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UNIVERSITY of OULU

TEKNILLINEN TIEDEKUNTA

**REMOVAL OF PERFLUORINATED COMPOUNDS
BY COAGULATION-FLOCCULATION**

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TIIVISTELMÄ

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Tiivistelmä <p>Perfluorattujen yhdisteet ovat kemiallisia yhdisteitä, joissa on hiili-fluorisidos. Perfluorattuja yhdisteitä käytetään useissa kuluttajatuotteissa. Työn tavoitteena oli selvittää kirjallisuuden pohjalta kuinka hyvin koagulaatio-flokkulaatiomenetelmä poistaa perfluorattuja yhdisteitä vedestä. Haluttiin myös selvittää kirjallisuuden avulla perfluorattujen yhdisteiden esiintymistä luonnossa. Työssä pyrittiin selvittämään yhdisteiden pitoisuusmääriä maaperässä, luonnonvesissä, jäteveden puhdistuslaitoksissa ja juomaveden puhdistuslaitoksissa.</p> <p>Työn tutkimusmenetelmänä käytettiin kirjallisuustutkimusta, keskittyen alan uusimpiin mahdollisiin julkaisuihin. Perfluorattuja yhdisteitä esiintyy maailmanlaajuisesti maaperässä, luonnonvesissä, sekä jäteveden puhdistuslaitoksissa että juomaveden puhdistuslaitoksissa. Koagulaatio-flokkulaatiomenetelmällä pystytään poistamaan perfluorattuja yhdisteitä vedestä, Poistumistehon hyötysuhde tavallisella koagulanteilla ei ole yhtä tehokas kuin uusilla koagulanteilla, kuten esimerkiksi luonnonmukaisilla koagulanteilla.</p>			
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ABSTRACT FOR THESIS

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Abstract <p>Perfluorinated compounds are chemical compounds with carbon-fluorine bond, they are used in commercial products. The goal of this thesis was to find out how coagulation-flocculation method remove perfluorinated compounds from water. Occurrence of perfluorinated compounds in waters and soil were researched and methods of observing these concentrations in the nature. Different concentrations on different points of waste water treatment plants and drinking water treatment plants were also researched. Main focus was to study different coagulation methods.</p> <p>Research methods used in this thesis included research of previous studies, focusing on most recent studies. Findings were that perfluorinated compounds can be found worldwide, both soil and water. Perfluorinated compounds can be removed from water by coagulation-flocculation process. It was also found that the removal efficiency by using different coagulant methods varied. Using conventional coagulants did not reach as good removal efficiency as when enhanced coagulation was being used. The best removal rate was achieved when natural M.oleifera or CBHyC was used as a coagulant.</p>			
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ABSTRACT

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INTRODUCTION

Perfluorinated compounds have been noticed as emerging environment threat in the past years. Due to the health and environmental risks, there has been on-going research to find an efficient way to remove PFCs from water. Perfluorinated compounds are widely used in consumer products, but use of them are being redistricted more and more. There are different kinds of perfluorinated compounds, but most recognized are perfluorooctane sulfonates (PFOS) and perfluorooctanoates (PFOA).

Samples to detect perfluorinated compounds are usually handled with solid phase extraction method, because it is the most commonly used extraction method for aqueous samples. Perfluorinated compounds have been recognized in water samples worldwide in oceans, lakes and rivers. There is given examples and concentration rates presented in this thesis. Perfluorinated compounds can also be acknowledged at waste water treatment plants and drinking water treatment plants, examples of concentration rates can also be found in this thesis.

Main focus on this thesis is review of coagulation-flocculation processes and how perfluorinated compounds can be removed using this method. Different coagulants and their removal efficiencies were compared.

PERFLUORINATED COMPOUNDS

1.1 Structure of perfluorinated compounds

Perfluorinated organic compounds or perfluorochemicals (PFC) are chemical compounds that are characterized by their carbon – fluorine bond, which is the most stable bond in organic chemistry. Because of the stable bond, perfluorochemicals are more thermally and chemically stable than hydrocarbon compounds. (Lange *et.al.* 2006) Perfluorinated compounds have a hydrophobic perfluorinated carbon tail and hydrophilic ionic head. (Arvaniti *et.al.* 2014) There are many different kinds of perfluorochemicals, but most important compounds are perfluoroalkyl substances (PFAS), perfluorooctane sulfonates (PFOS) and perfluorooctanoates (PFOA), and this thesis will focus on those. These chemicals are widely used in consumer products and they can be considered as a toxicological concern. (Lange *et.al.* 2006) Perfluoroalkyl substances are used in textiles, in outdoor clothing, for durable water repellency (DWR). (Van Der Veen *et.al.* 2016) PFOS and PFOA occur as active ingredients, impurities or as degradation products of derivates, for example in water, oil and stain repellents for textiles, leather and paper. (Lange *et.al.* 2006) Below the chemical structures of PFOS and PFOA in figure 1 and 2 are shown.

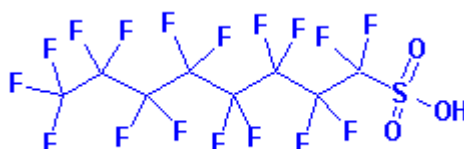


Figure 1: Structure of perfluorooctanesulfonic acid (PFOS). Resource: Fluoride action network

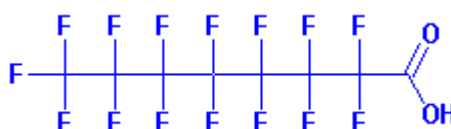


Figure 2: Structure of Perfluorooctanoic acid (PFOA).

Resource: Fluoride action network

1.2 Environmental causes

The occurrence of perfluorinated compounds have been issued one of the emerging problems in the environmental chemistry especially in aquatic environment, concentrations varying between pg and ng per liter (Ahrens 2011). There are also studies showing that PFCs can be transported atmospherically (Martin *et.al.* 2006). The main concern is the environmental persistence of PFCs and the ability to bioaccumulation. Due to possible impact on humans and wildlife, perfluorooctane sulfonate and its salts has been added to list of persistent organic pollutants (POP) in Stockholm Convention in 2009. (Stockholm convention Annex B 2009) However new PFC classes (e.g. perfluoroalkyl phosphonates (PAPs)) are still being produced (Ahrens 2011).

In the environment PFCs can degrade to long-chain perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFASs) (Martin *et.al.* 2006). Long-chain PFOS and PFOA are more toxic in the environment than short-chain (less than 7 carbon molecules) PFCs. Short-chain compounds are more mobile and have a lower bioaccumulation potential. (Gellrich *et.al.* 2012) Perfluorinated compounds are released to the environment during the manufacturing, storage, and transport and also later in the product use and disposal (Paul *et.al.* 2008).

1.3 Toxicity

Perfluorinated compounds can be recognized as an ecological risk to the environment as well as toxicological risk to the human population. Water contamination can be recognized near old manufacturing facilities. Through these water contaminations people are exposed to perfluorinated chemicals. (Lau *et.al.* 2009)

Since first perfluorinated compounds were produced in 1940s and 1950s, there was not yet any testing method for these compounds. Also the potential health effects on human were not yet acknowledged. (Lindstrom *et.al.* 2011) By the early 2000s a measurable quantities of PFCs could be found in almost every human blood samples worldwide, PFOS being the dominant group (Kannan *et.al.* 2004). The effects of PFCs have been tested on different laboratory animals and the toxicokinetics of different PFCs vary

between different animal species and gender. In conclusion it is difficult to estimate the human health effects. (Lindstrom *et.al.* 2011)

PFOS and PFOA are weakly lipophilic, bind to proteins and are very water soluble. The principle binding protein partner is albumin. In human blood PFCs bind to serum proteins. (Lange *et.al.* 2006) Humans can be exposed to PFCs by dietary uptake or by being in contact with products that have been treated with substances containing PFCs. Different food groups e.g. fish, drinking water, meat and dairy products have been found to contain traces of PFCs. (Stahl *et.al.* 2011) In human body perfluorinated compounds mainly accumulate in kidney, liver and muscle tissues (Lange *et.al.* 2006).

OBSERVATION OF CONCENTRATIONS IN NATURE

2.1 Analytical methods

The most analyzed perfluorinated compounds are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). There are multiple different factors that can have a high influence on the results on water samples. These are sampling method, sampling container, sampling depth and sampling period. (Ahrens 2011)

Solid phase extraction (SPE) method is the most commonly used extraction method for aqueous samples (Ahrens 2011). Solid phase extraction is a method where liquid with suspended or dissolved compounds are separated with each other by their physical or chemical properties (Hennion 1999). The goal in solid phase extraction is to concentrate compounds so that the detection is possible, without SPE the concentrations in samples are below detection limit. SPE consist of three or four steps, which must be done carefully to have reliable results. The first step is conditioning the solid sorbent with suitable solvent. Usually methanol is used for this purpose. Methanol is used as solvent, because it does not interact between the compounds and sorbent. The second solvent followed by methanol is water or aqueous buffer that has the same pH and ionic strength with the sample. In the second step the sample is percolated through the solid sorbent, volume ranging from 1 mL to 1 L. The sample is added to the column by gravity, pumping, aspirated by vacuum or with automated system. The sample flow-rate through the sorbent should be generated so low enough to enable retention of the analytes but still high enough so that the duration is not too long. In the second step the analytes are concentrated to the sorbent. The third step in the solid phase extraction is washing of the solid sorbent with a solvent. The third step is not mandatory. In aqueous matrices, a drying step is usually made after washing, to remove traces of water from solid sorbent. The fourth and the final step is elution. In the final step the interactions between analytes and sorbent is disrupted. The elution solvent is methanol or acetonitrile. (Camel 2003) Usually there is also a filtration step with samples with high suspended particulate matter (SPM) to avoid blocking SPE cartridges. During this filtration step, perfluorinated compounds may be adsorbed into the equipment. The SPE method can be used for both long and short chain PFCs. (Ahrens 2011)

Retention of the trace elements on the solid sorbent is required for preconcentration. The mechanism of retention depends on the sorbent. Different mechanisms include simple adsorption, chelation or ion-exchange, last of which is most commonly used for perfluorinated compounds. Ion exchange sorbents contain anionic or cationic functional groups that can exchange the counter-ion. The charged functional groups of analytes and the oppositely charged functional groups of sorbents have electrostatic attraction. Ion exchange can be done with pH modification, in strong or weak sites. They refer to the fact that strong sites are present as ion-exchange sites in every pH. Weak sites are only present when pH values are smaller than greater than the pKa. Strong sites are quaternary amines (anion exchange) and sulfonic acid groups (cation exchange). Weak sites are primary, secondary and tertiary amines (anion exchange) and carboxylic acid groups (cation exchange). (Camel 2003)

After preconcentration, samples are usually analyzed with high performance liquid chromatography that is coupled with mass spectrometry (LC-MS or HPLC-MS). HPLC-MS is used to detect, identify and separate chemicals of particulate masses in the presence of other chemicals. While using the HPLC-MS method it must be recognized that there might be adsorbing from or to the used instruments, this has to be concerned when deciding the used materials of instruments. (Ahrens 2011)

2.2 Occurrence of perfluorinated compounds

2.2.1 Concentration rates in oceans and soils

Perfluorinated compounds can be detected worldwide in the nature both soil and water (Lau *et.al.* 2009). Yamashita *et.al.* studied in 2005 the concentrations of perfluorinated acids in oceans. Their study included open water samples from the Atlantic and Pacific Oceans and samples from coasts of different Asian countries. PFOA and PFOS were found in 80% of the samples analyzed.

Since 2005 there has been several studies worldwide examining different oceans and their concentrations in perfluorinated compounds. Ahrens *et.al.* studied in 2010 the concentrations in the North Sea, Baltic Sea and Norwegian Sea. Their study indicated that the concentrations are higher near the coast compared to the offshore sea. The range of the concentrations varied from offshore Norwegian Sea with 100 pg/L to 22 080 ng/L in river Seine (Ahrens *et.al.* 2010). In surface water samples collected from 22 different

locations from North Pacific to the Arctic Ocean the concentration varied between 230 pg/L and 840 pg/L. (Cai *et.al.* 2012) These different concentrations are represented in table 1.

Table 1: Concentrations of perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHS), perfluorononanoate (PFNA) and perfluorooctanoic acid (PFOA) in oceans at different locations.

Location	Year	PFOS (pg/L)	PFHS (pg/L)	PFNA (pg/L)	PFOA (ng/L)	Reference
Coastal area of China	2005	23–9680	<5–1360	2.0–692	243–15,300	Yamashita <i>et.al.</i> 2005
Coastal area of Hong Kong	2005	70–2600	<5–311	22–207	673–5450	Yamashita <i>et.al.</i> 2005
Central to Eastern Pacific Ocean (surface water)	2005	1.1–20	0.1–1.6	1.0–16	15–62	Yamashita <i>et.al.</i> 2005
Baltic Sea	2011	n.d. – 350	-	10–42	25–455	Ahrens <i>et.al.</i> 2010
Open North Sea	2011	n.d. – 70	-	40–50	20–70	Ahrens <i>et.al.</i> 2010

nA= Number of samples analyzed, n.d. = not detected

Perfluorinated compounds can be found in the soil. For their ability to be highly soluble in water, they do not bind well to soil or sediments. From soil, PFCs can be migrated to groundwaters. (Davis *et.al.* 2007) Sepulvado *et.al.* (2011) studied from 2004 to 2007 the occurrence of PFCs in biosolids and biosolids-amended soils following the land application of municipal biosolids. PFOS were the most detected perfluorinated compound in both biosolids with 80 – 219 ng/g and biosolids-amended soil 2 – 483 ng/g. Their study indicated that when increasing the biosolids loading rate, the concentrations of PFCs in soil grew.

Naile *et.al.* (2010) studied the occurrence of perfluorinated compounds in water, soil and sediment in coastal areas of Korea in 2010. Their study indicated that the concentrations of PFCs are much lower in soil and sediment compared to concentrations in the water. In their study either soil or sediments did not have greater PFOS concentration than 2.0 ng/g.

2.2.2 Occurrence at waste water treatment plants

Perfluorinated compounds can be detected in sewage sludge. Loganathan *et.al.* (2007) studied the existence of perfluorinated compounds at various stages of two different waste water treatment plants (WWTP) during various seasons in 2005. The stages where samples were collected at first plant were influent, oxidation ditch water, oxidation ditch solids, clarifier water, effluent, reactivated liquid, reactivated sludge and final solid waste. At the second plant the stages where the samples were collected were influent, aeration supernatant, aeration–mixed liquid suspension solids (MLSS), reactivated sludge supernatant, reactivated sludge, effluent, ash basin water and sludge cake (before and after burning). The predominant PFCs in the samples of their study were PFOA and PFOS. Study made in Denmark by Bossi *et.al.* in 2008 also showed that PFOA and PFOS were the dominant perfluorinated compounds in both effluent and influent waste water. Both studies indicated that the concentrations increased in the effluent water. Concentrations found in these studies can be seen in table 2 and the difference between concentrations on influent and effluent waters can be seen in table 3. The increased concentrations in effluent waste water after many treatment steps may result from an additional source of perfluorinated compounds within the process. The increase may be result from biodegradation of precursors such as perfluoroalkyl phosphates (PAPS), fluorotelomer alcohols (FTOHs) or fluorotelomer sulfonates (FTS). (Sinclair & Kannan, 2006)

Table 2: Concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in sludge samples at different waste water treatment plants globally.

Location	WWTPs analyzed	PFOS (ng/g)	PFOA (ng/g)	Sample	Reference
United States of America	2	8.2 – 993 (dry weight (solid sample))	8.3 – 219 (dry weight (solid sample))	Sludge	Loganathan <i>et.al.</i> (2007)
Denmark	6	4.8 – 74.1 (dry weight)	3.4 – 19.7 (dry weight)	Sludge	Bossi <i>et.al.</i> (2008)
Spain	12	below detection limit – 4.99	below detection limit – 0.69	Sludge	Gómez- Canela <i>et.al.</i> (2012)
Germany	3	2.08 – 4.45	0.59 – 1.21	Sludge	Gómez- Canela <i>et.al.</i> (2012)
Hong Kong	3	3.1 - 7304.9	1.3 – 15.7	Sludge	Ma <i>et.al.</i> (2010)

Table 3: Concentrations of PFOA and PFOS in influent and effluent waters in different waste water treatment plants.

Location	PFC	Season	Influent (ng/L)	Effluent (ng/L)	Reference
United States of America, Kentucky	PFOA	Winter	83	155	Loganathan <i>et.al.</i> (2007)
		Spring	184	183	
		Summer	100	122	
		Fall	22	149	
United States of America, Kentucky	PFOS	Winter	8.1	14	Loganathan <i>et.al.</i> (2007)
		Spring	11	8.0	
		Summer	16	13	
		Fall	7.0	28	
United States of America, Georgia	PFOA	Winter	30	102	Loganathan <i>et.al.</i> (2007)
		Summer	50	52	
		Fall	2.0	6.7	
United States of America, Georgia	PFOS	Winter	7.9	13	Loganathan <i>et.al.</i> (2007)
		Summer	7.8	9.3	
		Fall	2.5	1.8	
Denmark, 6 different WWTP	PFOS	Not defined	6.8	6.1	Bossi <i>et.al.</i> (2008)
			2.4	12.8	
			5.2	6.4	
			7.1	7.9	
			2.3	6.7	
			3.3	<1.5	
Denmark, 6 different WWTP	PFOA	Not defined	19.9	13.2	Bossi <i>et.al.</i> (2008)
			<2.0	15.2	
			15.2	17.6	
			11.7	16.3	
			5.5	14.9	
			18.6	<2.0	

2.3 Perfluorinated compounds in drinking waters

Due to being highly soluble to water, perfluorinated compounds are being concerned as a contaminant to drinking waters, perfluorooctanoic acid (PFOA) being the most common perfluorinated compound detected (Boone *et.al.* 2014). The European Commission has added perfluorooctane sulfonate (PFOS) in the list of priority hazard chemicals that must be monitored in water areas in the EU, setting Environmental Quality Standard (EQS) of 0.65 ng/L in fresh water. (European Commission, Directive 2013/39/EU)

Takagi *et.al.* (2008) studied the concentrations of perfluorooctanoic acid (PFOA) and PFOS in tap water in Japan during 2006-2007. Their study varied different sources of fresh water, including rivers, lakes, subsoil and ground water. Drinking water treatment plants (DWTP) also had different process stages for treating the fresh water. PFOS concentration varied from 0.26 ng/L to 22 ng/L in all raw water samples. In 90% samples analyzed, the concentration was below 10 ng/L. PFOA concentration varied from 5.2 ng/L to 92 ng/L in all raw water samples, also changing of the seasons and source of the raw water affected on the concentration of the samples. Concentrations of PFOS and PFOA in tap water were ranging from 0.16–22 ng/L and 2.3–84 ng/L. The best removal rate was discovered in DWTP which used activated carbon as one of the filtrating step and changed activated carbon material once or twice a year.

Quinones and Snyder (2009) studied the concentration of different perfluorinated compounds in seven different drinking water treatment plants in United States of America. The sources of the water in DWTP's were in most of the cases surface water and treatment processes varied in the DWTPs. In almost every case the PFC concentrations were comparable in finished drinking water samples to raw water samples. In their study the only removal they observed was at utility that used microfiltration and reverse osmosis in waste water treatment. Domingo *et.al.* (2012) studied the concentrations of PFCs in Spain; they studied raw water, after the purification process and consumption location (public water fountains). In their study the highest concentrations were PFOA (2.40 ng/L) and PFOS (1.81 ng/L). Significant differences in PFC concentrations between specific sampling points of the distribution network were not found. This means that neither PFC is removed nor combined in the purification process or during the transportation in the distribution. Their study indicated that all of the PFCs analyzed, with the exception of PFBA, showed lower concentrations after purification process. Concentrations found in these studies are collected in table 4.

Table 4: Concentrations of PFOA and PFOS in tap water samples globally.

Country	PFOS (ng/l)	PFOA (ng/l)	Reference
USA—West Virginia	—	3550	Paustenbach <i>et. al.</i> (2007)
Japan	0.16 – 22	2.3 – 84	Takagi <i>et. al.</i> (2008),
Germany	0 – 22	22 – 519	Skutlarek <i>et. al.</i> (2006)
Canada	—	0.2	Lien <i>et. al.</i> (2006)
Sweden	0.3 – 0.8	1.3	Lien <i>et. al.</i> (2006)
Malaysia	0.1	0.1	Lien <i>et. al.</i> (2006)
China	1.5 – 13.2	1.1 – 109	Lien <i>et. al.</i> (2006)
Thailand	0.1 – 1.9	0.2 – 4.6	Lien <i>et. al.</i> (2006)

There are different potential methods to degrade and remove perfluorinated compounds such as PFOA and PFOS from aqueous environment: chemical methods e.g. advanced oxidation and photocatalytic processes and physical methods such as precipitation or adsorption or combination of both. (Fujii *et.al.* 2007) The next chapter will focus on the coagulation-flocculation method.

REMOVING OF PERFLUORINATED COMPOUNDS BY COAGULATION-FLOCCULATION

3.1 Coagulation-flocculation process

Coagulation-flocculation is a process which can be used to remove colloidal compounds and suspended particles from water. In coagulation phase hydrophobic colloids are destabilized by neutralizing the forces with coagulants e.g. ferrous sulfate, aluminium sulfate, ferric chloride and cationic polymers. In the following flocculation step these neutralized particles form bridges between the flocs creating larger aggregates or flocs. Flocculants can be e.g. cationic and anionic polymers such as polyferric sulfate (PFS) and organic polyacrylamide (PAM). Once flocculated particles have formed into larger particles they are separated or removed with filtration, flotation, settling or straining. (Fu & Wang 2011) Different coagulants and their removal efficiencies can be found in table 5.

3.2 Different mechanisms

Two common types of coagulation is usually used in drinking water treatment: the first one is conventional coagulation which is used to remove turbidity particles and some organic pollutants and the second one being enhanced coagulation which is a practice where an excess amount of coagulant is used for turbidity removal to achieve better removal of organic pollutants. (Xiao *et.al.* 2013) Also using different coagulants have effect on purification efficiency.

Xiao *et.al.* studied in 2013 the removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) by coagulation and how different solution pH and coagulant dosage effects on the removal rate. PFOS and PFOA removal was minimal with conventional coagulation. However using enhanced coagulation, which uses excess of the coagulant, compared what is needed for turbidity removal. The conclusion in the study was that the coagulant dosage and solution pH had the biggest impact on the removal of PFOS and PFOA from surface water. By increasing the coagulant dosage and lowering the pH they could achieve the best removal percentage.

In 2011 Deng *et.al.* studied the effect of using polyaluminium chloride (PACl) in coagulant treatment to remove PFOS from surface water. In the study it was also investigated how solution pH, different temperature, effects of coagulant dose and the initial turbidity effects on removal of PFOA and suspended solids in the water. The ideal dosage of polyaluminium chloride was indicated to be 10 mg/L. The solution pH in the study was adjusted between 5.0 – 9.0, and the initial turbidity decreased when the pH increased. The temperature was tested on 5 °C, 15 °C, 25 °C and 35 °C. The influence of low temperature on the hydrolysis of the coagulant and increases water viscosity, this results in low coagulation efficiency. The amount of PFOA in aqueous phase grew when the solution temperature increased. Meanwhile the residual turbidity decreased a little bit when the solution temperature grew from 5 °C to 35 °C. Because the coagulation efficiency was low in low solution temperature, the residual turbidity was high. Lower temperature caused the collision efficiency to lower down. The higher the solution temperature, the higher the collision efficiency, results good results for the coagulation. In their study the coagulation efficiency in lower initial turbidity was low and the formations of aggregates were not efficient. However in high turbidity the surface water contained more suspended solids, which can absorb more PFOA and therefore having lower residual concentrations of PFOA in water.

Bao *et.al.* did a study in 2014, where they removed PFOS and PFOA from surface water using alum ($\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \times 6\text{H}_2\text{O}$) and polyaluminium chloride (PACl) as a coagulants, like in the previous studies mentioned. They also investigated the effect of different pH values and amount of natural organic matter. Even in the beginning of their experiment the removal rate in the initial pH and after adding 50mg/L of ferric chloride was 32% for PFOA and ~12% for PFOS. When the pH was adjusted to 4, removal rates for PFOA was ~47.6% and for PFOS was 94.7%. When the NOM concentration increased, the removal rate was lowered, because of the competitive adsorption between NOM particles and PFOA and PFOS on the surface of the flocs and coagulants.

Zhao *et.al.* (2016) compared conventional coagulants (e.g. PACl) to hybrid coagulant, which in this study was organic-inorganic CBHyC. It was prepared by the covalent bond of C-Si and Si-O-Al, the Si source in this study was silane coupled with octadecyl-ammonium group. Different Si/Al ratios (0.15, 0.3 and 0.6) and basicity (B) values (1.0, 2.0 and 2.5) were tested to determine the best removal of perfluorooctanoic

acid from water. The best result was obtained with CBHyC with 0.3 Si/Al ratio and 0.2 B value, which had 99.6% removal rate of PFOA from water and it is also tolerant for pH change. When the Si/Al molar ratio was increased, the removal performance of PFOA was increased.

Yu *et.al.* (2016) studied using coagulation as a first treatment stage in removing perfluorooctanoic sulfonates from water, the second treatment stage was nanofiltration. As a coagulant they used AlCl_3 , and when the coagulant concentration reached 0.60 mmol/L the PFOS removal rate was 60%. They also noticed that the removal of PFOS enhanced when humic acid (HA) was added to the solution. PFOS was adsorbed to HA molecules. PFOS can be removed together with HA during the coagulation after the adsorption. However, PFOS cannot be removed entirely by conventional coagulation.

Pramanik *et.al.* (2015) did a comparative study of different removing methods of PFOA and PFOS in drinking water treatment. One of the methods compared was coagulation. Different coagulants were tested, including conventional alum ($\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$), PACl and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). They also tested natural coagulant *M.oleifera*. The initial dose of 5 mg/L resulted in removal efficiencies of PFOA and PFOS 18% and 23% for alum and 6% and 8% for ferric chloride. When using *M.oleifera* as a coagulant, removal efficiencies were 32% for PFOA and 38% for PFOS; these results are higher than using conventional coagulants. Better results in the removal may be due to bigger floc area, which resulted in better adsorption. When the coagulant dosage was increased in all cases, the removal efficiency increased. In their study the removal efficiency grew also when pH was decreased. When the pH decreases, the flocs are positively charged and induce electrostatic attraction with anionic PFOS and PFOA molecules. The best solution pH in their study was 4.

Table 5: Different coagulants and their removal rates.

Water type	Coagulant	Optimum conditions	Removal (%)	Reference
Surface water in Beijing	Polyaluminium chloride	pH 7.5, temperature 25 °C, 10 mg/L coagulant dosage 0.2 mg/L PFOA	PFOA 90%	Deng <i>et.al.</i> (2011)
Synthetic surface water	Alum and ferric chloride	coagulant dosage >60 mg/L pH 4.5 – 6.5	<35% for PFOA and PFOS	Xiao <i>et. al.</i> (2013)
Synthetic surface water	Alum and ferric chloride and polyaluminium chloride	pH 4, coagulant dosage 50 mg/L	PFOA 47.6%, PFOS 94.7%	Bao <i>et.al.</i> (2014)
Deionized water	CBHyC	Si/Al ratio 0.3, basicity 2	PFOA 99.6%	Zhao <i>et.al.</i> (2016)
Deionized water	AlCl ₃	pH 7.5, coagulant dosage 0.60 mmol/L	PFOS 60%	Yu <i>et.al.</i> (2016)
Feed water from local reservoir	M.oleifera	pH 4, dosage 20 mg/L	PFOA 32% and PFOS 38% (in initial dosage of 5 mg/L and pH 7.5)	Pramanik <i>et.al.</i> (2015)

CONCLUSIONS

Subject of this thesis was the removal of perfluorinated compounds from water by coagulation-flocculation. Due to the occurrence of perfluorinated compounds worldwide and their negative impact on health and environment, it is important to find a solution to remove them efficiently.

Concentrations of perfluorinated compounds in the nature are well recognized. Different concentrations of water and soil world-wide are presented in this thesis. The concentrations should get lowered with time; the best way to achieve this is to decrease the use of perfluorinated compounds in all the industries, where they are being used. There are also notable concentrations of perfluorinated compounds in waste water and drinking water treatment plants worldwide.

Different coagulants are being studied all the time, because they are being used widely in waste water and drinking water treatment plants. Removal efficiencies with conventional ways are not that efficient compared to enhanced coagulation. The best removal rate was reached with hybrid coagulant CBHyC, with 99.6% removal efficiency from spiked deionized water with PFOA. Also using natural *M.oleifera* as a coagulant showed promising results in removing PFOA and PFOS from feed water.

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