_8FOSA, d_3-N-MeFOSAA, d_5-N-EtFOSAA, d-N-MeFOSA, d-N-EtFOSA, d_7-N-MeFOSE, d_9-N-EtFOSE, all purchased from Wellington Laboratories (purity 99%).

The injection standard, $^{13}C_8$ PFOA, was added before instrument analysis and was used to calculate the recovery of the internal standards and quality control.

3.2 Water samples

Six different water types, taken from four different places in Sweden, were used for the experiments. The reason for using water from different places was so they would contain DOC with different character to see whether this affects the removal efficiency of PFASs. The collected water samples included Krycklan (C4), Bolmen (BO), Tostarp (TO) and WWTP Kungsängsverket in Uppsala (EB) (figure 3). The water C4 was divided into two fractions, where half of the water was exposed to UVC radiation and is called hereafter UV. The last water sample has been cultivated using algae, in laboratory and is called hereafter SA.

Four of the used waters (i.e. C4, UV, BO and TO) contained DOC with terrestrial origin that primarily originates from decomposed plant materials, known as allochthonous origin. This type of DOC is hydrophobic and has a high molecular weight. The two remaining waters (i.e. EB and SA) did not have terrestrial origin instead they contain organic matter produced by bacteria and algae, known as autochthonous origin. This type of DOC is more hydrophilic and has a lower molecular weight (Leeheer, 2004).

C4: C4 was collected in a river located at Vindeln municipality, Västerbotten (Figure 3). The catchment area for this water is mainly coniferous and is dominated by wetland assuring that the organic material is allochthonous.

UV: The C4 water sample was divided into two fractions, where half of the water (UV) was exposed to UVC radiation. The UVC light changes the structure of the DOC, making it more bioavailable and the average molecular weight decreases (Bertilsson & Tranvik, 2000).

BO: BO was collected in the lake Bolmen, located in western Småland (Figure 3). The catchment area for this lake mainly contains coniferous making the DOC allochthonous. The water from this lake is used as drinking water.

TO: TO was collected in a stream named Tostarp located in Skåne, south of Ljungbyhed (Figure 3). This catchment area is dominated by deciduous forest and the organic material is allochthonous.

Figure 3. Map showing the different sample point for the waters. UV is from the same place as C4. Sa was cultivated in laboratory. Picture taken from Nilsson and Wängdahl (2014).

EB: Water was also collected from the WWTP Kungsängsverket in Uppsala (Figure 3). Treatment in this WWTP is done in three steps; mechanical, biological and chemical. Water was collected after the biological treatment.

SA: The last water was collected at SLU where Millipore water had been cultivated, using algae, in laboratory. This water contained DOC formed only in water (autochthonous) without contributions from surrounding catchment.

The data in table 2 below are provided from another master study conducted at the same time and in the same manner as this study (Nilsson and Wängdahl, 2014). The table shows that pH were around the same for all waters, as well as amount DOC. For EB a significantly higher amount of anions was present and both conductivity and alkalinity were higher. More detailed information regarding the different water samples can be found in Nilsson and Wängdahl (2014).

Table 2. Characteristics of the six different waters used for this study where type, pH, conductivity, concentration DOC, alkalinity and anions (sulfate, nitrate, chloride and fluoride) was measured. Data taken from another master study (Nilsson and Wängdahl, 2014)

Water	Type	pH	Conductivity S m^{-1}	DOC (mg L^{-1})	Alkalinity (mM)	SO_4^{2-} (µM)	NO_3^- (µM)	Cl^- (µM)	F^- (µM)
C4	Wetland	7.6	18	9.0	0.20	nd	nd	36	0.8
UV	Wetland, UVC radiation	7.5	14	7.0	0.22	nd	nd	35	nd
Bo	Coniferous	7.4	26	9.1	0.80	8.6	59	74	6,8
To	Deciduous	6.7	26	6.1	0.57	11	50	74	4.6
Eb	WWTP After biofilter	7.3	295	7.0	7.80	230	150	890	23
Sa	Protein	8.1	34	9.6	1.77	4.3	27	43	5.1

nd = not detected

3.3 Water treatment techniques

All experiments were performed in laboratory, under a constant temperature of 20 °C. The amount of water available was limited since the different water types were sent from different parts of Sweden, therefor duplicates could not be made for each water and treatment. For all experiments except the NF membrane, a standard chemical reactor (flocculator, KEMIRA) was used to be able to adjust stirring rate and time (Figure 4). The method for this study can be divided into two parts; part one focus on the different treatment techniques described in this (chapter 3.3) and part two focuses on the chemical analysis of the water samples for PFASs (chapter 3.4).

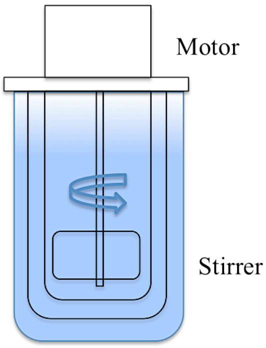


Figure 4. Schematic picture showing beaker with flocculator used for stirring using MIEX, $FeCl_3$ and PAC.

3.3.1. MIEX®

The MIEX® resin used in this study was MIEX® Gold resin, obtained from Lovö WWTP where it had already been used for pilot trials with a bed volume of approximately 1000 bed volumes. To be able to compare the different water types, the amount of MIEX® added to the water was scaled to fit the amount of DOC. This was done by using water from BO as standard water, scaling the amount MIEX® added depending on how much lower the DOC was compared to BO. For the waters with high DOC concentration (i.e. C4, UV, BO, SA) a dose of 5 mL L^{-1} MIEX® was used, according to the dosage used at Lovö wastewater treatment plant. For two of the waters, TO and EB, 3.5 mL and 4 mL MIEX® was added, due to lower DOC concentrations. The amount MIEX® resins used in the experiment were prepared a day before, the doses were measured into 15 mL tubes and then stored in refrigerator (Appendix B).

A volume of 1000 mL were used for the six different water and weighed into 1000 mL beakers; duplicates were done for C4 and UV. A pre sample of all waters was collected before the MIEX® treatment began, pH measurements on the untreated water was also performed. The MIEX® resins were added to the different beakers and with the help of a flocculator the samples were stirred at a rate of 250 rpm for 15 min, then for 5 min the MIEX® resins settled before taking out approximately 80 mL of sample and measuring pH (appendix B).

3.3.2. Coagulation with $FeCl_3$

For the experiments using $FeCl_3$ the volume of water being used was changed from 1000 mL to 700 mL, to make sure it would be enough water for all experiments remaining.

The flocculant used for the $FeCl_3$ experiment was KEMIRA PIX-111 that is a liquid flocculants that contains active trivalent iron ions. Iron content in the chemical is 13.8% (+- 0.4%) (Kemira Kemi AB, 2013). The dose PIX used was 41 μL L^{-1} (i.e. 28.7 μL in 700 mL of water) which corresponds to a $FeCl_3$ dose of 8 mg L^{-1}. The dose was based on the amount normally used in Ringsjö drinking water treatment plant, where the water from *BO* is used as raw water and where they use the same flocculant for coagulation. Also for this treatment the dose $FeCl_3$ used was scaled for TO (19.3 μL) and EB (19.5 μL) since these two waters contained lower DOC concentration than the rest of the waters.

The six different water types were weighed into 1000 mL beakers; duplicates were done for BO and EB. A pre sample of all waters was collected before the treatment began, pH measurements on the untreated water was also performed. As mentioned earlier, for the $FeCl_3$ to work efficiently a pH value between 4.9-5.2 was desired. Test titrations were performed on each water type to obtain the right amount of base or acid, depending on water, to achieve the right pH. When right amount of base and acid was determined the PIX containing the flocculants were added at the same time as the base (NaOH) or acid (HCl) by using automatic pipette. With the help of flocculator the samples were stirred for 30 sec at a speed of 350 rpm, then stirred slowly for 20 min (40 rpm), followed by a settling time of 60 min, this according to consultation with Ringsjö (Appendix B). After sedimentation, approximately 80 mL of samples were collected and pH was recorded (Appendix C).

3.3.3. Powdered activated carbon (PAC)

The PAC experiments was performed the same way as the MIEX experiment, using 700 mL of each water due to lack of water. The PAC used for these experiments was Norit W90 with a total surface area of 725 m^2/g and a particle size D10 of 17 μm (Cabot, 2014). For the waters with high DOC concentrations a normal dose of PAC was used, 20 mg L^{-1}, this according to the dosage used at the Norrvatten WWTP. A scaling of amount of PAC to compensate for amount DOC was also done for two of the waters, TO and EB, with a dose of 13.6 mg L^{-1} and 13.5 mg L^{-1}, respectively. For one water (C4) two higher dosages was also used, 50 mg L^{-1} and 100 mg L^{-1}, in order to investigate whether increased dose PAC increases the removal efficiency.

The six different water types were weighed into 1000 mL beakers. A pre sample of all waters was collected before the treatment began, pH measurements on the untreated water was also performed. The different PAC doses were weighed on aluminum foil so it could easily be added into the water (Appendix D). The PAC was added to the different beakers and with the help of a flocculation machine the sample was stirred at a rate of 250 rpm for 15 min, then for 5 min the PAC settled before taking out approximately 80 mL of each sample and measuring pH.

3.3.4. NF Membrane

Experiment design for the NF membrane was developed in consultation with the manufactures of the membrane module (Pentair, Enschede, The Netherlands). The membrane module used was a X-Flow T/RX-300 manufactured from Pentair. A NF membrane was used, also manufactured from Pentair, of model HFW 1000. It is an x-flow hollow-fiber membrane with 120 fibers and operates at 0.5 m/s cross flow. It is a hydrophilic membrane that has a negatively charged surface with a diameter size of 0.8 mm and the membrane area is 40 m^2 (Pentair, 2014; Pentair, 2006). The membrane has a MWCO around 500 D (Keucken, 2013).

A pre sample of all waters was collected before the treatment began, pH measurements on the untreated water was also performed. The membrane module was connected to an external plastic container (7 L), this to avoid iron contamination since rust was detected in the container attached to the module (Figure 5). For treatment with NF membrane five liters of water was required. For the NF, a stabilization period was required to stabilize the membrane where the water had to recycle through the membrane module for approximately 45 min. After the stabilization period the filtration through the membrane began and samples were taken from the permeate filtrated through the membrane. Permeate samples were collected at three different times during the treatment. The first sample was collected from the permeate right after stabilization; whilst the other two samples were collected after 25% (~ 1.5 h) and 50 % (~ 3h) of the feed volume was filtrated. All samples were collected at a volume of approximately 80 mL. No duplicates were done for the NF membrane treatment since the amount of water was not sufficient.

During the entire treatment, which took between 2.5-3.5 h depending on water type, the transmembrane pressure (TMP) was kept at one bar (Equation 4) (Pentair, 2006).

$$\left(\frac{P2+P3}{2}\right) - P1 = 1\,Bar \qquad (4)$$

where P1, P2 and P3 are the pressure for each manometer (Figure 5).

The flowrate of permeate was monitored continuously to detect possible fouling. A constant rate of permeate was desired. The rate differed between different waters and ranged between 0.76–1.0 Lh^{-1}. To ensure the temperature was constant, at approximately 20 °C during the entire run, the feedtank was placed in a waterbath and the temperature was continuously monitored (Appendix E).

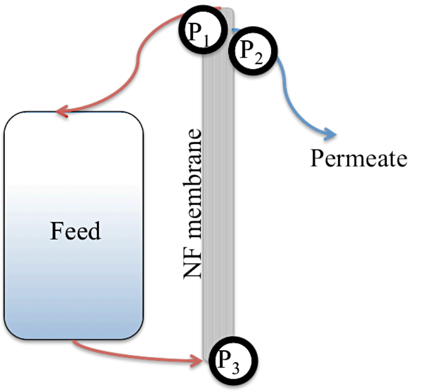


Figure 5. Schematic picture showing lab setup with an external container, NF membrane and manometers.

Prior to each treatment run the membrane module was cleaned. This was done by first letting a solution containing 500 ppm NaOCl circulate through the membrane module for approximately 30 min followed by circulation of five liters of Millipore water for approximately 45 min.

3.4 Chemical analysis

3.4.1 Blank and positive control

Since PFASs are widely spread in our environment and commonly used in our daily life products, precaution had to be taken to make sure that the samples were not contaminated during experiments and analyzes. Running blanks for each experiment, always in duplicates, made it possible to make correction regarding this. For NF membrane one blank was run and three samples were collected during the treatment. This was done to consider possible contamination of the samples from equipment, air or by something else in the laboratory environment that can contribute to contamination.

Positive controls (n=3) were performed for the experiment using the flocculator, but no MIEX®/$FeCl_3$/PAC was added to the beakers. Positive controls were also performed for the NF membrane treatment method (n=3). Water was run through the membrane machine without the membrane. The positive controls were used to compensate any loss of compounds due to adsorption to the walls of the beakers, tubing, the flocculator or evaporation into the air. The concentration levels of PFASs for the specific treatment technique were corrected by the average loss of the positive control samples for the flocculator and NF membrane treatment technique, respectively (Appendix A). The water used for the positive controls was C4. This water was used for all positive controls due to the fact that more C4 was available compared with the other water types.

3.4.2 PFAS analysis in water

Prior to the extraction of the PFASs all samples were filtrated to remove particles that had not been removed through sedimentation. This was done using a glass microfiber filter (GF/C, Whatman), Werner Glass Filtration equipment and vacuum. Before filtration all glass material was first rinsed with ethanol, dish washed and then burned at 400°C over night and finally rinsed carefully with methanol. After filtration the water samples were stored in refrigerator at + 4°C.

Extraction of PFASs was done through solid-phase extraction (SPE), according to Ahrens et al., (2009), using Oasis Wax cartridges (Waters, 6 cc, 150 mg, 20 µm, Ireland) and a SPE workstation (Appendix F). In order to correct for PFAS loss during the extraction and concentration, each sample was spiked with 100 µL of PFAS internal standard (20 pg μL^{-1}) prior to the SPE. The SPE-setup was preconditioned by rinsing the cartridges with, 4 mL ammonium hydroxide in methanol, followed by 4 mL of methanol and finally 4 mL Millipore water. The cartridges were then loaded with approximately 80 mL water sample. The water flow through the cartridge was regulated to one drop per second, this was done by using vacuum pump. When all water had passed through, the cartridges were washed with 4 mL 25mM ammonium acetate buffer in Millipore water. Before the elution, leftover water was removed using a centrifuge for 2 min at 3000 rpm. The elution was carried out with 4 mL methanol and 4 mL 0.1% ammonium hydroxide into a 15 mL PP-tube. The samples were concentrated using nitrogen evaporat (N-EVAP™112) to 1 mL (Appendix F). Finally an injection standard, 10 µL InjS of 200 pg μL^{-1}, was added to the samples and they were analyzed for PFAS using liquid chromatography-mass spectrometry (HPLC-MS/MS).

4. Results

4.1 Quality assurance and quality control

The concentration of the blanks was set to calculate the method detection limit (MDL); a total of eight blanks were used (Equation 5).

$$MDL = \bar{C}_{blanks} + 3 * SD_{blanks} \qquad (5)$$

Mean concentration and standard deviation of the blanks and MDLs for the four different treatment techniques are listed in table 3 below. Since the different techniques exhibited very different concentrations for the blanks, blanks and MDLs are listed separately.

Table 3. Mean blank concentration (± standard deviation (SD)) and method detection limit (MDL) for the blanks using MIEX®, $FeCl_3$, PAC and NF membrane

Compound	**MIEX®**		**$FeCl_3$**		**PAC**		**NF membrane**	
	Blank (ng L^{-1}), n=2	MDL (ng L^{-1})	Blank (ng L^{-1}), n=2	MDL (ng L^{-1})	Blank (ng L^{-1}), n=2	MDL (ng L^{-1})	Blank (ng L^{-1}), n=3	MDL (ng L^{-1})
PFBA	1.4 ± 0.39	2.6	9.7 ± 0.77	12	0.96 ± 0.57	2.66	17 ± 5.6	34
PFPeA	4.1 ± 0.38	5.2	5.8 ± 4.3	19	0.19 ± 0.04	0.30	26 ± 10	58
PFHxA	nd	0.05	2.2 ± 0.36	3.3	nd	0.05	40 ± 15	85
PFHpA	nd	0.05	0.4 ± 0.015	0.47	nd	0.05	58 ± 19	114
PFOA	nd	0.05	277 ± 11	309	12 ± 16	60.2	90 ± 62	277
PFNA	nd	0.05	0.26 ± 0.36	1.4	nd	0.05	202 ± 266	1000
PFDA	0.89 ± 1.3	4.7	2.9 ± 2.5	10	0.12 ± 0.17	0.64	267 ± 315	1212
PFUnDA	1.9 ± 1.9	8.0	2.8 ± 2.6	11	0.25 ± 0.13	0.65	219 ± 119	575
PFDoDA	3.9 ± 2.3	11.0	2.3 ± 1.5	6.7	0.03 ± 0.04	0.15	167 ± 48	310
PFTeDA	0.91 ± 0.70	3.0	2.3 ± 1.3	6.1	3.1 ± 1.4	7.3	17 ± 2.1	24
FOSA	1.6 ± 0.93	4	25 ± 25	100	0.52 ± 0.09	0.78	207 ± 198	802
PFBS	nd	0.05	6.0 ± 4.0	18	nd	0.05	60 ± 19	118
PFHxS	nd	0.05	0.0 ± 0.0	0.05	nd	0.05	61 ± 28	146
PFOS	0.21 ± 0.30	1.1	1.5 ± 0.21	2.2	0.10 ± 0.14	0.53	165 ± 241	887

[a] nd = not detected, MDL set to 0.05

The recoveries of the ISs, added prior to extraction, were calculated for individual samples using equation 6 (Table 4).

$$Recovery\ IS\ (\%) = \frac{Area_{IS(sample)}}{\overline{Area}_{IS(calibration)}} \times \frac{Area_{InjS(calibration)}}{\overline{Area}_{InjS(sample)}} \times 100 \qquad (6)$$

Table 4. Recovery for the extraction of the water samples for individual internal standard (IS), with corresponding PFAS used for quantification (n=93)

Internal standard (IS)	Recovery (%)	Corresponding PFAS
$^{13}C_4$ PFBA	84 ±10	PFBA
$^{13}C_2$ PFHxA	73 ±10	PFPeA, PFHxA, PFHpA
$^{13}C_4$ PFOA	87 ±10	PFOA, PFBS, PFOS
$^{13}C_5$ PFNA	68 ±15	PFNA
$^{13}C_2$ PFDA	84 ±12	PFDA
$^{13}C_2$ PFUnDA	98 ±18	PFUnDA
$^{13}C_2$ PFDoDA	87 ±15	PFDoDA, PFTeDA
$^{18}O_2$ PFHxS	76 ±13	PFHxS
$^{13}C_8$ FOSA	75 ±13	FOSA

4.2 MIEX®

The removal efficiency for PFASs using MIEX® showed a wide distribution ranging from 0-87% removal (Figure 6). The different water types (i.e. C4, UV, BO, TO, EB, SA) showed varying removal efficiency for individual PFASs and also for the removal of DOC ranging from 0% (EB) to 72 % (C4).

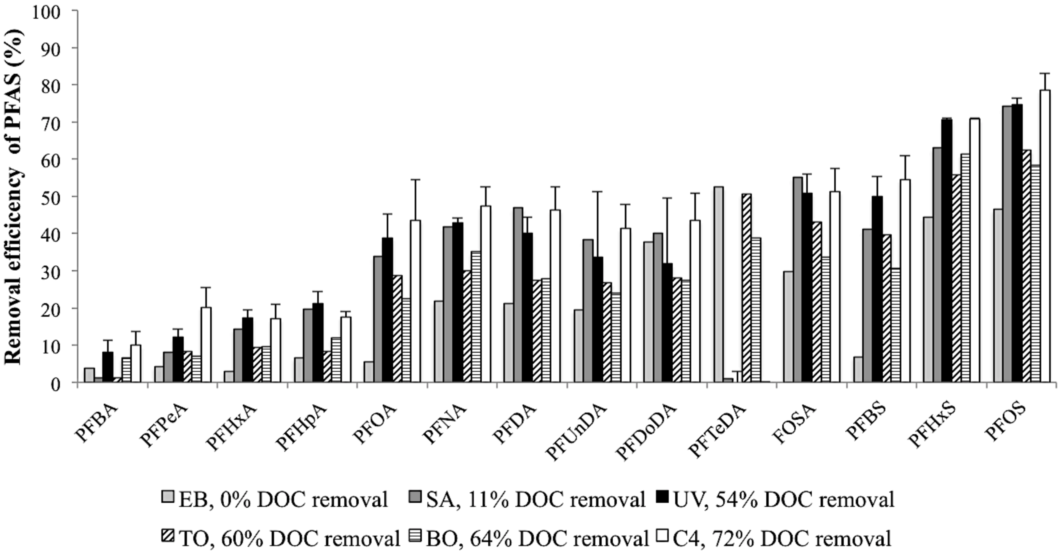


Figure 6. Removal efficiency for PFASs in different water types when treated with MIEX® resins. Waters are presented with corresponding DOC removal in ascending order. Average removal efficiency of individual PFASs for treatment for water C4 and UV (*n*=2).

The removal efficiency for individual PFASs depended on the perfluorocarbon chain length and functional group, the removal efficiency is presented as average of all six waters (Figure 7). For PFCAs, the removal efficiency increased from 6.1 ± 2.7% for the C_3 perfluorocarbon chain PFBA to 39 ± 6.3% for the C_8 PFNA and decreased to 18 ± 17 % for the C_{13} PFTeDA. For PFSAs, the removal efficiency increased from 41 ± 11% for the C_4 perfluorocarbon chain PFBS to 68 ± 8.1% for the C_8 PFOS. In addition, the removal efficiency depended on the functional group showing the highest removal efficiency for the C_8 perfluorocarbon chain PFSA (PFOS) with 68 ± 8.1 % followed by C_8 FOSA with 46 ± 6.6 % and C_8 PFCA (PFNA) with 39 ± 6.3 %. The same pattern could be seen for the C_4 and C_6 PFASs. C_4 perfluorocarbon chain PFBS, had the higher removal efficiency of 41 ± 11%, followed by C_4 perfluorocarbon chain PFPeA with 12 ± 4.2 %. Also C_6 perfluorocarbon chain PFHxS had the higher removal efficiency of, in average, 63 ± 6.6%, followed by C_6

perfluorocarbon chain PFHpA with 15 ± 4.1 %. There was no removal of PFTeDA (C_{13}) for the water types C4 and UV, which resulted in a high standard deviation for this compound.

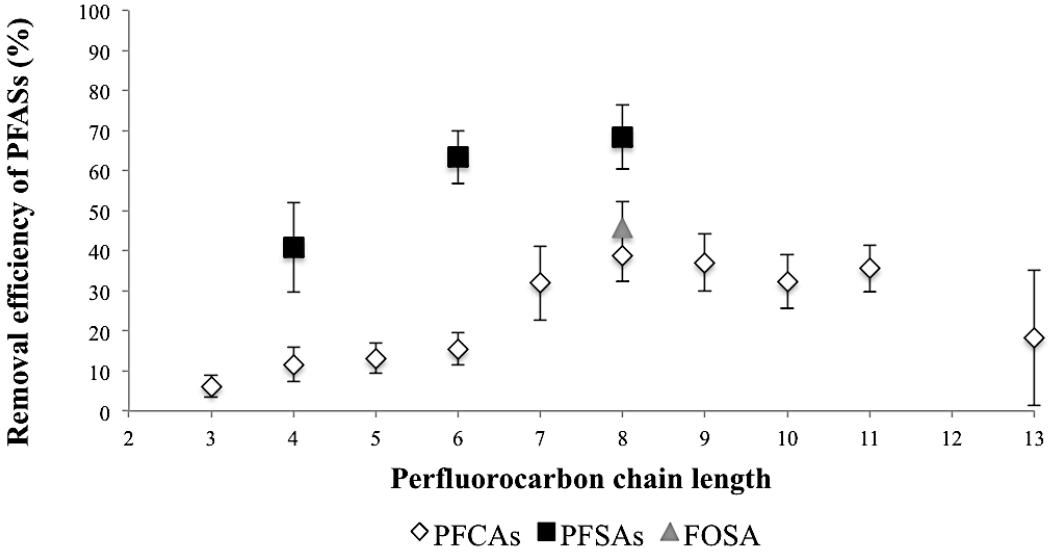


Figure 7. Average removal efficiency of individual PFASs for all water types using MIEX® depending on the perfluorocarbon chain length (*n*=8).

4.3 Coagulation with $FeCl_3$

Removal efficiency for individual PFASs depended on the perfluorocarbon chain length and functional group, the removal efficiency is presented as average of all six waters (Figure 8). For both the PFCAs and the PFSAs an increase in removal efficiency could be seen, where for PFCAs, the increase ranged, in average, from 1.9 ± 0.62 % for the C_3 perfluorocarbon chain PFBA to 78 ± 7.6 % for the C_{13} perfluorocarbon chain PFTeDA. For PFSAs, the removal efficiency increased from, in average, 2.3 ± 2.3 % for the C_4 perfluorocarbon chain PFBS to 12 ± 10 % for the C_8 PFOS. Furthermore, the removal efficiency depended on the functional group showing the highest removal efficiency for the C_8 perfluorocarbon chain FOSA with, in average, 35 ± 10 % followed by C_8 PFSA (PFOS) with 12 ± 10 % and C_8 PFCA (PFNA) with 9.0 ± 7.7 %. For PFASs with the same perfluorocarbon chain (C_4 and C_6) only a slightly higher removal could be seen for the PFSAs, with an average removal of 2.3 ± 2.3 % for C_4 PFBS compared to 1.2 ± 0.96 % for C_4 PFPeA and an average removal of 4.9 ± 5.7 % for C_6 PFHxS followed by 3.5 ± 2.7 % for C_6 PFHpA.

The reason for the large error bars for the PFCAs having a chain length of 10 and 11 was the difference in removal efficiency for the different water types. For PFUnDA (C_{10}) a removal of only 5.0 % was obtained for TO, while for SA 74 % was removed. The same distribution was seen for PFDoDA (C_{11}) where 86 % was removed in SA but only an average of 18% for EB. For treatment with $FeCl_3$ the different water types (i.e. C4, UV, BO, TO, EB, SA) showed varying removal of DOC ranging from 31% (EB) to 82% (C4) (Appendix C).

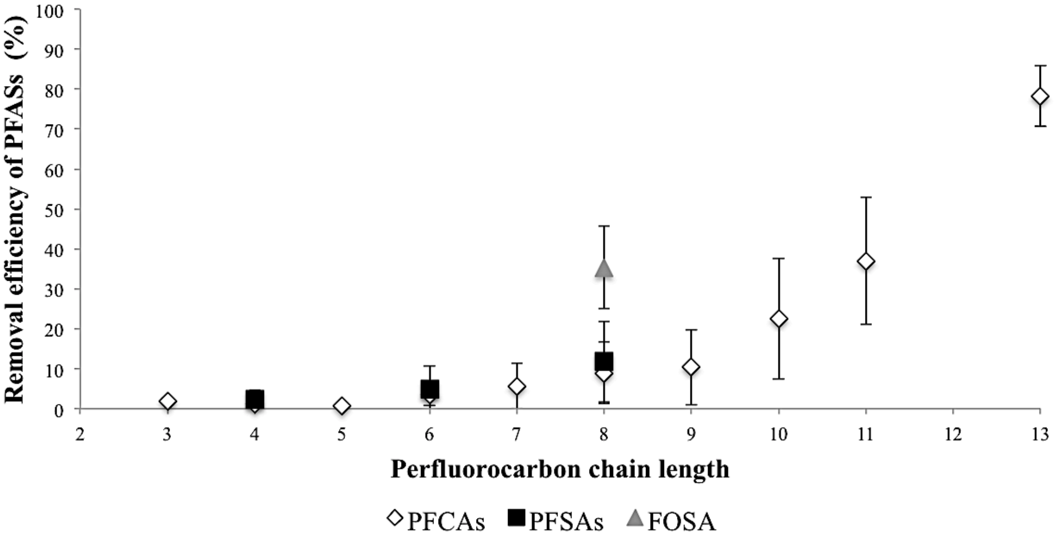


Figure 8. Average removal efficiency of individual PFASs using $FeCl_3$ depending on the perfluorocarbon chain length (*n*=8).

4.4 PAC

An increase in removal efficiency with the perfluorocarbon chain length can be seen for both PFCAs and PFSAs, the removal efficiency is presented as average of all six waters (Figure 9). For PFCAs, the removal efficiency increased from 2.2 ± 1.7 % for the C_3 perfluorocarbon chain PFBA to 21 ± 16 % for the C_{13} perfluorocarbon chain PFTeDA. For PFSAs, the removal efficiency increased from 4.2 ± 3.7 % for the C_4 perfluorocarbon chain PFBS to 16 ± 3.7 % for the C_8 PFOS. For PFASs with different functional groups but same perfluorocarbon chain length there were only slightly higher removal efficiency for PFSAs than PFCAs. The removal of C_8 perfluorocarbon chain FOSA was somewhat higher than both PFCA and PFSA, with a removal of 31 ± 11% for FOSA followed by C_8 PFOS with 16 ± 3.7% and C_8 PFNA with 14 ± 6.7 %. For PFASs with the same perfluorocarbon chain (C_4 and C_6) only a slightly higher removal could be seen for the PFSAs, with an average removal of 4.1 ± 3.8 % for C_4 PFBS compared to 2.5 ± 1.6 % for C_4 PFPeA and an average removal of 9.9 ± 3.5 % for C_6 PFHxS compared to 6.6 ± 2.1 % for C_6 PFHpA. The reason for the large error bars for PFTeDA (C_{13}) was the difference in removal efficiency for the different waters, with a removal of 0 % for SA and 51 % for BO.

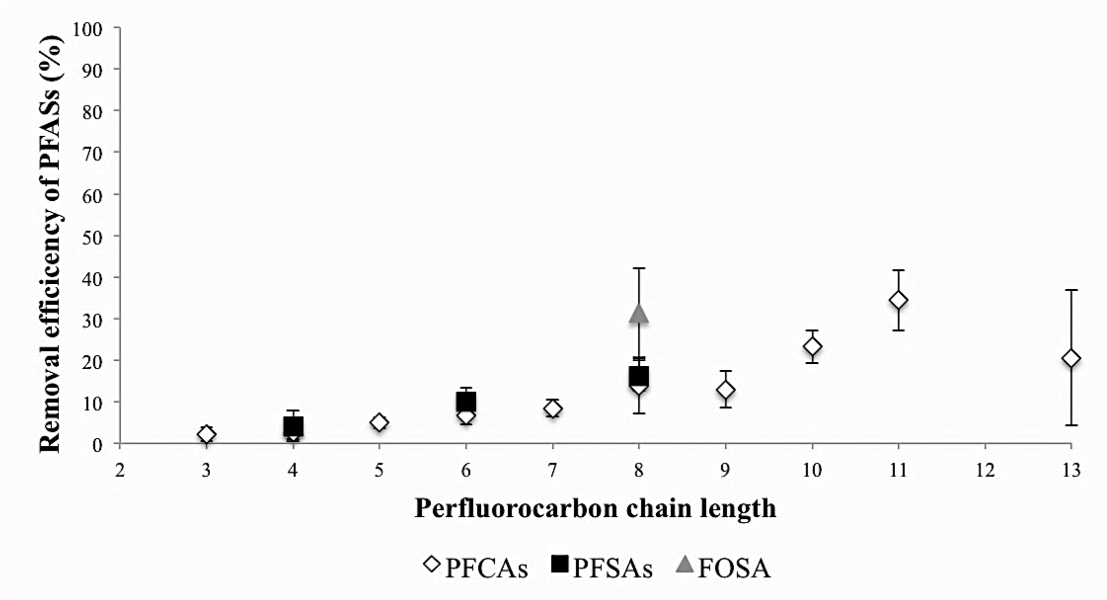


Figure 9. Average removal efficiency of individual PFASs using PAC (20 mg L^{-1}) depending on the perfluorocarbon chain length (*n*=7).

The comparison of the removal efficiency using different PAC dosage (i.e. 20, 50 and 100 mg L^{-1}) is illustrated in figure 10. An increase in removal efficiency with increased dosage can be seen, where removal of PFASs ranged from 2-41% for the lowest dose, 8% to 78% for a PAC dose of 50 mg L^{-1} and 12% to 92 % for the highest dose of 100 mg L^{-1}.

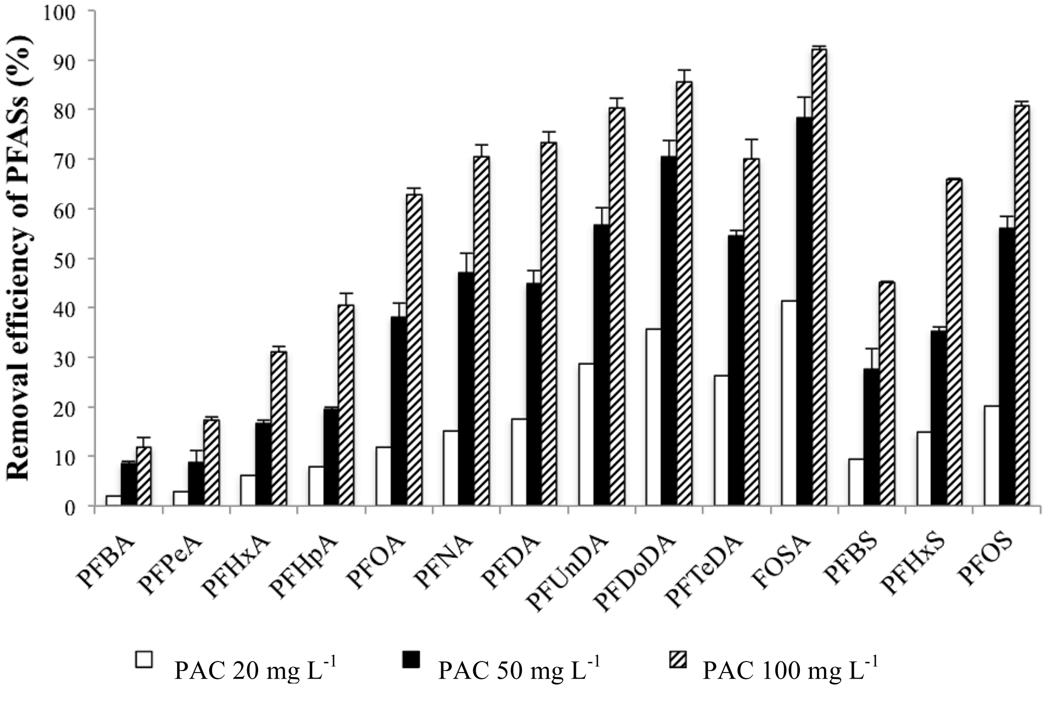


Figure 10. Average removal efficiency using different doses PAC with C4 water using PAC 20 mg L^{-1} (*n*=1), 50 mg L^{-1} (*n*=2) and 100 mg L^{-1} (*n*=2).

4.5 NF membrane

Figure 11 below illustrates removal efficiency with NF membrane for individual PFASs depending on perfluorocarbon chain length, functional group and molecular weight, the removal efficiency is presented as average of all six waters. The removal efficiency for PFCAs increases from 25 ± 7.1 % for the C_3 perfluorocarbon chain PFBA to 59 ± 7.0 % for the C_{13} perfluorocarbon chain PFTeDA. For PFSAs, the removal efficiency increased from 35 ± 13 % for the C_4 perfluorocarbon chain PFBS to 69 ± 3.0 % for the C_8 PFOS. In addition, removal efficiency depended on functional group, where PFSAs showed a higher removal than the PFCAs with same perfluorocarbon chain. For C_8 PFSA (PFOS) removal was 69 ± 3.0 % compared to C_8 FOSA with 61 ± 4.1 % and C_8 PFCA (PFNA) with 59 ± 11 %. The same pattern could be seen for PFSAs and PFCAs with perfluorocarbon chain of C_4 and C_6, with a removal for C_4 PFBS of 36 ± 13 % compared to 25 ± 7.1 % for C_4 PFPeA and for C_6 PFHxS a removal of 57 ± 9.6 % compared to 35 ± 10 % for C_6 PFHpA. Furthermore, figure 11 indicates that removal efficiency depends on molecular weight, PFSAs having a slightly higher removal efficiency compared to PFCAs with slightly higher molecular weight. PFOS, with a molecular weight of 500.16 D and removal of 69±3.0 %, whiles PFDA, with a molecular weight of 513.10 D had a removal of 57 ± 11 %.

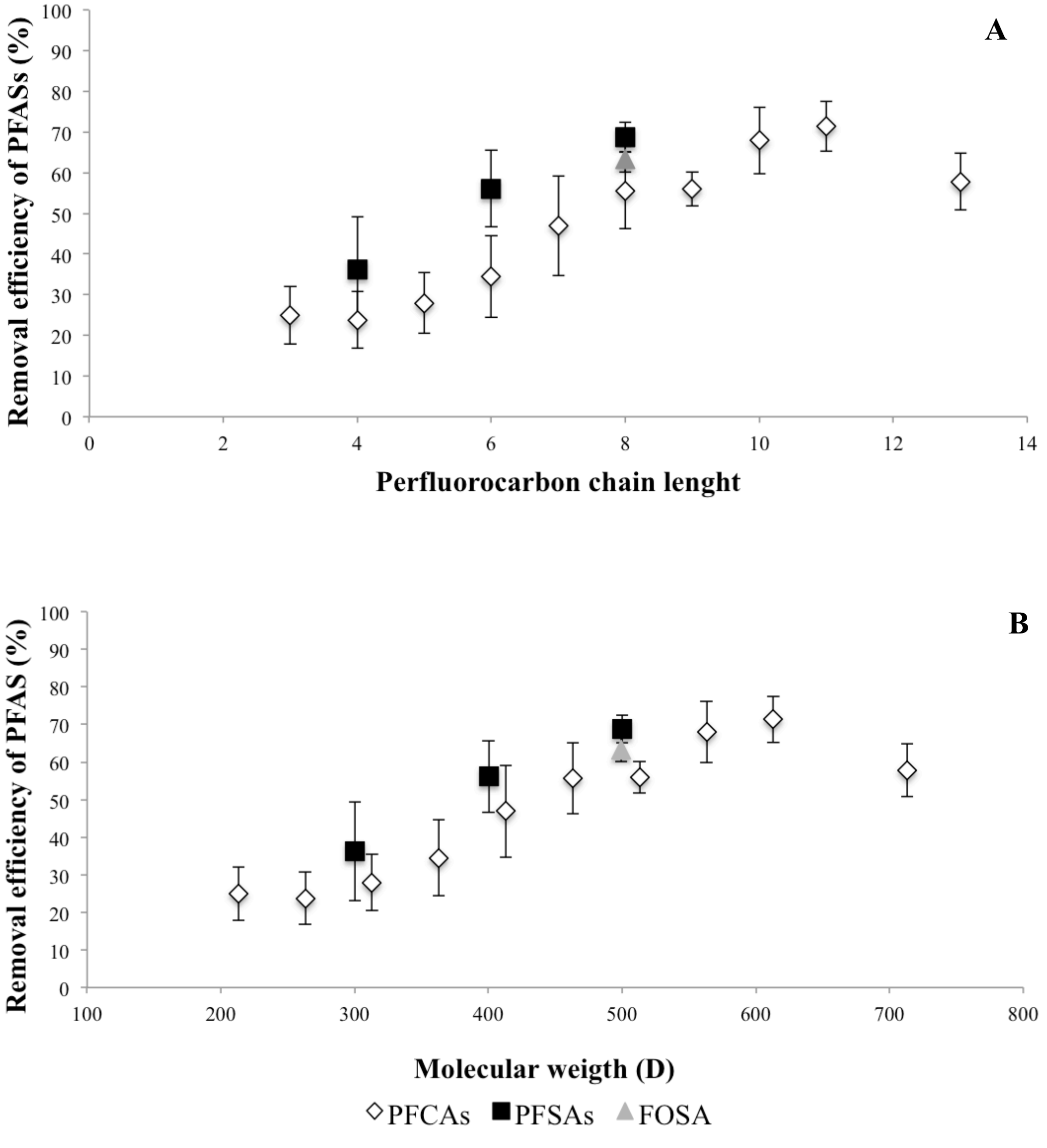


Figure 11. Average removal efficiency of individual PFASs using NF membrane depending on A) perfluorocarbon chain length (*n*=6) and B) molecular weight (*n*=6).

Figure 12 shows the removal efficiency for PFBA in permeate after stabilization period (45 min) and after 50% of treatment (~ 3h). Most of the removal took place in the first sampling of permeate, right after stabilization (45 min). For short-chained PFCAs (C≤6) a significant decrease (student's t-test $p<0.05$) in removal efficiency was obtained between the first sample taken, after stabilization, and sample taken after 50% of treatment (Appendix E). For the other PFASs no significant decrease in the removal efficiency after 50 % of treatment occurred (student's t-test $p<0.05$).

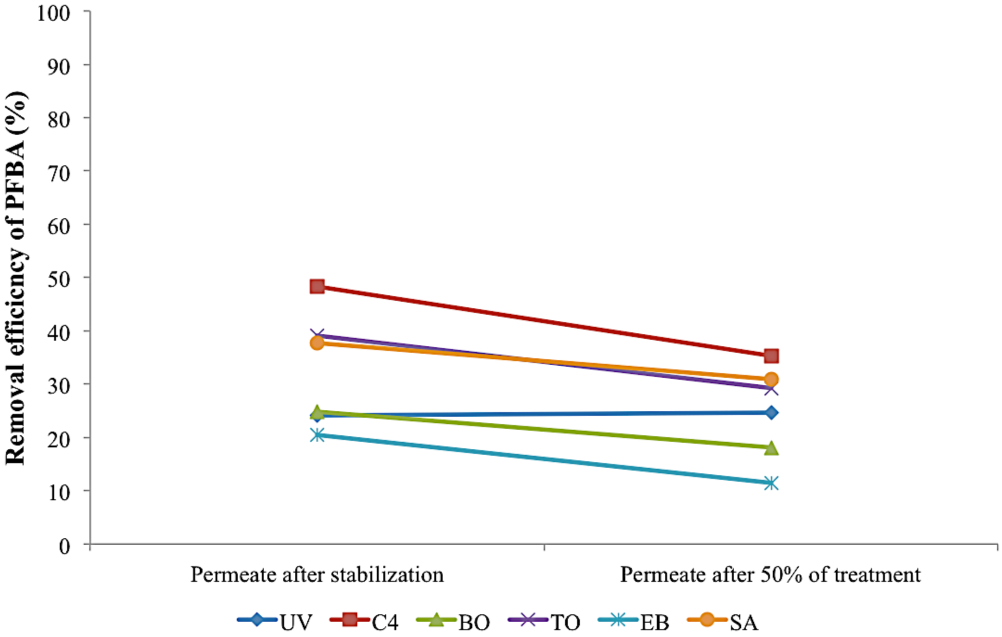


Figure 12. Removal of PFBA during different stages in treatment with NF membrane.

4.6 Comparison between different treatment techniques

The removal efficiency for individual PFASs using different treatment techniques showed a wide distribution (Figure 13). An average of all water was taken for each treatment technique. Removal efficiency ranged between 6.1 ± 2.7% and 68 ± 8.1% for MIEX®, 0.8 ± 1.0 % and 78 ± 7.7% for $FeCl_3$, 2.2 ± 1.7% and 34 ± 7.2 % for PAC (20 mg L^{-1}), and for the NF membrane the removal efficiency ranged between 24 ± 6.9 % and 75 ± 8.3%.

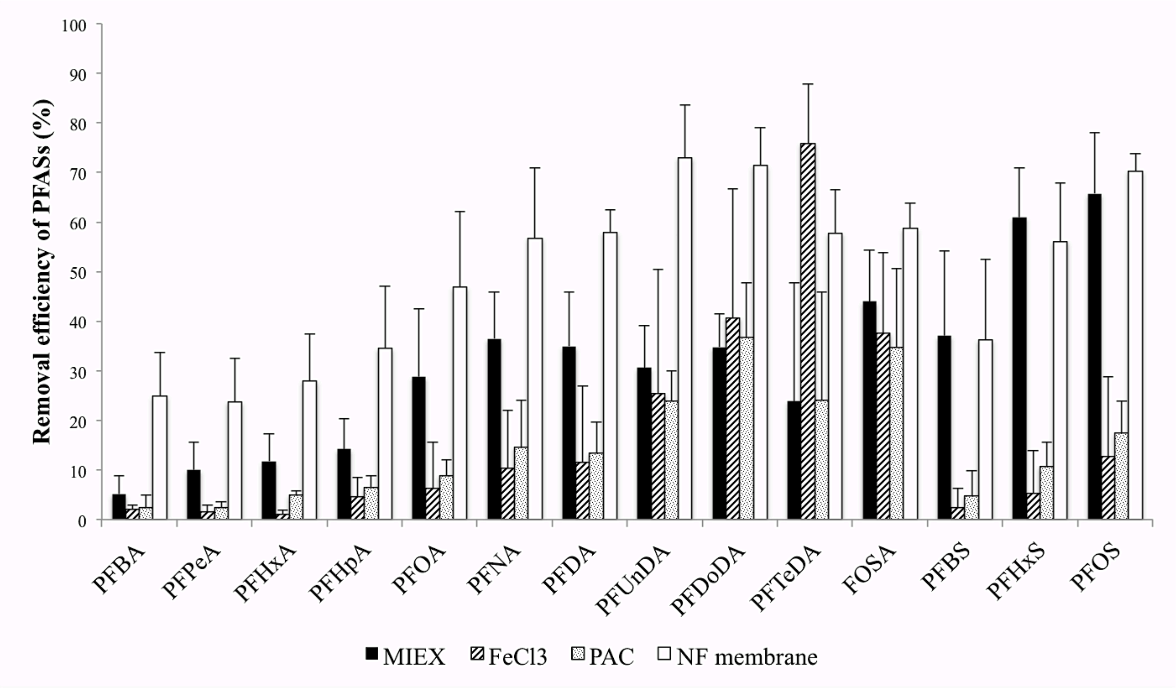


Figure 13. Removal efficiency for individual PFASs presented as average of all six waters, some with duplicates, using MIEX (*n*=8), $FeCl_3$ (*n*=8), PAC 20mg L^{-1} (*n*=7) and NF membrane (*n*=6).

4.7 Correlation of the removal efficiency with pH, Fr, HIX and absorbance of DOC (UV_{254})

The removal of PFNA, FOSA and PFOS (C_8) was correlated to the Freshness (Fr), humification index (HIX), pH and adsorption of DOC (UV254) for the six used waters (Table 5). Due to lack of time multiple linear regression were only made for three of the PFASs and there might be other trends that was not discovered in the study. Data for different characteristics were obtained from previous study by Nilsson and Wängdahl (2014) (Appendix G).

For MIEX®, a significant correlation of removal efficiency to Fr was found for FOSA and PFOS (C_8) (student t-test, $p<0.05$, Tabel 5), which show an increase in removal efficiency for lower Fr. A significant trend was also found when correlating PFNA with Fr and HIX, where low values for both Fr and HIX lead to an increase in removal efficiency of PFNA using MIEX®. For $FeCl_3$, PFNA, FOSA and PFOS correlated significantly with pH (student t-test, $p<0.05$) where removal efficiency increased when high pH. For PAC and NF membrane, the correlation with DOC characteristics was generally low. For PAC, only FOSA correlated with the UV_{254} (student t-test, $p<0.05$), where a high UV_{254} value lead to a higher removal of FOSA. For NF membrane a significant trend (student t-test, $p<0.05$) was found when correlating PFNA with HIX, which show an increase in removal efficiency when higher HIX (Table 5).

Table 5. Summary of results from statistical analysis using multiple linear regression with r^2-value from Pearson correlation and *p*-values from student's t-test comparing the removal efficiency of PFASs (%) with Freshness (Fr) and humification index (HIX) pH, and adsorption of DOC (UV254)). Factors which gave a significant correlation ($p < 0.05$) are shown in brackets above the p and r^2 value while factors with no significant correlation ($p > 0.05$) are not shown[a]

		PFNA	**PFOS**	**FOSA**
		(Fr, HIX)	**(Fr)**	**(Fr)**
MIEX®	r^2	0.97	0.67	0.62
	p	0.0002	0.03	0.02
$FeCl_3$		**(pH)**	**(pH)**	**(pH)**
	r^2	0.88	0.52	0.83
	p	0.0006	0.04	0.002
PAC			**(UV_{254})**	
	r^2	NS	0.78	NS
	p	NS	0.02	NS
NF membrane		**(HIX)**		
	r^2	0.79	NS	NS
	p	0.07	NS	NS

[a] NS =not significant

5. Discussion

In general, the removal efficiency increased with increased perfluorocarbon chain length (Figure 13). This can be seen for all PFASs and for all treatments. However, the different treatments showed slightly different curves when removal efficiency was plotted against perfluorocarbon chain length. For MIEX®, PAC and NF membrane tendencies for a sigmoid curve could be seen while for $FeCl_3$ the curve increased exponential (Figure 14).

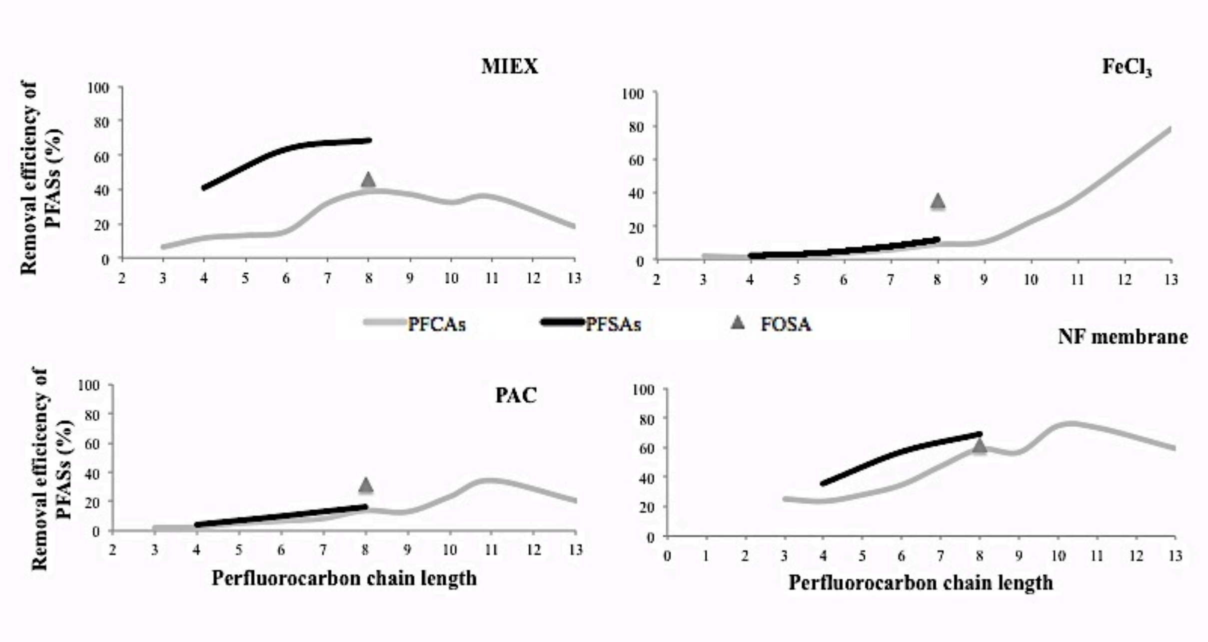


Figure 14. The differenct curves showing removal of PFCAs (grey line), PFSAs (black line) and FOSA (trangle) for all four different treatment techniques.

Removal efficiency was also dependent on the functional group where PFSAs were removed for all treatments more efficiently than PFCAs. Results from all treatment techniques showed a higher removal efficiency for PFSAs than for PFCAs. FOSA also had a tendency to be removed more efficiently than PFCAs. However, it differed between treatment techniques whether FOSA was removed more efficiently than PFSAs. When comparing PFNA, PFOS and FOSA, all with a perfluorocarbon chain length of 8 but different functional groups, FOSA had the highest removal efficiency using $FeCl_3$ and activated carbon. On the other hand, for NF membrane and MIEX®, the removal efficiency was greater for PFOS in comparison to FOSA and PFNA. The estimated pK_a values for the different PFASs increased, PFOS (pK_a = -3.27 – 0.14) < PFNA (pK_a = -0.2 – 4.2) < FOSA (pK_a = 6.2-6.5) (Benskin et al., 2012; Rayne and Forest, 2009; Goss, 2007; Zhou et al., 2009; Brooke et al., 2004). PFASs with lower pK_a values are expected to have a greater tendency to diffuse and thereby bind to the MIEX® resins and the negatively charged NF membrane. According to Ahrens (2011) FOSA has shown a strong ability to adsorb to particles, which could be an explanation for FOSA being removed more efficiently when treated with $FeCl_3$ and PAC where adsorption is the main mechanism for removal. Meanwhile, for MIEX and NF membrane the PFASs that are the most hydrophobic (FOSA<PFNA<PFOS) and having the highest MW (i.e. PFOS (MW=500.16 D), FOSA (MW=499.18D), PFNA (MW=463.09D)) were removed in greater extent.

5.1 MIEX®

The removal efficiency for PFASs differed between the different compounds using anion-exchange resins (Figure 6). This is in agreement with previous studies, showing that the treatment with anion exchangers gives higher removal efficiency for PFASs with longer perfluorocarbon chain (Appleman et al., 2013b; Deng et al., 2010). This can partly be seen for results in this study where PFASs with a perfluorocarbon chain C>6, were removed between 18-39% for PFCAs and between 6-15% for the shorted-chained PFCAs(C≤6) same trend can be seen for PFSAs (Figure 7). There seem to be a change in removal efficiency for PFCAs with a perfluorocarbon chain C_3-C_7 (from 6.1% to 32%), the removal efficiency was relatively stable from C_7-C_{11} (from 32% to 36%), and the removal efficiency decreased to 18% for PFTeDA (C_{13}). This was valid for all water types except EB. There might be two different processes for removing short-chained and long-chained PFCAs. The short-chained PFASs (low molecular weight) are capable of being removed through diffusion into the resins, and adsorb faster to the resins than long-chained PFASs (Du et al., 2014; Slunjski et al., 2000). On the other hand, the long-chained PFASs are more likely removed through hydrophobic interaction, thus the higher K_{ow} value a chemical has the more hydrophobic it is and are more easily removed through hydrophobic interaction with the MIEX® resins than chemicals with lower K_{ow} value (Rahman et al., 2013). For PFCAs, the K_{ow} value increases with increased perfluorocarbon chain length (Wang et al., 2012) (Table 1). However, the removal efficiency was relatively stable for the longer perfluorocarbon chained PFCAs. This indicates that the hydrophobic interaction has only a low influence on the removal efficiency for PFASs.

Removal efficiency was dependent on functional group where PFSAs were removed more efficiently (41-68%) than PFCAs (6–39 %). When comparing PFASs with different functional group but same perfluorocarbon chain (i.e. C_4, C_6, C_8) the removal of PFSAs was higher (41%, 63%, 69%, respectively) compared to corresponding PFCAs (12%, 16%, 39%, respectively). FOSA (C_8) was removed more efficiently than corresponding PFCA (PFNA), with an average removal of 46 ± 6.6% compared to 39 ± 6.3 % for PFNA. However, removal was higher for PFOS (C_8), with an average removal of 68 ± 8.1 %, than for FOSA. These results were expected since PFSAs are estimated to have lower pK_a values (<<0) than both PFCAs (pK_a= -0.2 – 4.2) and FOSA (pK_a= 6.2 - 6.5)(Goss, 2007; Zhou et al., 2009; Brooke et al., 2004; Benskin et al., 2012; Rayne and Forest, 2009), since low pK_a indicates that these compounds have a higher tendency to exchange with the negatively charged chloride on the MIEX® resins.

No significant trend were found between PFAS removal and DOC removal for the MIEX® treatment (student's t-test, p>0.05 for all compounds and water, Appendix B). This is also evident when comparing EB and SA, which were the two waters with the lowest DOC removal. In figure 6 it is shown that SA (DOC removal =11%) was one of the waters having overall the highest removal efficiency of PFASs though one of the water having the lowest DOC removal, while EB (DOC removal = 0 %) had the lowest removal efficiency of PFASs and the lowest DOC removal. The water EB contained a much higher amount of anions (1268 μM) than the rest of the waters (< 200 μM, Table 2). The higher content of anions might reduce the removal efficiency of PFASs due to the competition of the anions with PFASs for the sorption to the anions exchange resins (Rahman et al., (2013)).

Significant correlations were obtained when correlating FOSA and PFOS (C_8) with freshness (Tabel 5). The higher Fr value obtained the lower removal efficiency for FOSA and PFOS. Freshness is a DOC character where a high Fr value means a higher amount of fresh carbon in the water and indicates a high content of autochthonous matter (i.e. SA and EB) (Wilson and Xenopoulos, 2009). Autochthonous material are hydrophilic and therefore less able to be removed through hydrophobic interaction with the MIEX® resins. It can be expected that the removal of PFASs would increase when the competition of DOC is lower for water with high freshness value. Lowest *p*-value (student's t-test) was obtained for FOSA (p=0.02, r^2=0.62) followed by PFOS (p=0.03, r^2=0.57), meaning the trend is stronger for FOSA and least evident for PFOS in terms of correlation to freshness. This is also in relatively good agreement with the K_{ow} values for the two PFASs (log K_{ow} for FOSA =5.62, log K_{ow} for PFOS =6.43)(Wang et al., 2011) making FOSA more hydrophilic. One of the main sources for PFASs to sorb to organic matter is believed to be hydrophilic interaction (Chen et al., 2012; Jeon et al., 2011). A reason for the decrease in PFAS removal might be that PFASs that are more hydrophilic might interact more with the hydrophilic DOC and be remained in the water.

A significant trend was also obtained when correlating PFNA with both Fr and HIX (Table 5) showing a decrease in removal of PFNA with high values for both Fr and HIX. A high HIX indicates a more allochthonous and hydrophobic DOC (i.e. C4, UV, BO, TO) at the same time as high Fr value indicates autochthonous and hydrophilic DOC (i.e. SA and EB). When treating the more hydrophobic waters, hydrophobic interactions occur in greater extent between the DOC and the MIEX® resins, making the DOC matter outcompete the PFNA. However, when treating the hydrophilic waters hydrophilic interactions might occur between the DOC and the PFASs. No significant trends were seen when correlating PFOS and FOSA (C_8) with HIX. It could be expected that PFOS would also obtain a significant correlation when compared with HIX since PFOS has a higher log K_{ow} value (PFOS (log K_{ow}=6.42), PFNA (log K_{ow}=5.92) (Wang et al., 2011)), making PFOS more hydrophobic than PFNA.

5.2 Coagulation with $FeCl_3$

Results show that conventional treatment using coagulation with $FeCl_3$ has, overall, low removal efficiency (Figure 8). For PFCAs and PFSAs with perfluorocarbon chain C≤10 an average removal of 1-12% were obtained. For PFCAs with longer perfluorocarbon chain (C>9) (i.e. PFUnDA, PFDoDA and PFTeDA) as well as FOSA (C_8) the average removal increased, showing the highest average removal for PFTeDA of 78 ± 7.6%. As expected, and shown in previous studies, conventional treatment using $FeCl_3$ is not an efficient treatment technique for removing the entire range of PFASs (Xian et al 2012; Appleman et al., 2013b).

There were almost no differences in removal when comparing PFCAs and PFSAs with same perfluorocarbon chain (i.e. C_4, C_6, C_8). However, a difference in removal efficiency was observed for PFNA, PFOS and FOSA, which have different functional group. FOSA had considerably higher removal efficiency (35 ± 10%) than PFNA (9.0 ± 7.7%) and PFOS (12 ± 10%). Since adsorption is one of the most important mechanisms for removal using $FeCl_3$, FOSA with strong adsorption ability has a greater tendency to be removed (Ahrens, 2011).

No significant trend was found between PFAS removal and DOC removal using coagulation with $FeCl_3$ (student's t-test, $p>0.05$ for all compounds and water, Appendix C). In appendix C it is shown that TO and BO have the same DOC removal, 68% and 69%, but quite different removal efficiency for PFASs. For TO, PFASs ($C\leq6$) were removed between 0% to 5% and removal for PFASs ($C>6$) ranged from 0% to 89%. For BO, on the other hand, removal of PFASs ($C\leq6$) ranged from 0% to 2% and ranged between 0-60% for PFASs ($C>6$). This indicates that the DOC content has only a small influence in the removal efficiency of PFASs.

When performing the treatment with $FeCl_3$ it is crucial, in order to get high removal efficiency, to end up in acceptable pH range (4.9-5.2) when adding both the $FeCl_3$ coagulant and acid or base. The pH values for each experiment are listed in appendix C, where it is shown that for all experiments pH was within the interval desired and therefore conditions should be good for removal. Significant correlations were obtained when correlating PFNA, FOSA and PFOS (C_8) with pH (Tabel 5). The higher pH obtained the higher removal efficiency of PFNA, FOSA and PFOS. The reason for this is hard to predict when pH is not a DOC characteristic. However, a change in pH might change the charge of the DOC, making the DOC less negatively charged, an in that way have an indirect impact.

The blanks that were run with $FeCl_3$ obtained high concentrations of some PFASs (Table 3). This could be due to difficulties in cleaning the stirrers of the flocculator. Other materials, such as the beakers, where rinsed with methanol and burned in an oven at 400°C, but this could not be done with the stirrers. PFASs could then have adsorbed onto the stirrers and ending up in the blanks. However, the concentrations in the samples were at least 10 times higher compared to the blanks. The high concentrations in the blanks could be a problem if the experiments were performed at lower concentrations.

5.3 PAC

The average removal efficiency for PFASs, using a PAC dose of 20 mg L^{-1}, were rather low for all PFASs in this study, with an average removal < 35% (Figure 9). An increase in PAC dose showed an increase in removal, where for a PAC dose of 50 mg L^{-1} average removal ranged between 8.5-78 % and for a dose of 100 mg L^{-1} the average removal was between 12–92% (Figure 10). In previous studies good removal efficiency (typically >60%) was obtained when using PAC at similar doses as the lowest in this study (i.e. 25 mg L^{-1} (Hansen et al., 2010) and 30 mg L^{-1} (Yu et al., 2014)). When comparing results from this study with a previous study performed by Hansen et al., (2010), with low initial PFASs concentrations (73 ng-1.4 μg L^{-1}), much higher removal efficiency (60-90%) was achieved (Hansen et al., 2010). A reason for this could be the difference in initial DOC concentration, where for this study the DOC concentrations where in the range of mg L^{-1} (Table 2), while a much lower DOC concentration was used in the previous study (ng L^{-1}). The much lower removal efficiency, compared to study by Yu et al., (2014), might be due to the environmental relevant concentrations used in this study (μg L^{-1}), while the study performed by Yu et al., (2014) used PFAS concentrations in the range of mg L^{-1}.

Results showed that an increase in perfluorocarbon chain length leads to an increase in removal efficiency for all three doses (Figure 10). However, even at the highest PAC dose (100 mg L^{-1}), the removal efficiency for the short-chained PFASs ($C<6$)

was below 50 %. The costs would be higher for water treatment plants using a dose of 100 mg L^{-1} continuously, but it might be a strategy to use this high dose when high concentrations of PFAS can be expected and in combination with other treatment techniques.

When comparing PFASs with the same perfluorocarbon chain length but different functional group there were almost no difference in removal between PFCAs and PFSAs (Figure 9). Almost no differences in removal were obtained when comparing PFPeA (C_4) and PFBS (C_4), with an average removal of 2.5 ±1.6% and 4.2 ± 3.7% respectively. Removal of C_6 PFCA (PFHpA) was also similar to C_6 PFSA (PFHxS), with an average removal of 6.6 ±2.1% and 9.9 ±3.5% respectively. Though, a difference could be seen when comparing PFASs with C_8 (i.e. PFNA, PFOS, FOSA). FOSA had considerably higher removal efficiency (31 ±11%) than PFOS (16 ±3.7%) and PFNA (14 ±6.7%). FOSA is predicted to have a much higher pK_a value (pK_a= 6.2 - 6.5) than PFOS (pK_a<<0) and PFNA (pK_a= -0.2 – 4.2) (Benskin et al., 2012; Rayne and Forest, 2009; Goss, 2007; Zhou et al., 2009; Brooke et al., 2004). FOSA has also shown to bind very strongly to particles, which could be a reason for the much higher removal (Ahrens, 2011).

The removal efficiency of PFASs varied between the different water types (C4=2.0-41%, UV=3.3-44%, BO=0.0-56%, TO=3.1-49%, EB=2.0-45%, SA=0.0-20%) even though all waters had about the same low removal of DOC with a range between 0 to 4 % (Appendix D). No significant trend was found between PFAS removal and DOC removal using PAC (student's t-test, $p>0.05$ for all compounds and water, Appendix D). However, the difference in removal between the different waters might be an indication that removal is dependent on the characteristics of the waters. It would be expected that waters containing hydrophobic DOC matter (i.e. C4, UV, BO, TO) would have lower removal efficiency due to the ability that active carbon possesses, to strongly sorb to hydrophobic organic compounds (Hansen et al., 2010). Contrarily to this, results show that these hydrophobic waters had the same or even higher removal efficiency than the hydrophilic waters (i.e. SA, EB) (Appendix D). When comparing removal efficiency of waters SA and EB, both hydrophilic and with a DOC removal of 0%, the removal of PFASs varied. Removal of PFASs (C>6) ranged from 0% to 20% for SA and 14% to 45% for EB (Appendix D). This indicates that the characteristics of the water might play an important part regarding removal efficiency. A previous study performed by Chowdhury et al., (2012) has shown that the concentration of DOC was considered to be the main influence factor on the adsorption of PFAS. When treating other organic compounds with PAC, same tendencies have been seen where the removal efficiency has been reduced due to the competition with organic matter (Appleman et al., 2013a). Since removal efficiency was not as high as in previous studies, this might be an indication that DOC concentrations may have had a significant influence.

No significant correlations were obtained when correlating PFNA, FOSA and PFOS (C_8) with Fr, HIX or pH (Tabel 5). However, a significant correlation was obtained when correlating FOSA with UV_{254} where higher UV_{254} values lead to a higher removal of FOSA. A low UV_{254} value indicated hydrophilic DOC (Machenbach, 2007), making the less hydrophilic waters (i.e. C4, UV, BO, TO) remove FOSA in greater extent. Activated carbon has sown the ability to strongly sorb hydrophobic organic compounds (Hansen et al., 2010). The hydrophobic DOC might sorb to the

PAC outcompeting the FOSA. However, no significant trends were seen when correlating PFOS and FOSA with UV_{254} making it hard to draw any conclusions.

When using the flocculator for the PAC experiment, the powder initially had a tendency to stick to the stirrers, after time less and less powder could be seen on the stirrers but there is still a risk not all PAC was active during the treatment.

5.4 NF membrane

The removal efficiency using NF membrane showed the highest removal efficiency of all treatments (24-75%) (Figure 11). Removal efficiency increased with increased perfluorocarbon chain, for short-chained PFASs ($C \leq 6$) the removal ranged in average between 24% and 57% while for long-chained PFASs ($C > 6$) average removal ranged between 47% and 75% (Figure 11). Results from previous studies indicate good removal efficiency (i.e. removal >90%), when using NF membrane (Appleman et al., 2013a; Tang et al., 2007). When comparing results from this study with a previous study performed by Appleman et al., (2013a), with low initial PFAAs concentrations (1 $\mu g\ L^{-1}$) and using both deionized water and artificial ground water, much higher removal efficiency (>93% for both water types) were found in the previous study. The study performed by Tang et al (2007) also obtained a higher removal (90-99%) for PFOS but in this study the initial PFOS concentrations was much higher (10 $mg\ L^{-1}$). As mentioned before, the low (more environmental relevant) concentrations of PFOS used for spiking in this study could be the reason for the lower removal efficiency compared to Tang et al (2007). This indicates that the removal efficiency of PFASs using NF membrane is concentration dependence and thus a higher sorption kinetic for higher PFAS concentrations under non-equilibrium conditions.

Removal efficiency was dependent on the functional group where PFSAs were removed in greater extent than PFCAs and FOSA when comparing PFASs with same perfluorocarbon chain. PFOS had an average removal of 69 ± 3.0%, FOSA of 61 ± 4.0% and PFNA of 59 ± 11%. This could be explained by PFOS having both higher MW (500.16 D) and higher log K_{ow} value (6.43) compared to PFNA (MW= 463.09 D, log K_{ow}=5.92) and FOSA (MW=499.18 D, log K_{ow}=5.62) (Wang et al., 2011). A higher MW makes the compound more prone to remain in the feed since the removal is dependent on MWCO.

Since the efficiency of the NF membrane is categorized by the MWCO it would be expected that there would be a change between the compounds that have a smaller MW (500D), these would pass through the membrane and the larger compounds would be blocked by the pores of the membrane. Since no change can be seen in the degree of removal efficiency at MW ≥500 D, it can be assumed that there are other factors besides MWCO contributing to the removal. The membrane has a negatively charged surface; this should expose the negatively charged PFASs to a repulsive force when they come in contact with the membrane. If the membrane would have had a positively charged surface it is possible that removal would be higher when an attraction between PFASs and the membrane could occur and contribute to the removal. The membrane is hydrophilic making it possible for hydrophilic interactions between the membrane and the hydrophilic functional group of the PFASs. It is possible that this interaction is just as important as the MWCO. The log K_{ow} value is estimated to be lower for the short-chained PFASs, making them more hydrophilic

(Table 1). It is possible that the short-chained PFASs are partly removed through hydrophilic interaction.

PFSAs have a slightly higher removal efficiency compared to the PFCAs with similar MW (Figure 11). PFHxS (MW= 400.14D) with an average removal of 60 ± 9.6% was almost removed in the same extent as PFNA (MW=463.09), with an average removal of 59 ± 11%. PFOA (MW=413.08) with a molecular weight similar to PFHxS are removed in less extent (47 ± 12%) compared to PFHxS (60 ± 9.6%). This shows that MWCO might not be the only factor, which has an influence on the removal efficiency. One reason for this might be that the PFSAs have lower K_{ow} values and are more hydrophilic than PFCAs with the same MW, making the tendency for hydrophilic interaction greater for PFSAs.

No significant trend (student's t-test, $p>0.05$ for all compounds and water) could be seen for correlation between PFAS and DOC removal (Appendix E). However, a significant trend was obtained when correlating PFNA with HIX (Tabel 5). A high HIX lead to an increase in the removal efficiency of PFNA. A high HIX indicates a more allochthonous material (i.e. C4, UV, BO, TO) and a more hydrophobic DOC. For water with more hydrophobic DOC, the hydrophobic part of PFNA could interact with the hydrophobic DOC forming particles that might have a too large MW to pass through the membrane and in this way remain in the feed (Chen et al., 2012; Jeon et al., 2011). However, no significant trends were seen when correlating PFOS and FOSA (C_8) with HIX making it hard to draw any conclusions.

The blank that was run though the membrane obtained high concentrations of PFASs (Table 3). This may be an indication of PFASs being adsorbed onto tubes and on the membrane, since the blank were run treating some of the spiked waters. Between each treatment the entire module was cleaned with a cleaning solution (i.e. 500 ppm of NaOCl), but this was only done to prevent algae growth in the membrane and to prevent the membrane from getting clogged. It seems that PFASs sorbed to tubes and walls were not sufficiently removed during the cleaning, which needs to be considered for future studies. However, for this study the average concentrations in the blank was, for most compounds, less than 10 % of the concentrations obtained in the samples. The concentrations of the blank are therefore considered to negligible in terms of impact on the samples. For future studies, it is recommended to improve the cleaning procedure and to run a blank between each treatment to see exactly how much is being adsorbed to the materials.

The permeate flow through the membrane was constant during the treatment process (i.e. 0.71-0.87 L h^{-1} depending on water type), which indicates that probably no fouling occurred during the treatments (Appendix E). Figure 12 shows the different removal efficiencies in permeate between sampling after stabilization and sampling after 50% of treatment. The last samples taken (i.e. after 50% of treatment (~3 h)), were used for all results in this study where removal efficiency is presented. A significant decrease in removal efficiency was obtained for short-chained PFCAs ($C \leq 6$) (Appendix E). This means that for some PFASs, the removal was somewhat higher in the permeate right after stabilization period than what is shown in the figures. Once the treatment with the NF membrane began, the water volume in the feed tank decreased while the concentration of PFASs increased in the feed tank. It might be possible that the decrease in removal efficiency between the first permeate sample and the last is due to this increase of PFAS concentration in the feed tank, whereas the NF membrane cannot filtrate the increasing concentration and maybe the hydrophilic interactions will decrease due to increased concentration. A better cleaning between each treatment might have exhibited the same removal efficiency or a higher removal in the last samples taken (i.e. after 50% of treatment (~3 h)) as in the samples taken after stabilization period (45 min).

5.5 Comparison between the different treatment techniques

The average removal efficiency varied a lot between the different treatment techniques (Figure 13). Overall, NF membrane exhibited the highest removal, ranging from 24 ± 6.9 % to 75 ± 8.3%. The treatment with NF membrane was also the only technique that had an average removal of short-chained PFASs ($C \leq 6$) >20%. However, even though NF membrane exhibited the highest removal of PFASs, this technique also displayed high concentrations in blanks, making the cleaning of the membrane very important. When deciding what type of treatment to use it is important to also consider also the cost of each treatment. To implement a better cleaning technique for the NF membrane is necessary but this might contribute to membrane being a more costly technique, making it more cost-efficient to use PAC at the highest dose (100 mg L^{-1}) or using MIEX® resins with a higher dose instead. One option is also to combine different techniques, maybe first run the water through membrane and later on treat the water with MIEX resins. However, this would also be a rather expensive way of treating the water.

Since four of the waters contained hydrophobic DOC (i.e. C4, UV, BO and TO) and two contained hydrophilic DOC (i.e. EB and SA), it is possible that these DOC compounds would compete with PFASs for adsorption and places to bind to in the different treatment techniques. The PFASs with the lowest K_{ow} value (i.e. PFBA ($\log K_{ow}$= 2.82 – 2.91), PFPeA ($\log K_{ow}$=3.43 – 3.69), PFBS ($\log K_{ow}$= 3.90)(Rayne and Forest (2009); Wang et al (2011)) should have a higher tendency to form a hydrophilic interaction with DOC matter in EB and SA, and thus should have a lower removal efficiency for these water types. On the other hand, the more hydrophobic PFASs (i.e. PFTeDA ($\log K_{ow}$= 8.90), PFDoDA ($\log K_{ow}$= 7.77), PFUnDA ($\log K_{ow}$= 7.15)) (Wang et al (2011)) should interact with the hydrophobic DOC matter in C4, UV, TO and BO. However, no trends for removal efficiency and water type were found (Appendix B-E).

When comparing $FeCl_3$ and PAC (20 mg L^{-1}), two techniques where the main mechanism for removal is adsorption, similar trend could be seen in removal, where the removal efficiency of PFASs, except for removal of PFTeDA, ranged from 0.8% to 37% for $FeCl_3$ and 2.2% to 34% for PAC (figure 8 and 9). The two treatments exhibited quite similar removal efficiency even though the removal of DOC for the treatments was very different. DOC removal with $FeCl_3$ ranges between 31-82%, while removal with PAC ranged between 0-4%. This indicates that removal of PFASs is not dependent on DOC removal.

Some PFASs might interact with the DOC (Chen et al., 2012; Jeon et al., 2011) and form colloids during treatment with MIEX®, $FeCl_3$ and PAC. However, these colloids might not be large enough to be removed through sedimentation and remain in the water. In this way, they would not be able to interact with the resins, $FeCl_3$ or activated carbon. This could be a reason why the NF membrane technique had a higher removal efficiency of short-chained PFASs than the other techniques. If these colloids would form they might be too large to be able to pass through the membrane.

Results on DOC concentrations and DOC removal were obtained from a master study performed by Nilsson and Wängdahl (2014) at the same time and in the same manner as this study. One source of error could be possible differences in pH and temperature between this study and the study performed by Nilsson and Wängdahl, which in turn could affect the removal efficiency for DOC. However, the source of error is considered to be rather minor and should not contribute to unreliable evaluation of results.

Results would be more reliable if there had been more replicates done for each water and treatment. In this study only batch-tests were performed which only gives a snapshot of reality and all experiments were performed in laboratory environment. It would be desirable to see how these techniques would perform in large-scale pilot-tests. Results might differ when the treatment processes are upscaled to normal size. For the NF membrane treatment a new membrane was used. There is always a small risk that over time DOC would affect this membrane. However, if the cleaning of the membrane is done adequately, this should not affect the removal capacity. The MIEX$^{®}$ used, on the other hand, provides a better understand regarding the method's expected capacity since it were resins that had already been used.

6. Conclusions

Perfluoroalkyl substances are a group of compounds with different chemical properties depending on perfluorocarbon chain length and functional group. In this study, the focus has been set on three PFAS classes, i.e. PFCAs, PFSAs and FOSA. Removal efficiency for six different water types containing different DOC was investigated using four different treatment techniques including MIEX®, $FeCl_3$, PAC and NF membrane. For all techniques, removal efficiency depended on both the perfluorocarbon chain length as well as functional group.

Results have shown a general increase in removal efficiency with increasing perfluorocarbon chain length for PFCAs and PFSAs. Removal efficiency also depended on functional group. This is in good agreement with the first of the hypotheses for this study that stated that the removal efficiency for PFASs would differ depending on perfluorocarbon chain length and functional group. PFSAs and FOSA were removed in greater extent than PFCAs when comparing compounds with the same perfluorocarbon chain length. This was applied for all treatment techniques. Meanwhile, when comparing C_8 PFSA (PFOS) and C_8 FOSA a difference in removal was seen between the different techniques. FOSA had a higher average removal than PFOS when using $FeCl_3$ and PAC, while when using MIEX® and NF membrane PFOS was removed in greater extent than FOSA.

No significant trend could be found regarding the removal efficiency and the content of DOC in the waters (Appendix B-E) which was assumed in the second hypothesis. However, some correlations were found between the DOC character and the removal efficiency of PFNA, FOSA and PFOS (Table 5). However, more statistical analysis is needed for the other PFASs, which could not be performed in this study due to the lack of time. It is interesting to note that the removal efficiency for all treatments in this study was lower than previous studies reported (Appleman et al., 2013a; Deng et al., 2010; Hansen et al., 2010; Tang et al., 2007). The previous studies were performed with low DOC concentrations or in absence of DOC, whereas this study was performed with natural waters of varying DOC, which indicates that the DOC might have reduced the removal efficiency for PFASs. Another explanation for the lower removal efficiency in this study compared to other studies is that low concentrations of PFASs (i.e. more environmental relevant concentrations) were used in this study compared to previous studies (Appleman et al., 2013a; Deng et al., 2010; Hansen et al., 2010; Tang et al., 2007). However, further studies regarding the correlation of the removal efficiency of PFASs with the DOC characteristics are needed to get a better insight between the interactions of the DOC character and PFASs.

When comparing different treatment techniques it is more relevant to look at average removal efficiency for all six waters instead of comparing the different waters separately. The water being treated in drinking water treatment plants usually contains a mixture of DOC character. It can be concluded that the NF membrane exhibits the best removal efficiency for both short- and long chained PFASs (in average, 51%). This was not according to the hypothesis of this study, which stated that PAC would be the treatment exhibiting the highest removal. However, the NF membrane technique has a low removal efficiency for the short-chained compounds (24-57%). A combination of different treatment techniques could be an option to increase the removal efficiency. For WWTPs, where coagulation with $FeCl_3$is already a technique that is commonly used, it would be desirable to combine coagulation with some other treatment. Combining membrane with activated carbon or MIEX® could be a way of removing more of the short-chained PFASs in drinking water. A larger PAC dose can also be used when concentrations are expected to exceed normally encountered levels.

Since short-chained PFASs (C≤6) seem to be difficult to remove from drinking water it would be good to try to reduce the occurrence of these PFASs. However, this is difficult to achieve when there are still many precursors being produced that have the ability to degrade to short-chained PFASs (Benskin et al., 2013). It is therefore crucial to further develop and investigate methods regarding the removal of PFASs. It is also important to work towards a more strict regulation regarding production and emission, as well as working toward a phase out of these compounds.

More research is needed to understand the interaction between PFASs and DOC in water and how removal efficiency is affected by the presence of DOC. Future studies are also needed to investigate the influence of other factors such as pH, conductivity, alkalinity etc. It would be desirable to carry out studies where only one type of water is being used but with different concentration of DOC. Since PFAS contaminated water is both a growing and critical problem it is necessary to find treatment techniques with the ability to remove >85% of all PFASs, not only the long chained PFASs. Each treatment technique used in this study exhibited generally poor removal efficiency (< 78%). It is still essential to find both a technical but also cost-effective way to remove PFASs from drinking water and wastewater. Therefore, more studies should be carried out combining different treatment techniques to find a way of removing short chained as well as long chained PFASs.

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8. Appendix

Appendix A – Positive Control

Positive controls (n=3) were performed for the experiment using the flocculator, but no MIEX$^{®}$/FeCl$_3$/PAC was added to the beakers (Table A1). Positive controls (n=3) were also performed for the NF membrane treatment method (Table A2). Water was run through the membrane machine without the membrane. The positive controls were used to compensate any loss of compounds due to adsorption to the walls of the beakers, tubing, the flocculator or evaporation into the air.

Table A1. Results from running positive control for treatment with flocculator (*n*=3). 0 refers to concentration in sample prior to treatment. Average PC is the mean value between PC.1 and PC.2. PC.3 was excluded since it contained elevated concentrations.

	0 (ng L^{-1})	**PC.1 (ng L^{-1})**	**PC.2 (ng L^{-1})**	*PC.3 (ng L^{-1})*	**Average PC (ng L^{-1})**	**Conc. lost in PC (ng L^{-1})**
PFBA	4704	4389	4671	*9082*	4530	173
PFPeA	3600	3269	3544	*6301*	3406	193
PFHxA	3665	3424	3694	*6437*	3559	106
PFHpA	3572	3304	3511	*6088*	3407	165
PFOA	4214	3929	4328	*8612*	4128	86
PFNA	4451	3898	4413	*9537*	4156	295
PFDA	2381	2192	2471	*3544*	2332	49
PFUnDA	2033	2083	2383	*3484*	2233	0
PFDoDA	1803	2054	2452	*3538*	2253	0
PFTeDA	590	618	962	*1301*	790	0
FOSA	2866	3336	3731	*8568*	3534	0
PFBS	4164	3745	4130	*8357*	3938	226
PFHxS	3338	3227	3709	*6456*	3468	0
PFOS	2341	2108	2441	*5034*	2274	66

Table A2. Results from running positive control with NF membrane. 0 refers to concentration in sample prior to treatment.

	0 (ng L^{-1})	**PC.1 (ng L^{-1})**	**PC.2 (ng L^{-1})**	**PC.3 (ng L^{-1})**	**Average PC (ng L^{-1})**	**Conc. lost in PC (ng L^{-1})**
PFBA	4102	3848	3594	3651	3697	404
PFPeA	3320	2925	3007	3025	2986	335
PFHxA	3271	2946	2894	2925	2922	349
PFHpA	3200	3003	2945	2948	2965	235
PFOA	3721	3284	3184	3182	3217	504
PFNA	3594	3171	3114	2802	3029	565
PFDA	2142	1815	1771	1599	1728	413
PFUnDA	1768	1262	1304	1131	1232	536
PFDoDA	1485	907	888	794	863	622
PFTeDA	673	380	386	350	372	301
FOSA	2386	767	0	0	256	2130
PFBS	3947	3072	3078	3222	3124	823
PFHxS	3674	2963	2713	2725	2800	873
PFOS	1948	1592	1573	1402	1522	425

Appendix B - MIEX®

The amount MIEX® resins used in the experiment were prepared a day before, where the doses were measured into 15 mL tubes and then stored in refrigerator (Figure B1). Figure B2 shows two off the beakers during the treatment with MIEX®.

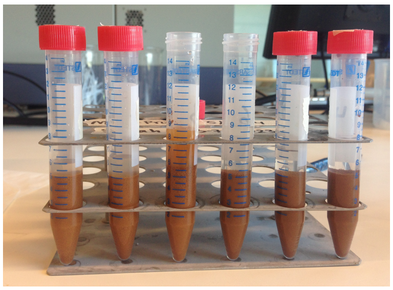

Figure B15. Tubes filled with approximately 5 mL of MIEX®. For the tube in the middle, MIEX® had just been added and had not yet settled.

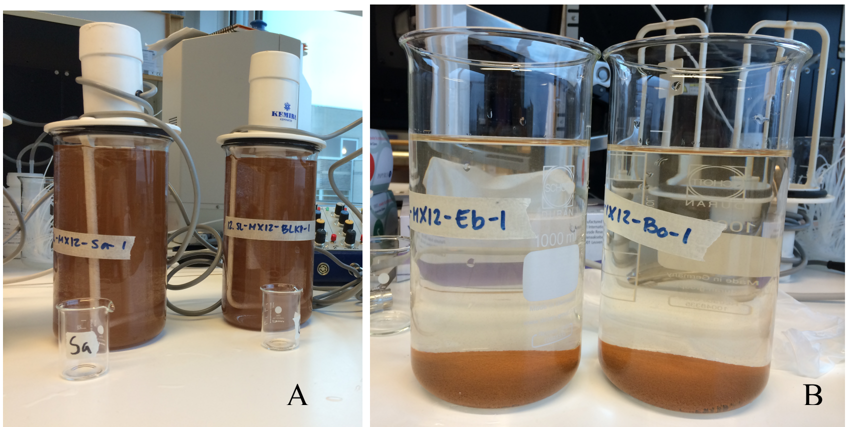

Figure B2. Figure A shows MIEX® experiment during stirring with flocculator. Figure B shows samples after 15 min of sedimentation.

Results showing pH values, the amount of water used for the treatment and amount of samples taken after treatment with MIEX® (Table B1). There are almost no changes in pH when comparing pH values before treatment (zero sample) and after treatment.

Table B1. Measured pH, weight in beaker and weight of the sample for each water type using MIEX®.

Sample	Date	pH	Weight water in beaker (g)	Weight water in sample (g)	MIEX (mL)
Eb-0	2014-02-27	7.2	-	86	-
Bo-0	2014-02-27	7.4	-	88	-
To-0	2014-02-27	7.4	-	85	-
Sa-0	2014-02-27	7.6	-	77	-
UV-0	2014-02-27	7.3	-	86	-
C4-0	2014-02-27	7.2	-	84	-
Eb-1	2014-02-27	7.3	1000	84	4
Bo-1	2014-02-27	7.4	1000	79	5
To-1	2014-02-27	7.5	1000	84	3.5

Sa-1	2014-02-27	7.5	1000	84	5
UV-1	2014-02-27	6.5	1000	86	5
UV-2	2014-02-27	6.8	1000	85	5
C4-1	2014-02-27	7.0	1000	84	5
C4-2	2014-02-27	7.0	1000	84	5

Removal efficiency of PFAS in correlation with removal of DOC for each water type, when using MIEX$^{®}$ (Figure B3).

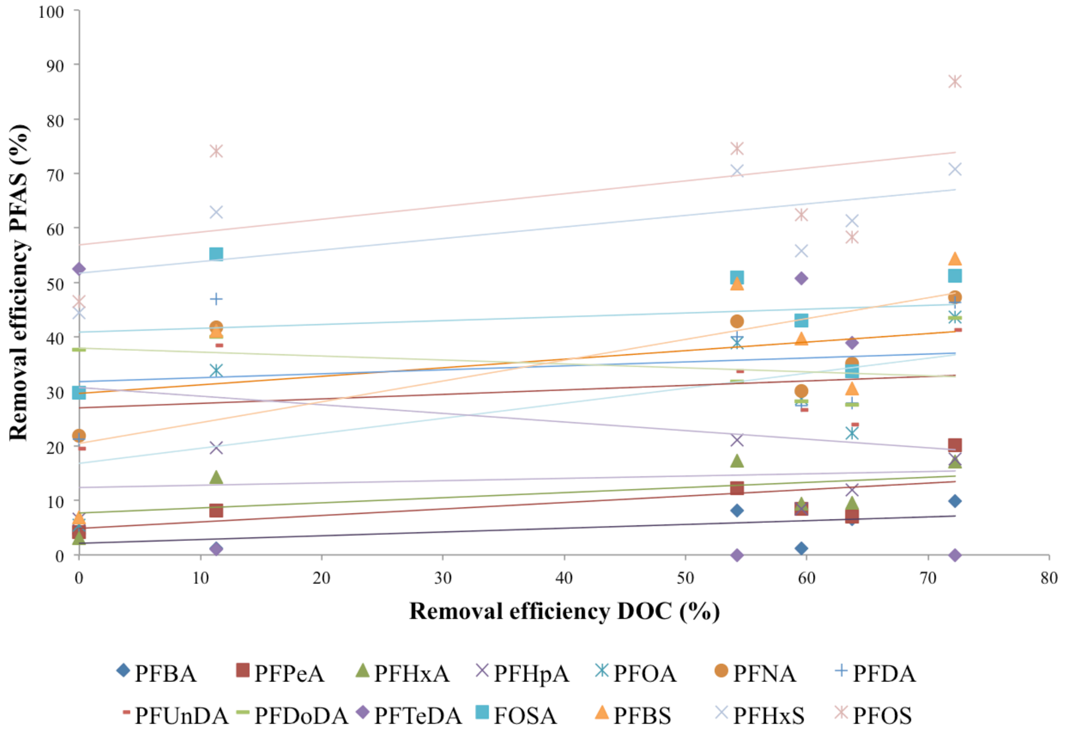

Figure B3. Removal efficiency for PFASs plotted against removal efficiency of DOC using MIEX$^{®}$ resins (n=6).

Results from statistic test, student t-test and Pearson test, looking for significant trend when comparing PFASs removal with DOC removal using MIEX$^{®}$ (Table B2).

Table B2. Summery of results from statistic test with r-value from Pearson test and p-values from student's t-test when comparing removal efficiency of PFASs (%) and DOC removal (%) for MIEX$^{®}$ treatment.

Compound		
	r	p
PFBA	0.574	0.234
PFPeA	0.64	0.171
PFHxA	0.512	0.299
PFHpA	0.208	0.692
PFOA	0.609	0.2
PFNA	0.503	0.31
PFDA	0.201	0.703
PFUnDA	0.29	0.577
PFDoDA	-0.332	0.52

PFTeDA	-0.182	0.73
FOSA	0.205	0.697
PFBS	0.677	0.139
PFHxS	0.643	0.168
PFOS	0.449	0.372

Appendix C - $FeCl_3$

Performing treatment with flocculator for water C4 using $FeCl_3$ (Figure C1).

Figure C1. Figure A shows $FeCl_3$ experiment during slowly stirring with flocculator. Figure B shows samples after approximately 30 min of sedimentation.

Results from measuring pH, the amount of water used for the treatment and amount of samples taken after treatment with $FeCl_3$ (Table C1). The pH values for all samples where in within the range required for best removal.

Table C1. Measured pH, weight in beaker, weight in sample and dose PIX for each water type using $FeCl_3$.

Sample	Date	pH	Weight water in beaker (g)	Weight in sample (g)	Dose PIX (µL)
C4-0	2014-03-07	7.0	-	84	-
UV-0	2014-03-10	7.2	-	90	-
To-0	2014-03-11	7.0	-	83	-
Sa-0	2014-03-21	7.4	-	80	-
Eb-0	2014-03-12	7.2	-	83	-
Bo-0	2014-03-11	6.9	-	87	-
C4-1	2104-03-07	5.0	700	87	28.7
UV-1	2104-03-10	5.0	700	82	28.7
To-1	2014-03-11	4.9	700	89	19.3
Sa-1	2014-03-21	4.8	700	85	28.7
Eb-1	2014-03-12	4.9	700	87	19.5
Eb-2	2014-03-12	5.3	700	87	19.5
Bo-1	2014-03-11	5.0	700	85	28.7
Bo-2	2014-03-11	5.1	700	88	28.7

The removal efficiency for PFASs using $FeCl_3$ showed a wide distribution ranging from 0-100% removal (Figure C2). The different water types (i.e. *C4, UV, BO, TO,* *EB, SA*) showed varying removal efficiency for individual PFASs and also for the removal of DOC ranging from 31% (EB) to 82 % (C4).

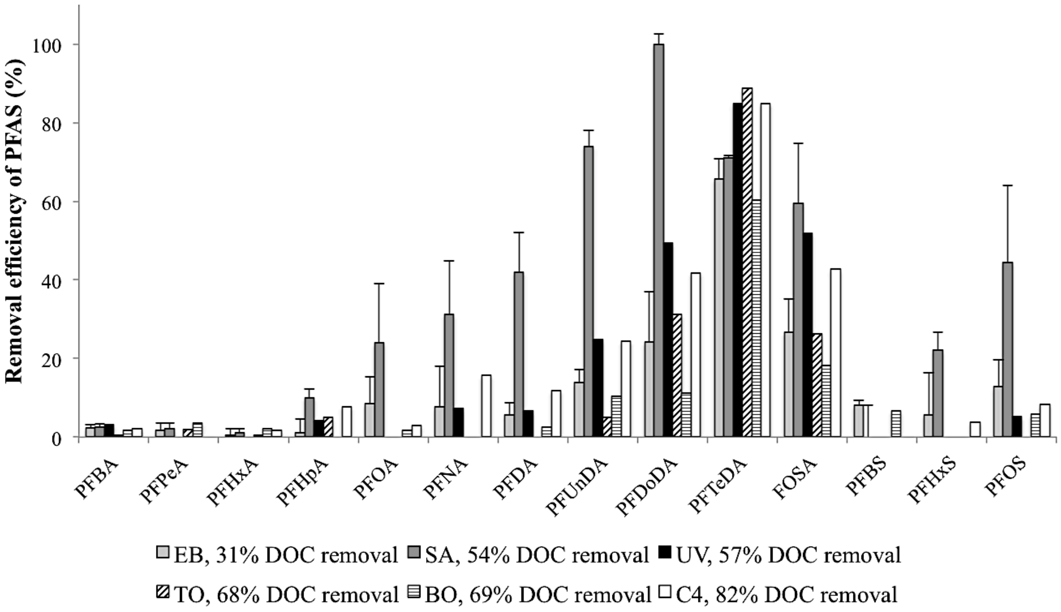

Figure C2. Removal efficiency for PFASs in different water types when treated with $FeCl_3$. Waters are presented with corresponding DOC removal in ascending order. Average removal efficiency of individual PFASs for treatment with water BO and E (n=2).

Removal efficiency of PFAS in correlation with removal of DOC for each water type, when using $FeCl_3$ (Figure C3).

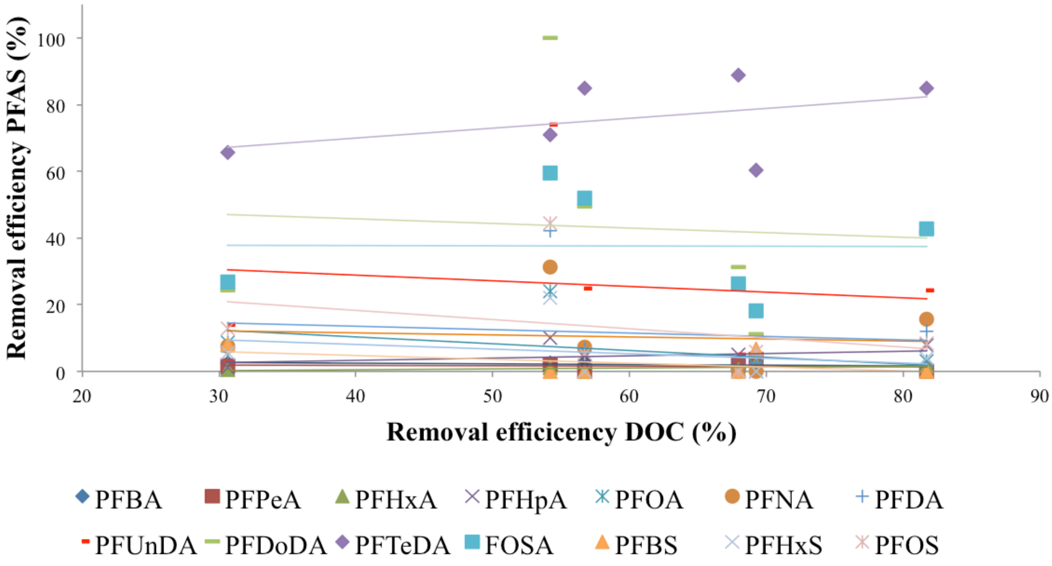

Figure C3. Removal efficiency for PFASs plotted against removal efficiency of DOC using $FeCl_3$ (n=6).

Results from statistic test, student t-test and Pearson test, looking for significant trend when comparing PFASs removal with DOC removal using $FeCl_3$ (Table C2).

Table C2. Summary of results from statistic test with r-value from Pearson test and p-values from student's t-test when comparing removal efficiency of PFASs (%) and DOC removal (%) for $FeCl_3$ treatment.

Compound		
	r	p
PFBA	-0.394	0.44
PFPeA	-0.13	0.806
PFHxA	0.568	0.24
PFHpA	0.312	0.547
PFOA	-0.385	0.451
PFNA	-0.091	0.864
PFDA	-0.115	0.828
PFUnDA	-0.119	0.822
PFDoDA	-0.078	0.883
PFTeDA	0.437	0.386
FOSA	-0.008	0.988
PFBS	-0.528	0.282
PFHxS	-0.283	0.587
PFOS	-0.3	0.564

Appendix D - PAC

The different PAC doses were weighted on aluminum foil so it could easily be added into the water (Figure D1). The PAC was added to the different beakers and with the help of a flocculation machine the sample was stirred.

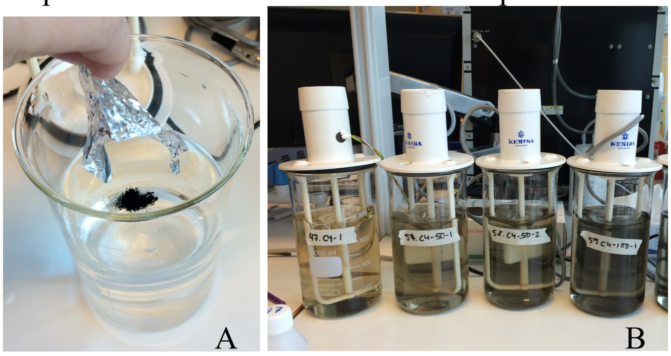

Figure D1. Figure A shows how the PAC was packed in foil and added into the beakers. Figure B shows how the samples from C4 are being stirred with the flocculator for three different dosage, 20 mg L^{-1} to the left. 50 mg L^{-1} the two beakers in the middle and 100 mg L^{-1} in the right beaker.

Results from measuring pH, the amount of water used for the treatment and amount of samples taken after treatment with PAC (Table D1).

Table D1. Measured pH, weight in beaker, weight in sample and PAC dose for each water type using PAC.

Sample	Date	pH	Weight water in beacker (g)	Weight in sample (g)	PAC dose (mg)
C4-0	2014-03-26	6.9	-	85	-
UV-0	2014-03-19	7.2	-	86	-
Sa-0	2014-03-20	7.6	-	73	-
Bo-0	2014-03-19	7.0	-	84	-
Eb-0	2014-04-02	7.2	-	86	-

To-0	2014-04-02	7.5	-	90	-
Eb-1	2014-04-02	7.4	700	83	9.5
To-1	2014-04-02	7.6	700	76	9.5
C4-1	2014-03-26	6.8	700	87	14
UV-1	2014-03-19	7.1	700	78	14
Bo-1	2014-03-19	6.9	700	76	14
Sa-1	2014-03-20	7.3	700	82	14
Sa-2	2014-03-20	7.3	700	83	14
C4-50-1	2014-03-26	6.8	700	87	35
C4-50-2	2014-03-26	6.9	700	86	35
C4-100-1	2014-03-26	6.9	700	87	70
C4-100-2	2014-03-26	7.0	700	88	70

As shown in figure D2, the removal efficiency of PFASs using PAC showed a wide distribution, ranging from 0-56% removal, whiles removal of DOC was low for all waters, ranging from 0-4%.

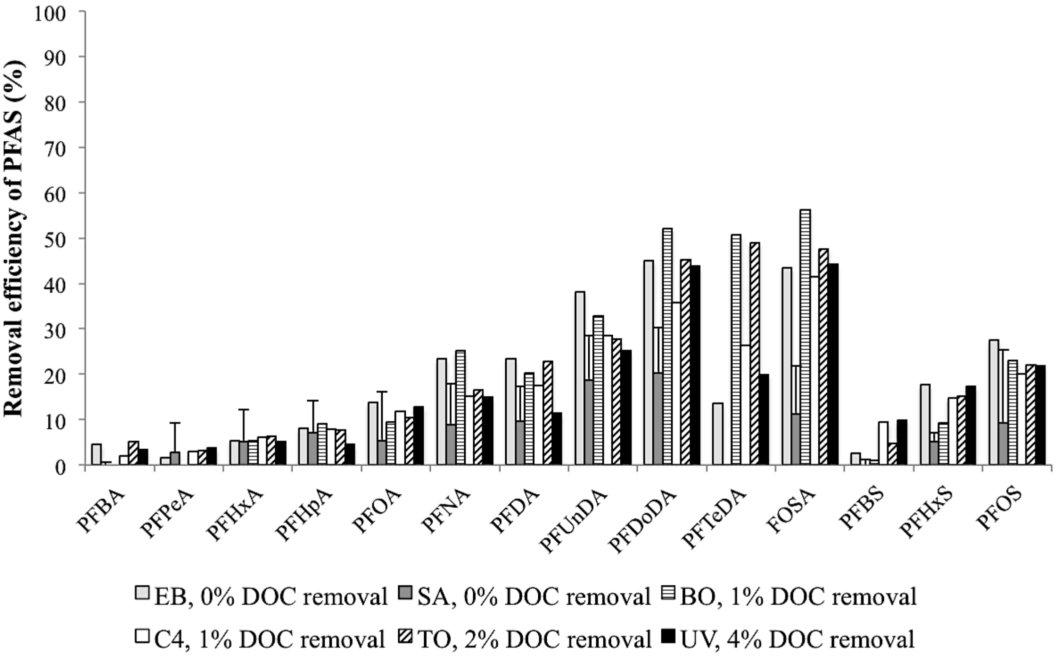

Figure D2. Removal efficiency for PFASs in different water types when treated with PAC (20 mg L^{-1}). Waters are presented with corresponding DOC removal in ascending order. Average removal efficiency of individual PFASs for treatment with water SA (*n*=2)

Removal efficiency of PFAS in correlation with removal of DOC for each water type, when using a PAC dose of 20 mg L^{-1} (Figure D3).

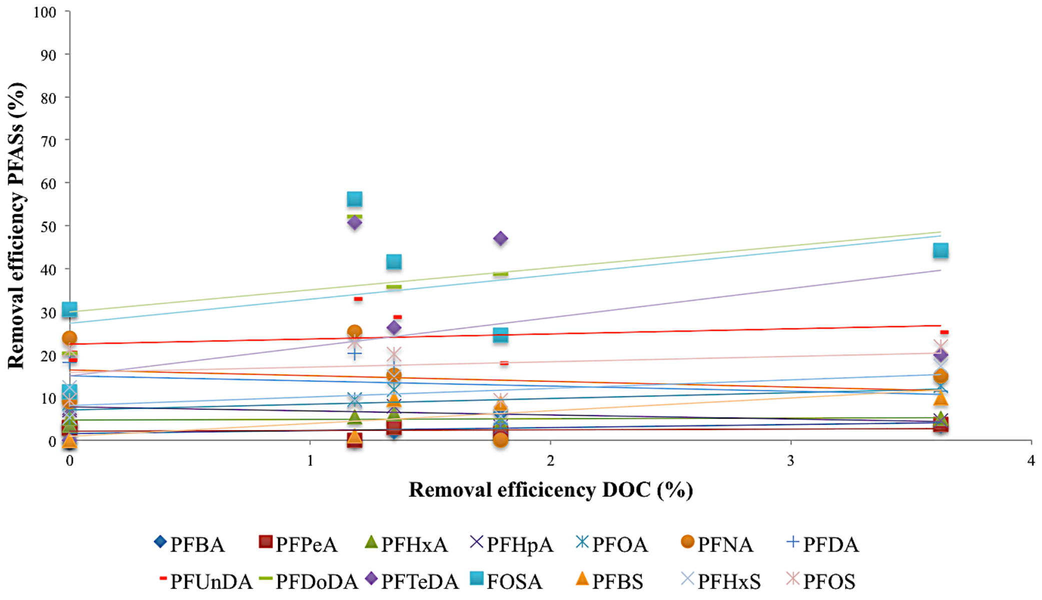

Figure D3. Removal efficiency for PFASs plotted against removal efficiency of DOC using a PAC dose of 20 mg L^{-1} (n=6).

Statistical test, student t-test and Pearson test, showed that no significant trend could be seen when correlating the removal of DOC and removal efficiency of PFASs using a PAC dose of 20 mg L^{-1} (Table D2).

Table D2. Summary of results from statistic test with r-value from Pearson test and p-values from student's t-test when comparing removal efficiency of PFASs (%) and DOC removal (%) using a PAC dose of 20 mg L^{-1}.

Compound		
	r	p
PFBA	0.396	0.437
PFPeA	0.176	0.738
PFHxA	0.232	0.658
PFHpA	-0.564	0.244
PFOA	0.563	0.244
PFNA	-0.19	0.718
PFDA	-0.258	0.621
PFUnDA	0.267	0.61
PFDoDA	0.622	0.187
PFTeDA	0.415	0.413
FOSA	0.474	0.343
PFBS	0.809	0.051
PFHxS	0.549	0.259
PFOS	0.263	0.615

Appendix E – NF membrane

Pictures shown the NF membrane module (Figure E1).

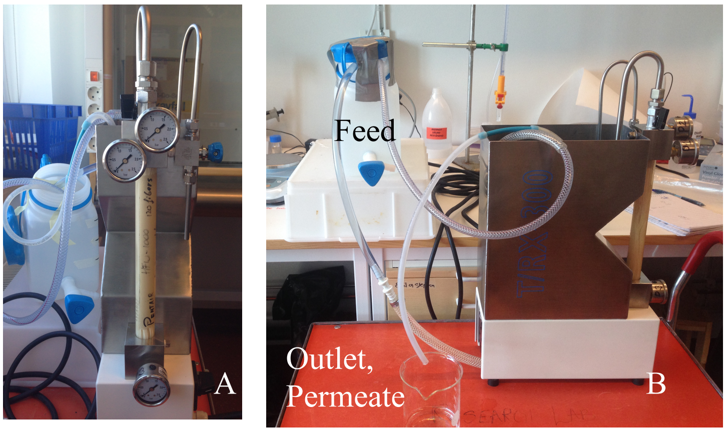

Figure E1. Figure A shows the NF membrane and manometers. Figure B shows the lab setup with an external container for the water.

Flow rate in permeate and temperature in feed tank during the entire run for each water (Table E1). Both flow rate and temperature were held constant during the entire run. Temperature were low in the beginning of the run when stabilization was occurring but once the filtration had started (45 min) the temperature was kept to around 21°C.

Table E1. Table showing temperature (°C) and rate (L h^{-1}) for each water run through the NF membrane.

	C4		UV		BO		TO		EB		SA	
Time (min)	Temp (°C)	Rate (Lh^{-1})	Temp (°C)	Rate (Lh^{-1})	Temp (°C)	Rate (Lh^{-1})	Temp (°C)	Rate (Lh^{-1})	Temp (°C)	Rate (Lh^{-1})	Temp (°C)	Rate (Lh^{-1})
0	14.2	-	14	-	11.6	-	11.5	-	13.2	-	11.5	-
30	18.5	-	18.4	-	16.7	-	15.5	-	17.7	-	17.9	-
60	19.4	0.86	19.2	0.83	19	0.73	18	0.8	19.2	0.71	19.1	0.77
90	21.4	0.84	20.8	0.81	20.9	0.76	19.2	0.79	21.1	0.73	20.1	0.76
120	21.2	0.87	21.8	0.79	21.5	0.79	20.3	0.79	22.1	0.8	21.1	0.75
150	21.7	0.85	21.7	0.8	21.6	0.76	21.4	0.78	22.5	0.76	21.3	0.76
180	21.8	-	21.5	0.82	21.7	0.77	21.5	0.76	22.2	0.73	21.2	0.76
210	-	-	21.3	-	21.5	0.76	-		22.0	0.73	21.1	-

Results from treatment with NF membrane for each of the samples show that there were no change in pH between the different sample times.

Table E2. Measured pH, weight in beaker and weight in sample for each water type using NF membrane. Samples named zero means samples taken before treatment.

Sample	Date	pH	Weight in container (g)	Weight sample (g)
UV-0	2014-04-07	7.2	-	80
Bo-0	2014-04-07	7.0	-	82
Eb-0	2014-04-08	7.4	-	80
To-0	2014-04-09	7.3	-	87

Sa-0	2014-04-10	9.1	-	86
C4-0	2014-04-14	7.2	-	85
UV-1	2014-04-07	7.1	5000	85
UV-2	2014-04-07	7.1	5000	85
UV-3	2014-04-07	7.1	5000	86
Bo-1	2014-04-07	7.1	5000	89
Bo-2	2014-04-07	7.1	5000	88
Bo-3	2014-04-07	7.1	5000	93
Eb-1	2014-04-08	7.6	5000	82
Eb-2	2014-04-08	7.9	5000	89
Eb-3	2014-04-08	8.0	5000	90
To-1	2014-04-09	7.3	5000	94
To-2	2014-04-09	7.3	5000	83
To-3	2014-04-09	7.2	5000	90
Sa-1	2104-04-10	9.0	5000	81
Sa-2	2014-04-10	8.9	5000	80
Sa-3	2014-04-10	9.0	5000	93
C4-1	2014-04-15	7.3	5000	91
C4-2	2014-04-15	7.2	5000	89
C4-3	2014-04-15	7.2	5000	89

The removal efficiency for PFASs using NF membrane showed a wide distribution ranging from 24-75% removal (Figure E2). The different water types (i.e. *C4. UV. BO. TO. EB. SA*) showed varying removal efficiency for individual PFASs and also for the removal of DOC ranging from 55% (EB) to 87 % (C4).

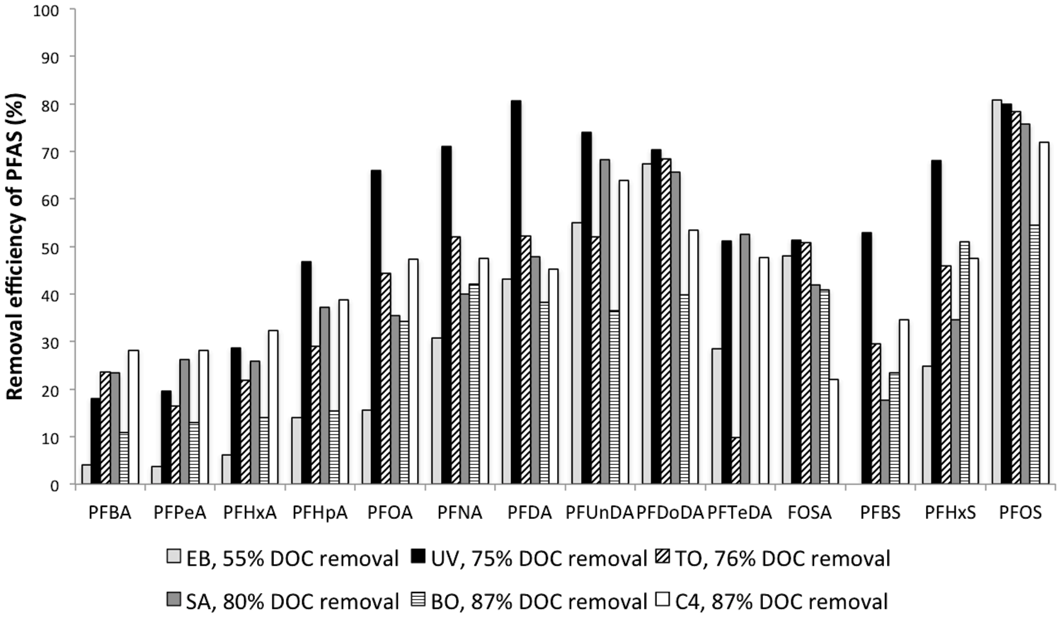

Figure E2. Removal efficiency for PFASs in different water types when treated with NF membrane. Waters are presented with associated DOC removal in ascending order.

Removal efficiency of PFAS in correlation with removal of DOC for each water type, when using NF membrane (Figure E3).

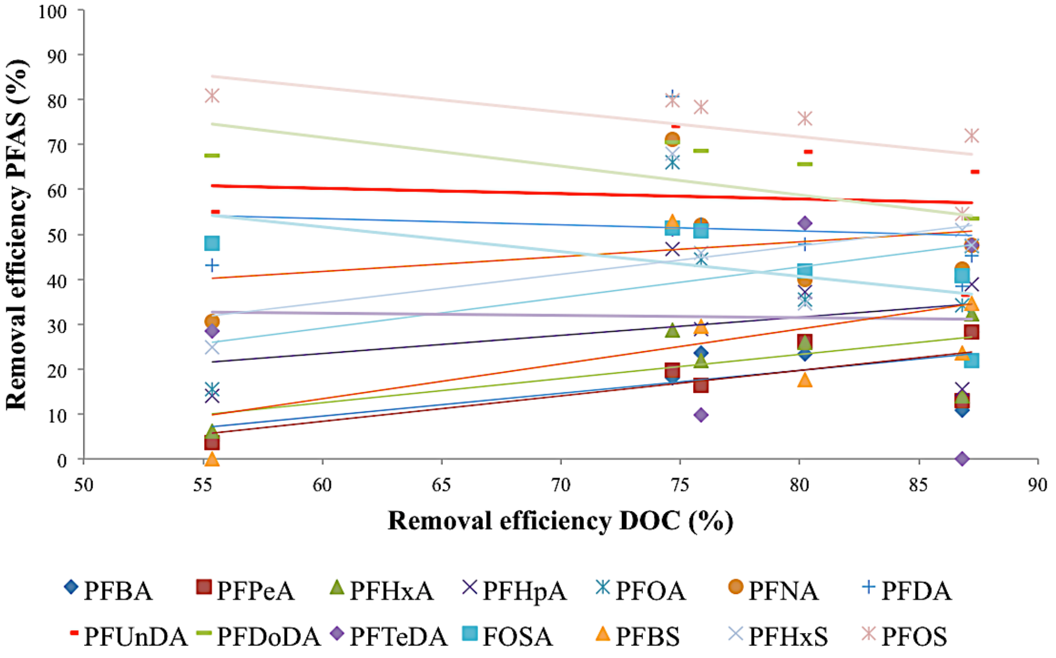

Figure E3. Removal efficiency for PFASs plotted against removal efficiency of DOC using NF membrane (n=6).

Statistical test, student t-test and Pearson test, showed that no significant trend could be seen when correlating the removal of DOC and removal efficiency of PFASs using NF membrane (Table E3).

Table E6. Summary of results from statistic test with r-value from Pearson test and p-values from student's t-test when comparing removal efficiency of PFASs (%) and DOC removal (%) using NF membrane.

Compound		
	r	*p*
PFBA	0.658	0.156
PFPeA	0.736	0.096
PFHxA	0.642	0.169
PFHpA	0.358	0.486
PFOA	0.477	0.339
PFNA	0.281	0.59
PFDA	-0.107	0.84
PFUnDA	-0.103	0.846
PFDoDA	-0.629	0.181
PFTeDA	-0.026	0.962
FOSA	-0.587	0.221
PFBS	0.515	0.296
PFHxS	0.502	0.31
PFOS	-0.647	0.165

Results from statistical test, student t-test, when comparing samples taken after stabilization (45 min) and samples taken after 50% of treatment (approx. 3h). Results show that there where only a significant ($p<0.05$) decrease in removal efficiency for the short-chained PFCAs (C<6) (Table E4).

Table E7. Correlations for treatment with NF membrane for the different compounds between the first sample and the last. Mean values for each compound of the six waters were taken for samples taken after stabilization (45 min) and the last sample taken after 50 % of treatment (~3 h) (*n*=6).

	Paired Differences					**t**	***p***
	Mean	**Std. Deviation**	**Std. Error Mean**	95% Confidence Interval of the Difference			
				Lower	Upper		
PFBA	-7.48	4.54	1.85	-12.24	-2.72	-4.04	.010
PFPeA	-11.66	5.74	2.34	-17.68	-5.65	-4.98	.004
PFHxA	-16.00	6.95	2.84	-23.29	-8.70	-5.64	.002
PFHpA	-13.33	12.58	5.13	-26.53	-0.13	-2.60	.048
PFOA	-7.26	7.41	3.02	-15.03	0.52	-2.40	.062
PFNA	-6.30	9.07	3.70	-15.82	3.22	-1.70	.150
PFDA	-2.41	5.89	2.41	-8.59	3.78	-1.00	.363
PFUnDA	-0.67	13.78	5.63	-15.13	13.8	-0.12	.910
PFDoDA	-0.67	7.97	3.25	-9.03	7.70	-0.21	.845
PFTeDA	1.68	4.68	1.91	-3.23	6.59	0.88	.420
PFBS	-10.58	11.98	4.89	-23.15	1.99	-2.16	.083
PFHxS	-3.17	5.49	2.24	-8.93	2.59	-1.42	.216

Appendix F- Chemical analysis

Extraction of all samples were made by using a SPE workstation and later on the samples were concentrated by using nitrogen evaporator (Figure F1).

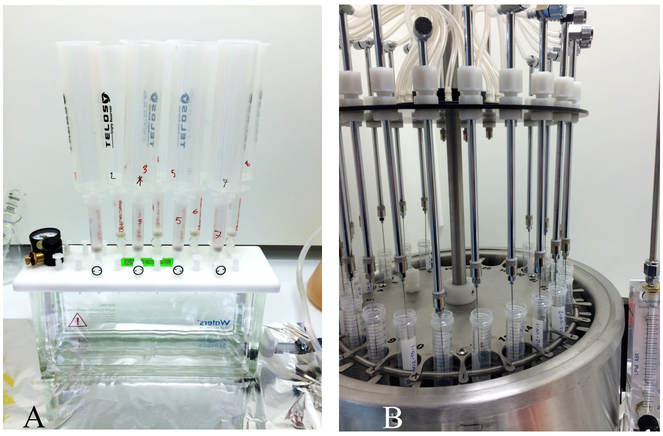

Figure F1. Figure A shows the SPE workstation with cartridges and reservoirs attached to it. Figure B shows the elution of samples using nitrogen evaporator.

Appendix G – Correlation of the removal efficiency with pH, Fr, HIX and absorbance of DOC (UV_{254})

Table G1. Summary of measured HIX, Fr, UV_{254} and pH for each treament and water. All data except pH (from this study) were obtained from Nilsson and Wängdahl (2014).

		HIX	**Fr**	**UV_{254}**	**pH**
MIEX	C4 1	0.94	0.36	0.42	7.6
	C4 2	0.94	0.36	0.42	7.6
	UV 1	0.96	0.27	0.32	7.5
	UV 2	0.96	0.27	0.32	7.5
	BO	0.93	0.51	0.36	7.4
	TO	0.95	0.45	0.24	6.7
	EB	0.87	0.90	0.14	7.3
	SA	0.93	0.45	0.12	8.1
$FeCl_3$	C4	0.94	0.36	0.42	7.6
	UV	0.96	0.27	0.32	7.5
	BO 1	0.93	0.51	0.36	7.4
	BO 2	0.93	0.51	0.36	7.4
	TO	0.95	0.45	0.24	6.7
	EB 1	0.87	0.90	0.14	7.3
	EB 2	0.87	0.90	0.14	7.3
	SA	0.93	0.45	0.12	8.1
PAC	C4	0.94	0.36	0.42	7.6
	UV	0.96	0.27	0.32	7.5
	BO	0.93	0.51	0.36	7.4
	TO	0.95	0.45	0.24	6.7
	EB	0.87	0.90	0.14	7.3
	SA	0.93	0.45	0.12	8.1
	SA	0.93	0.45	0.12	8.1
NF membrane	C4	0.94	0.36	0.42	7.6
	UV	0.96	0.27	0.32	7.5
	BO	0.93	0.51	0.36	7.4
	TO	0.95	0.45	0.24	6.7
	EB	0.87	0.90	0.14	7.3
	SA	0.93	0.45	0.12	8.1