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Combining PAC and HAOPs with Microgranular Adsorptive Filtration to Enhance Water Treatment

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Abstract

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Immense effort has been made over the past few decades to address the challenge of sustainable drinking water production. As a result of this endeavor, low- and high-pressure membrane filtration have been developed as a reliable and efficient water treatment technology. However, application of membranes is restricted due to fouling, which is accumulation of contaminants in the feed on the membrane surface or within membrane pores during filtration. Fouling severely deteriorates the process efficiency by increasing trans-membrane pressure (TMP) and lowering membrane permeability.

In drinking water treatment natural organic matter (NOM) is usually the main membrane foulant, causing fouling by restricting or blocking the pores and/or forming a gel layer on the membrane surface. NOM is also the cause of several other problems in drinking water treatment

such as affecting taste and odor, formation of harmful disinfection by-products (DBPs), and increasing the required dose of coagulant and adsorbent. Although conventional NOM pretreatment processes such as coagulation with metal-based coagulants or adsorption onto powdered activated carbon (PAC), can capture NOM to some extent, there is need for more efficient and economical methods that remove NOM and mitigate membrane fouling.

In the past few years, a novel pretreatment technology, called microgranular adsorptive filtration (μ GAF), has been developed by Benjamin's group at the University of Washington. This process integrates adsorption and granular media filtration. It is reported that μ GAF with heated aluminum oxide particles (HAOPs) can substantially remove NOM and mitigate the downstream membrane fouling. However, a previous effort for application of PAC in μ GAF failed partly because the PAC did not have a comparable NOM removal efficiency.

The research presented in this dissertation studied if any PAC can present the advantages that HAOPs offer in the μ GAF process. Three commercially available PACs were tested. PACs with different manufacturing conditions had distinct NOM removal efficiency and adsorption kinetics and when used in μ GAF, they had different efficiencies for capturing membrane foulants. Among the tested PACs, SA SUPER possessed a higher NOM removal efficiency and rate of adsorption. It effectively adsorbed high molecular weight (HMW) NOM molecules such as biopolymer fraction and humic substances, resulting in significant mitigation of the fouling of the downstream membrane. Overall, at low doses, it outperformed the other two PACs, performing comparable to HAOPs.

μ GAF substantially enhanced the performance of HAOPs and SA SUPER compared to batch adsorption. The enhancement, however, was more significant for HAOPs than SA SUPER. Size exclusion chromatography confirmed the increase in the removal efficiency of the HMW

biopolymer fraction and humic material when adsorbents were used in μ GAF. Utilization of the mixture of HAOPs and SA SUPER, both in batch adsorption and μ GAF, led to a significant increase in the total NOM removal efficiency and consequently a dramatic decrease in the DPB formation potential of the treated water.

SA SUPER was more effective than HAOPs in adsorbing fluorescent NOM both in batch and μ GAF. However, despite the reports in the recent years, no rational correlation was found between the removal of fluorescent NOM and mitigation of the downstream membrane fouling.

Effect of process parameters on μ GAF performance was also investigated for both HAOPs and PAC SA SUPER. It was reported that surface of the HAOPs layer is more effective than its depth in removing large humic substances. However, this effect was limited to HAOPs and the surface of the SA SUPER layer did not have the similar capability. On the other hand, increasing the depth of the SA SUPER layer at a fixed effective adsorbent dose, enhanced the removal of membrane foulants, whereas for HAOPs, it resulted in a slight decrease in the removal of humic substances due to the decrease in the ratio of the adsorbent surface layer to total volume of water treated. For both adsorbent, increasing the flux to the μ GAF unit, did not have a considerable effect on the process performance.

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DEDICATION

Wherever I am, whatever I achieve, you are always with me and I owe you forever.

Mahmoud and Setareh

Chapter 1. Introduction

Drinking water is a major challenge of the 21st century. Based on a WHO (World Health Organization)-UNICEF (United Nations International Children's Emergency Fund) report in 2014, more than 700 million people lack access to safe drinking water (WHO, 2014), and thus, during the past few decades, developing water treatment technologies that are both relatively cheap and efficient has been a major concern.

As a result of such development, membrane-based water treatment has become increasingly popular. Low-pressure membrane treatment, which includes microfiltration (MF) and ultrafiltration (UF), can remove particulate matter and pathogens and thus, assure high-quality drinking water at reduced cost (Gao et al., 2011). Despite its potential as a reliable alternative to conventional drinking water treatment (DWT), however, application of membranes is hindered by the accumulation of impurities from the feed inside or on the membrane (membrane fouling). Membrane fouling leads to increased trans-membrane pressure (TMP) at a constant flux or decreased flux at a constant pressure, leading to reduction in process efficiency.

Natural organic matter (NOM) is usually the main membrane foulant in drinking water treatment. NOM is a complex mixture of organic compounds, generated by the degradation of plants and microbial metabolism and is abundant in natural waters. From 1970 to 2002 more than 5,000 papers were published about natural organic matter characterization and fractionation and its effects on drinking water, and this number has continued to increase until now (Purdue, 2009). NOM molecules can cause fouling by adsorption onto the membrane pores and consequently restricting or blocking the pores and/or forming a gel layer on the membrane surface.

In addition to deterioration of membrane performance, NOM adversely affects the quality of water because of taste, odor and color, and it increases the required dose of coagulant, adsorbent and disinfectant in DWT processes. Reaction of NOM with oxidants during the disinfection process produces detrimental disinfection by-products (DBPs). Moreover, the presence of NOM enhances biological growth in water distribution networks. NOM levels in Europe and North America are gradually increasing due to global climate change (Skjelkvaale, 2003), and stricter regulations are being enforced on drinking water treatment. Therefore, there is need for efficient and economical methods that mitigate membrane fouling and also remove NOM.

The most common NOM pre-treatment processes upstream of the membranes are adsorption onto powdered activated carbon (PAC) and coagulation with metal-based coagulants such as aluminum sulfate or ferric chloride. Such processes can capture potential foulants before they reach the membrane or remove contaminants that membranes alone cannot effectively remove. However, neither coagulants nor PAC, can remove all fractions of NOM. Furthermore, although pre-adsorption and pre-coagulation can capture some foulants, sometimes coagulation flocs or PAC particles can exacerbate membrane fouling (Kim et al., 2008; Ma et al., 2014).

Benjamin's group has developed a novel pretreatment technology called microgranular adsorptive filtration (μ GAF). By pre-depositing a layer of adsorbent directly onto the membrane surface, this process integrates adsorption, granular media filtration and membrane filtration. The group has also synthesized an aluminum-based adsorbent called heated aluminum oxide particles (HAOPs) that, when used in the μ GAF process, is able to remove NOM substantially and also mitigate membrane fouling (Kim et al., 2010). Therefore, μ GAF provides both performance and cost efficiency. However, although there is a fair amount of experience for the μ GAF process with HAOPs, there is little information about its performance with PAC, the most commonly

used adsorbent in DWT. Additionally, HAOPs, like other metal-based adsorbents, is not capable of removing some fractions of NOM that can cause membrane fouling and/or other NOM related problems such as formation of DBPs.

This research proposal focuses on performance of the μ GAF process with PAC and the benefits of μ GAF process over conventional batch adsorption for removal of NOM and mitigation of membrane fouling. Since PAC and HAOPs represent two different classes of adsorbents with distinctive adsorption mechanisms, comparison of μ GAF-PAC systems with the available knowledge of μ GAF-HAOPs systems can provide a deeper understanding of the process mechanisms. Furthermore, application of mixtures of HAOPs and PAC will be investigated as an approach for increasing process efficiency.

Chapter 2. Background information

In this section, NOM characterization techniques and the role of NOM in membrane fouling and DBP formation are reviewed. The section also provides a survey of recent pretreatment methods used for NOM removal and the consequent decrease in membrane fouling and DBP formation potential.

2.1 NOM analysis

Natural organic matter (NOM) is a complicated mixture of organic compounds that is present in all natural waters and is the product of the degradation of plants and/or microbial metabolism-catabolism (Matilainen et al., 2011; Piccolo, 2001). NOM consists of a continuous spectrum of organic components, from highly aromatic to largely aliphatic, and its concentration and characteristics vary by climate and geology (Matilainen et al., 2011). Since the 1970s, thousands of research publications have been dedicated to developing a better understanding of NOM structure and behavior (Perdue, 2009).

However, the extreme complexity of NOM has made it impossible to identify all of its individual components (Croué et al., 2000). Thus, analytical methods have been developed to characterize NOM molecules based on broad physical or chemical properties. These practical methods are discussed below.

Total organic carbon

NOM and total organic carbon (TOC) are often used interchangeably, since in natural waters, synthetic organic contaminants typically account for a negligible fraction of the TOC (Leenheer and Croué, 2003). Typically, dissolved organic carbon (DOC) comprises around 90%

of the TOC (Tranvik and Wachenfeldt, 2009). TOC and DOC are the most commonly used indices in studies of NOM treatment processes.

Ultraviolet and visible (UV–Vis) absorption spectroscopy

Organic compounds that are aromatic or have conjugated double bonds absorb UV light. In NOM characterization, UV absorbance is typically analyzed at a single wavelength of 254 nm. Although absorbance at this wavelength is primarily by aromatic groups, UV_{254} is widely used as a surrogate for all DOC in natural waters (Korshin et al., 2009).

Specific UV-absorbance

Specific UV-absorbance (SUVA) is defined as the UV absorbance of a water sample normalized to the DOC concentration of the sample. There is a strong correlation between SUVA at 254 nm ($SUVA_{254}$) and the aromatic carbon content of NOM (Croué et al, 1999). Therefore, high $SUVA_{254}$ is an indicator of predominance of hydrophobic organic material such as humic substances in the NOM, and low $SUVA_{254}$ indicates a predominance of hydrophilic material (Edzwald and Tobiason, 1999).

XAD resin fractionation

Fractionation using XAD resins is the most common method for the separation of NOM into hydrophilic (HPI) and hydrophobic (HPO) fractions. Each fraction can be further separated into neutral, acidic and basic sub-fractions (Perdue, 2009; Matilainen et al., 2011).

XAD resin was first introduced to isolate NOM during the 1980s (Leenheer, 1981; Thurman and Malcolm, 1981), and it was subsequently chosen by the International Humic Substances Society (IHSS) as a standard method for isolating humic acid (HA) and fulvic acid (FA).

The fraction of the NOM that adsorbs to XAD-8 resin at $\text{pH} < 2$ is called the humic substances (HS). Humic substances are high-molecular-weight hydrophobic NOM molecules that typically have high aromaticity. The fraction of HS that is insoluble at $\text{pH} 1$ is called humic acids (HA), and the fraction that is soluble at $\text{pH} 1$ is called fulvic acids (FA) (Perdue, 2009). Typically, hydrophobic acids comprise more than 50% of the NOM in natural waters. However, due to the relatively low solubility of HA material, most natural waters contain 5 to 25 times more FA than HA (Leenheer and Croué, 2003; Perdue, 2009).

Although fractionation methods with resins have been extensively applied, disadvantages such as physical or chemical alterations of the NOM due to the extreme pH levels used in fractionation and the irreversible adsorption of NOM to the resin may influence the results (Song et al., 2009).

Fractionation of NOM with size exclusion chromatography (SEC)

Molecular weight and size distribution are important characteristics of NOM in drinking water treatment processes (Ho et al., 2013; Pelekani et al., 1999). The molecular weight (MW) of NOM molecules is reported to vary from a few hundred to greater than 100,000 Da (Tranvik and Wachenfeldt, 2009; Leenheer and Croué, 2003). Figure 2.1 presents the size distribution of different constituents of NOM in natural waters.

Among the available techniques for investigation of size distribution of the NOM, size exclusion chromatography (SEC) has the advantages of minimal sample preparation, simplicity of operation and low required sample volume (Ho et al., 2013). SEC columns include porous gel material. When a sample is injected into the column, small molecules interact more than large molecules with the internal pores, so larger molecules elute sooner (Pelekani et al., 1999).

Various factors can affect the NOM MW estimation by SEC, such as hydrophobic and/or

electrostatic interactions between the column packing and NOM, differences between the molecular structure of the calibration standards and the NOM, and detection methods (Zhou et al., 2000; Pelekani et al., 1999).

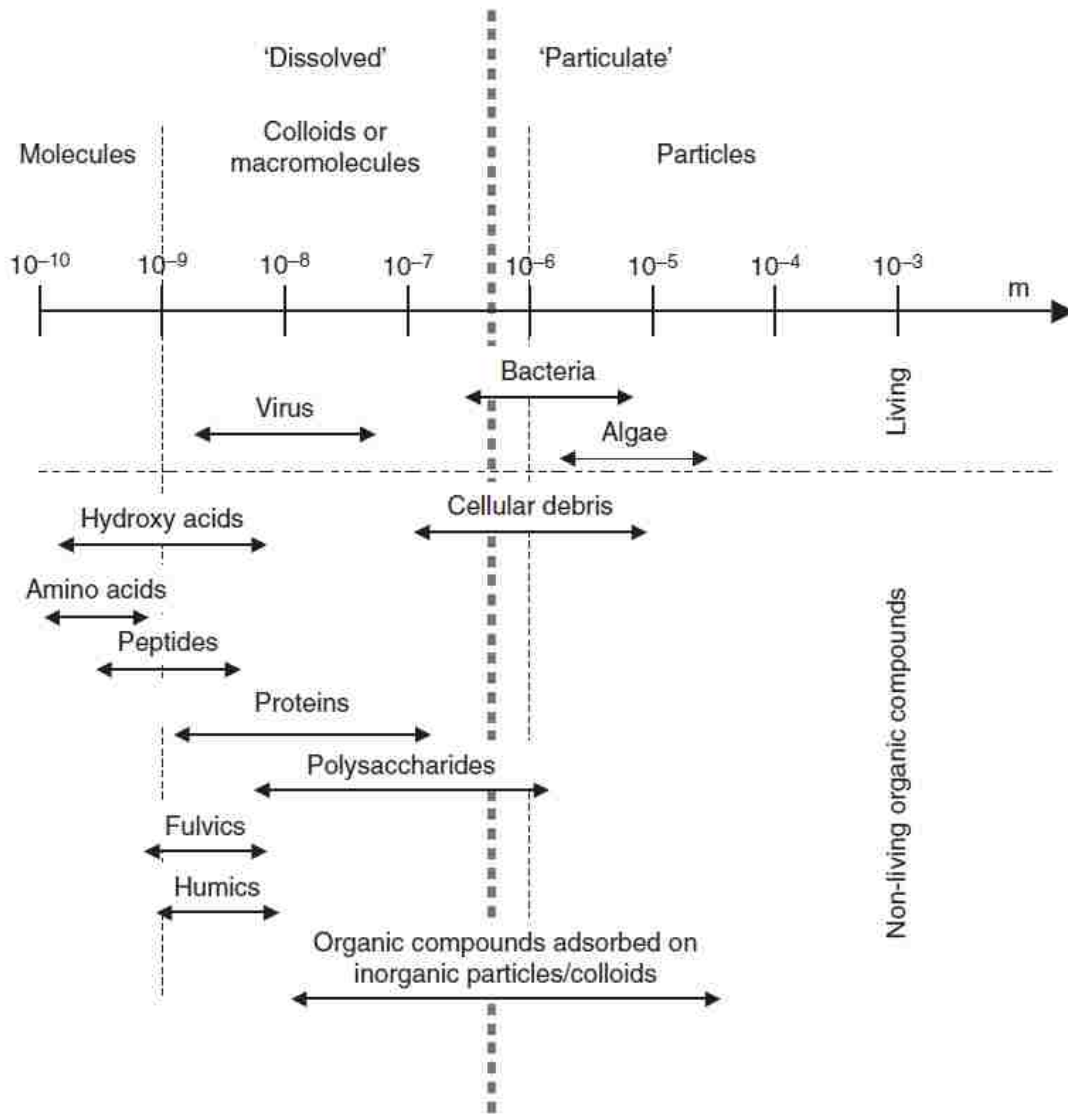


Figure 2-1 Size distribution of organic matter in natural waters (adopted from Tranvik and Wachenfeldt, 2009)

An eluent with a proper ionic strength at neutral pH can suppress the NOM-column

electrostatic interactions. Phosphate buffer solution at pH 6.8 with ionic strength adjustment using sodium chloride is a common eluent for NOM characterization (Her et al., 2002; Allpike et al., 2005). Also, using an aqueous eluent with 20% of an organic solvent such as methanol reduces the hydrophobic interactions. The molecular weight distribution (MWD) of NOM can be estimated by comparing the chromatograph with known molecular weight standards that have similar structure and solution behavior to NOM. Polystyrene sulfonate (PSS) and polyethylene glycol (PEG) are the most common standards in calibration of SEC columns (Korshin et al., 2009; Sarathy and Mohseni, 2007, Pelekani et al, 1999).

Detectors used for SEC analysis include single and variable UV-vis detectors (Matilainen et al., 2011), Fourier transform infrared (FTIR) analysis (Allpike et al., 2007), and 3D excitation/emission fluorescence detection (Wu et al., 2003, 2007a). The main disadvantage of UV detection is, as mentioned previously, its low response to NOM molecules with low UV absorbance such as aliphatic acids, proteins and polysaccharides. Therefore, during the past decade, on-line organic carbon detectors (OCD) have become popular. Huber et al. (2011) reported that five peaks could be distinguished in analyzing a surface water with high performance liquid chromatography (HPLC) with OCD. These peaks represent different NOM fractions that, in the order of decreasing apparent molecular weight (AMW), are identified as: biopolymers (such as polysaccharides, polypeptides, proteins and amino sugars), humic substances (humic and fulvic acids), building blocks (breakdown products of HS), low molecular weight acids, and low molecular weight neutrals (LMW alcohols, aldehydes, ketones, sugars, and also amino acids). Figure 2.2 shows the apparent molecular weight of these fractions and a chromatogram of a surface water from southern Taiwan (Lai, et al., 2015).

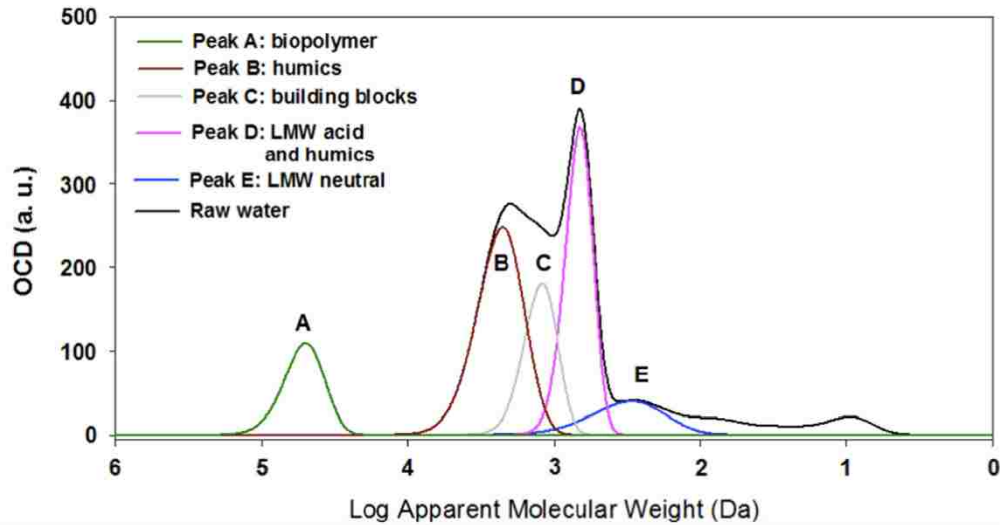


Figure 2-2 HPLCSEC-OCD chromatogram of different NOM fractions of a surface water (adopted from Lai et al., (2015))

Three-dimensional fluorescence excitation-emission matrix (F-EEM) spectroscopy

Three-dimensional fluorescence excitation-emission matrix (F-EEM) spectroscopy involves excitation of sample molecules and measurement of the emitted radiation over a range of wavelengths. It has gained popularity because of its high sensitivity, selectivity, and simplicity (Peiris et al., 2010; Baghoth et al., 2011).

There are various statistical methods for processing EEM data, among which parallel factor analysis (PARAFAC) has been commonly used recently. This method decomposes EEM spectra into distinct component groups associated with similar fluorophores (Shao et al., 2014).

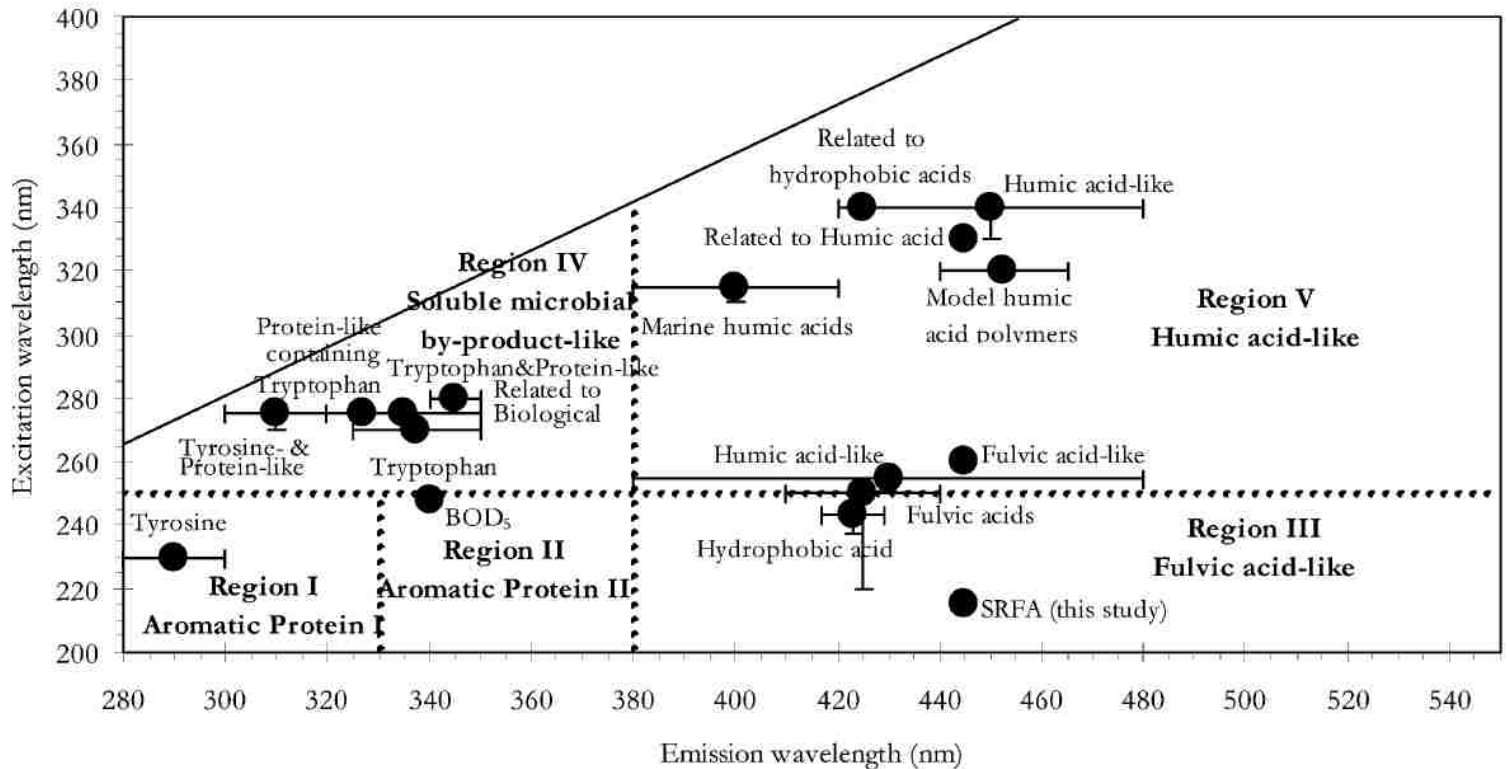


Figure 2-3 Location of different EEM peaks (adopted from Chen et al., 2003)

Fluorescent NOM is commonly categorized into three classes: humic-like, fulvic-like and protein-like substances. In interpreting EEM spectra, each class of molecules appears in a specific location in the excitation-emission space. For example, most peaks related to simple aromatic proteins appear at excitation wavelengths <250 nm and emission wavelengths <350 nm, whereas those for fulvic acid-like materials are at excitation wavelengths <250 nm and emission wavelengths >350 nm (Chen et al., 2003). Locations of the peaks of NOM fractions in EEM spectra are presented in Figure 2.3.

2.2 Low-pressure membrane fouling

Membrane fouling is a complicated phenomenon that depends on composition and

chemistry of the feed water, membrane properties, temperature, mode of operation and hydrodynamic conditions (Li and Elimelech, 2004). NOM has been identified as the major foulant in low-pressure membrane processes used for drinking water treatment, causing fouling by at least two mechanisms (Guo et al. 2012):

- 1- Adsorption onto the membrane pores, causing pore restriction or blockage
- 2- Formation of a gel layer on the membrane surface

These mechanisms are governed by size exclusion of solutes or chemical or electrical interactions, initially between the foulants and the membrane surface and later between foulants (Amy and Cho, 1999).

There is disagreement among researchers about the major NOM fractions responsible for membrane fouling. Until a decade ago, humic substances were considered to be the major foulant of low-pressure membranes by most researchers (Jones and O'Melia, 2000; Lin et al., 2000). For example, Yuan and Zydney (1999; 2000) reported that humic macromolecules are the main foulants of UF membranes and that fouling happens at the membrane surface. The effects of Suwannee river humic acid (SRHA, MW 10,000-30,000) and bovine serum albumin (BSA, MW 66,000) (as a surrogate of proteins) on fouling of UF membranes were investigated by Jones and O'Melia (2001). They found that SRHA could enter the pores and adsorb to the pore walls, whereas BSA was mostly retained on the membrane surface. Also, at a given mass of adsorbed material, humic acid caused more fouling than protein did. However, Fan et al. (2001) reported the fouling potential of different NOM fractions as: hydrophilic neutral compounds > hydrophobic acids > transphilic acids > hydrophilic charged compounds.

In recent years, the importance of the large MW hydrophilic fraction of NOM in both reversible and irreversible fouling of low-pressure membranes has been thoroughly investigated.

This fraction is also known as biopolymers and is thought to be comprised of polysaccharides and proteins. Biopolymers are rich in aliphatic carbons and hydroxyl groups (Leenheer, 2009; Yamamura et al., 2014a). One of the indicators of water with high biopolymer content is a lower SUVA₂₅₄ than water dominated by hydrophobic humic substances. Protein-like NOM is correlated with dissolved organic nitrogen (DON) levels, and high polysaccharide-like NOM results in high hydrophilic DOC levels in NOM fractionation (Amy, 2008). Typically, NOM of microbial origin, such as algal organic matter (AOM) (autochthonous NOM) or effluent organic matter (EfOM), contains higher levels of polysaccharide-like and/or protein-like foulants than NOM of a terrestrial origin (Amy, 2008).

Peldszus et al. (2011) studied fouling of a 400-kDa polyvinylidene fluoride (PVDF) hollow-fiber membrane fed with water from the Grand River (Canada). An upstream municipal sewage treatment plant discharge guaranteed the presence of biopolymers for the two years that the experiments were performed. Foulants causing irreversible and reversible fouling were analyzed by fluorescence EEMs spectroscopy. The results revealed a significant correlation between irreversible fouling and protein concentration. No significant retention of humic substances was observed, and therefore no strong correlation between humic substance concentrations and reversible or irreversible fouling was found. Colloid/particulate matter on the other hand, was found as a major contributor to reversible fouling. Kimura et al. (2014a) tested the fouling rate of a 0.1 µm PVDF membrane by waters from five different sources. Waters with higher protein-like intensities in EEM spectra and larger biopolymer peaks in LC-OCD chromatograms exhibited higher irreversible fouling potential. Also, a water with high humic content but low biopolymer content caused less reversible and irreversible fouling than a water with lower humic substance but higher biopolymer content. Yamamura et al. (2014) further illustrated the

dominant fouling effect of hydrophilic NOM fraction by filtering fractionated NOM through MF and UF membranes. At an identical DOC concentration, the hydrophobic fraction did not cause significant fouling, while the hydrophilic fraction severely fouled the membranes. However, the fouling of hydrophilic MF and UF membranes was less pronounced than that of hydrophobic membranes. Furthermore, they noticed that the HPI fraction from waters of different sources had different fouling intensities, even though all the fractions had equal DOC content. This result was in agreement with that of Halle' et al. (2009), who found that while biopolymer concentration is a key factor for irreversible fouling, its composition is of more importance.

Jermann et al. (2007) studied the role of polysaccharides and HS in fouling. Nordic Aquatic Humic Acid Reference and alginate (as a surrogate for polysaccharides) were used for fouling of a 100-kDa polyethersulfone (PES) membrane. HA induced mainly irreversible fouling by adsorption onto the membrane through hydrophobic interactions. Alginate, on the other hand, adsorbed only slightly, probably as a result of the electrostatic repulsion between PES and alginate, since both materials are negatively charged. When both HS and alginate were present in the feed solution, the mutual influence of the substances exacerbated fouling compared to the sum of the effects of each individual foulant (alginate, by forming a cake layer and decreasing HA permeation and HA, by narrowing the pores and increasing alginate retention and incorporation in the cake). The authors suggested that adsorbed HA can act as a bridge between the membrane and alginate, resulting in a more irreversible fouling layer. This result supports the finding of Lee et al. (2008) that low-MW NOM (0.3-1 kDa) initiates the fouling, but high-MW NOM (> 50 kDa) causes the bulk of the fouling. Yamamura et al. (2007b) also proposed that relatively low-MW humic-like substances start the fouling by adsorption onto the membrane, and larger MW hydrophilic NOM then accumulates on it.

2.3 DBP formation

One of the major problems related to the presence of NOM in drinking water production is the formation of disinfection by-products (DBPs) (Bond et al., 2010). DBPs result from reactions between NOM and disinfectant oxidants. Based on the NOM molecular characteristics and the applied disinfectant, two types of DBPs can form: carbonaceous DBPs (C-DBPs) and nitrogenous DBPs (N-DBPs) (Gan et al., 2013). On a mass basis, C-DBPs (which include trihalomethanes [THMs] and haloacetic acids [HAAs]) are dominant (Krasner et al., 2006). C-DBPs increase the risk of cancer and/or liver, kidney, or central nervous system problems. The US Environmental Protection Agency (EPA) has established a maximum contaminant level (MCL) of 80 µg/L for the sum of the concentrations of four THMs and 60 µg/L for sum of the concentrations of five HAAs.

N-DBPs are, however, not regulated by the US EPA. This group contains a variety of nitrogenous DBPs including N-nitrosamines, a group of derivatised amines that are carcinogens and mutagens. Among the nine N-nitrosamines that are classified as DBPs, N-nitrosodimethylamine (NDMA) is the most frequently detected, typically at nanogram per liter concentrations (Kristiana et al., 2013). N-nitrosamines are considerably more toxic than the regulated DBPs (Richardson et al., 2007).

It is believed that the hydrophobic fraction of NOM, which has high aromatic content, is the major source of THM and HAA precursors (Liang and Singer, 2003; Korshin et al. 2004; Leenheer and Croue, 2003). However, other NOM fractions can also contribute significantly to formation of DBPs. Hua and Reckhow (2007) investigated the formation of THMs and HAAs for different MW fractions and hydrophobicity groups of NOM from three drinking water plant influents in Canada and USA. They found that for the waters with high and medium SUVA₂₅₄

(4.4 and $2.8 \frac{L}{mg \cdot m}$, respectively) the hydrophobic NOM had higher potential for THM and HAA formation than the hydrophilic and transphilic fractions. However, all three hydrophobicity groups of the low SUVA water exhibited similar levels of THM and HAA precursors. For all three waters, the 0.5-3 kDa fraction of the NOM yielded the highest THM formation. On the other hand, while the <0.5 kDa fraction was the most productive fraction for dihaloacetic acid (DHAA), the >10 kDa and 3-10 kDa MW fractions had the highest trihaloacetic acid (THAA) formation yield. The authors concluded that, although a strong correlation exists between DBP formation and the SUVA value, depending on the water source, the low MW and hydrophilic fractions of NOM could also make significant contributions to DBP formation. These results were in agreement with those of Kitis et al. (2002), who tested two waters with different SUVA, MW distribution and, polarity. They observed that for the high SUVA water, higher MW fractions had higher DBP yields, whereas the 1-3 kDa fraction of the low SUVA water produced the highest HAA and THM yield. They also found that, although the hydrophobic fraction of the NOM was the most reactive in both waters, the hydrophilic fraction also contributed significantly to DBP formation.

Similar research has been done for N-DBP formation. Chen and Valentine (2007) studied NDMA formation from different NOM fractions by chloramination. They reported that the hydrophilic acid fraction forms more NDMA than the hydrophobic acid fraction. They also found that the basic fractions yield higher NDMA formation than the acidic fractions. Kristiana et al. (2013) investigated the formation of eight N-nitrosamines from different MW fractions of NOM and found that the <2.5-kDa fraction had the highest potential for N-nitrosamine formation by chloramination. These results are consistent with the higher nitrogen content of basic and hydrophilic fractions of NOM (Leenheer, 2009).

2.4 NOM pretreatment

In the previous sections, two NOM-related problems (membrane fouling and DBP formation) in drinking water treatment were introduced. Various approaches have been used to overcome these obstacles. In this section, innovative approaches for solving these problems are discussed.

Approaches for minimizing and controlling DBP formation include using alternative disinfectants such as chloramine or chlorine dioxide, and removal of DBP precursors prior to disinfection (EPA, 2006). However, changing the disinfectant does not necessarily solve the problem. For example, although chloramine produces lower THM and HAA levels than free chlorine, it significantly increases the levels of N-DBPs such as NDMA (Andrzejewski et al., 2005), and chlorine dioxide increases the formation of brominated DBPs (EPA, 2006). The second strategy does not generate alternative DBPs, and it can often be implemented with existing technologies. Therefore, NOM removal before disinfection is the most effective solution to control the formation of DBPs (Bond et al., 2010).

Various approaches have also been practiced for membrane fouling mitigation, such as switching from dead-end filtration mode to cross-flow mode (Belfort et al., 1994), flux adjustment (Howell et al., 1995), or using membranes with more fouling resistive material (Miyoshi et al., 2015). Here again, removing NOM foulants prior to membrane filtration is considered the best strategy to mitigate membrane fouling.

The most commonly used process for NOM removal is coagulation. Coagulation works well for removing high-MW NOM with high $SUVA_{254}$ values, but it does not remove low-MW NOM

with low $SUVA_{254}$ very efficiently. Table 2.1 presents an overview of the relationship between $SUVA_{254}$ and TOC removal during coagulation (Edzwald and Tobiason, 1999).

Table 2-1 Relationship between SUVA and DOC removal during coagulation (adapted from Edzwald and Tobiason, 1999)

$SUVA_{254}$	Composition	Coagulation	DOC Removal
> 4	Mostly aquatic humics, high hydrophobicity, high MM compounds	NOM controls, good DOC removals.	> 50% for alum, little greater for ferric.
2-4	Mixture of aquatic humics and other NOMs, mixture of hydrophobic and hydrophilic NOM, mixture of MMs.	NOM influences, DOC removals should be fair to good.	25–50% for alum, little greater for ferric.
< 2	Mostly non-humics, low hydrophobicity, low MM compounds.	NOM has little influence, poor DOC removals.	< 25% for alum, little greater for ferric.

Coagulation + powdered activated carbon (PAC) adsorption

Najm et al. (1998) conducted jar tests with Colorado River water and reported that a combination of enhanced coagulation and PAC adsorption reduced the total chemical dose required to produce drinking water that complies with US EPA DPB regulations. Uyak et al. (2007) carried out similar experiments with Terkos Lake water in Turkey, with average DOC and UV_{254} of 4.4 mg/L and 0.136 cm^{-1} , respectively. They found that coagulation with 100 mg/L FeCl_3 could achieve 45% DOC removal and 57% THM formation potential (FP) reduction. However, 40 mg/L FeCl_3 + 20 mg/L PAC achieved the same THMFP reduction and more DOC removal (nearly 60%).

The Effect of six water treatment processes (alum coagulation, magnetic ion exchange resin (MIEX) treatment, chlorination, ozonation, PAC adsorption, and biological sand filtration) on NOM removal was studied by Ho et al. (2013). They found that, although MIEX was capable of

removing more NOM over a broad range of molecular weight than any of the other processes alone, a combination of alum and PAC could remove even more NOM, with a wider range of molecular weight.

Two reports have been published describing the plant-scale application of PAC coupled with coagulation to enhance NOM removal. Carrière et al. (2009) found that application of 11 mg/L of PAC in a water treatment plant in Canada led to only 6.7% additional removal of NOM and that this removal was ineffectual at lowering THM formation potential in both plant and jar tests. However, Kristiana et al. (2011) reported that addition of 150 mg/L PAC to the enhanced coagulation process improved DOC removal by 70% and significantly decreased the chlorine demand in the pipeline at the South West water treatment plant in Australia, where the raw water had very high DOC (18.8-20.5 mg/L). Also, THM and HAA formation was reduced by up to 40 and 90%, respectively.

Membrane fouling reduction by a combination of coagulation and PAC adsorption has also been the subject of several research publications. In a 63-day test of two, 0.1- μm microfiltration membranes in parallel, trans-membrane pressure buildup for the membrane receiving water pretreated with 5 mg/L PAC and poly aluminum chloride (PACl, 0.8 mg Al/L) was substantially less than for the membrane receiving water that had been pretreated only by coagulation (Matsui et al., 2009). Yu et al. (2014) also investigated the long term (63 days) effect of PAC+alum pretreatment compared to alum pretreatment alone, on fouling of 0.03- μm PVDF ultrafiltration membranes. Both reversible and irreversible fouling were significantly mitigated by addition of 10 mg/L PAC with alum coagulation. Addition of PAC decreased the feed water DOC level, and fluorescence EEM analysis revealed that the concentration of protein-like material in the foulants inside the membrane pores also decreased. The effect of combined coagulation-adsorption pre-

treatment on ultrafiltration of secondary effluent was studied by Haperkamps et al. (2007). They tested four different commercially available PACs, and LC-OCD analysis indicated that each adsorbent had different adsorption efficiency for different organic fractions. Simultaneous coagulation and adsorption enhanced the membrane performance, apparently by increasing the removal of the biopolymer fraction. Gou et al. (2005) obtained a similar result, finding that combined pretreatment increased the operational flux by more than five-fold. However, pilot-scale experiments of Kweon et al. (2009) showed no significant difference on fouling reduction of UF membranes between PAC pre-treatment alone and combined adsorption-coagulation pretreatment.

Considering the different reported results for combined pretreatment with respect to both DBP formation and membrane fouling, it can be inferred that the efficacy of this process is strongly dependent on the type of the PAC and the characteristics of the source water in addition to the adsorbent and coagulant dosage.

Reduction of adsorbent particle size

NOM adsorption onto PAC is a relatively slow process and thus a considerable fraction of the adsorption capacity of the adsorbent would be untouched during a typical 1-2 hour contact time in water treatment (Ando et al., 2010). Reduction of the PAC particle size increases the adsorption rate (Najm et al. 1990). In addition, Ando et al., (2010) found that pulverizing PAC particles with median particle diameter of 11.8 μm to “super-fine” particles with median diameter of 0.73 μm significantly increases the NOM adsorption capacity. The ratio of the adsorption capacity of the super-fine PAC (SPAC) to the adsorption capacity of the regular PAC was lowest for the post-coagulation water that contained only low-MW NOM and highest for the Suwannee River Humic Acid. Adsorption of different MWs of PSS yielded a strong correlation

between the increased adsorption capacity due to pulverization and the size of the adsorbate molecules. Matsui et al., (2009) found that pulverizing PAC to sub-micron size increases the adsorption capacity of the adsorbent for membrane foulants. They observed similar TMP increase rates for a system pretreated with pulverized PAC and a system pretreated with regular PAC but with a five-fold higher dose.

Authors believed that the increased capacity is due to the increase in the mesopore volume of the adsorbent. However, the mesopore volume increase was too small to account for the enhancement of the adsorption capacity, and it was suggested that NOM adsorption mostly depends on the total external particle surface area of the adsorbent.

NOM removal by heated aluminum oxide particles (HAOPs)

HAOPs is a novel adsorbent first synthesized by Kim et al. (2008). Like other metal oxide adsorbents, it is believed that NOM adsorbs to HAOPs by binding to the hydroxide surface sites (Cai et al., 2008). Figure 2.4 presents the efficiency of different adsorbents, including HAOPs, for removing NOM from Lake Union (LU) water in batch adsorption tests. At small doses, HAOPs has a higher NOM removal efficiency than other adsorbents. However, at high adsorbent doses, the removal efficiency reaches a plateau, indicating that a fraction of NOM cannot adsorb onto HAOPs. A similar trend can be seen for alum and ferric chloride. On the other hand, PAC seems to be capable of removing almost all the organic matter in the water at high doses.

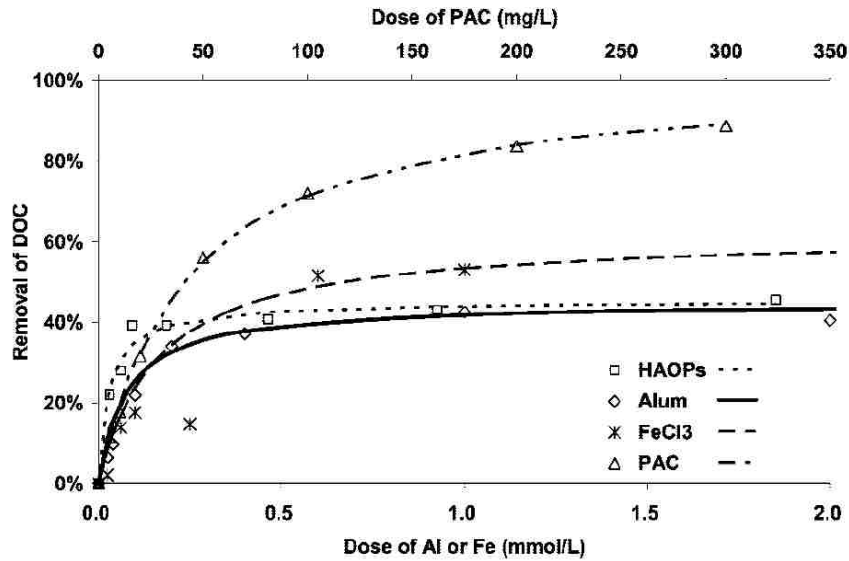


Figure 2-4 NOM removal from LU water by sorption onto various solids (Cai et al., 2008)

Further investigation revealed that the fraction of NOM that is not adsorbable on HAOPs is preferentially adsorbed onto PAC (Cai et al., 2008). Therefore, it seems that mixtures of HAOPs and PAC at low doses would have the potential to remove a wide range of NOM molecules.

Kim et al. (2008) compared the efficacy of NOM pretreatment for fouling reduction by HAOPs, heated iron oxide particles (HIOPs) and PAC. They found that batch reactors with HAOPs and HIOPs could remove some membrane foulants, but that the pretreatment performance was significantly improved when the HAOPs or HIOPs was pre-deposited on the membrane and the feed water was passed through the pre-deposited adsorbent layer before reaching the membrane.

Pretreatment by micro-granular adsorptive filtration (μ GAF) process

Granular media filtration has been reported to be effective in removing particulate matter prior to membrane filtration, resulting in longer filtration cycles (Sakol, and Konieczny, 2004). However, removal of soluble foulants by granular media filtration is very limited.

μ GAF combines granular media filtration and adsorption. Choo et al. (2004) pre-deposited iron oxide particles (IOPs) on the surface of UF membranes. Although the flux decline throughout the filtration cycle was lower than in a test without pre-treatment, the adsorbent particles themselves imposed hydraulic resistance, causing the initial flux to decline by nearly 50%. Zhang et al. (2003) pre-loaded heated iron oxide particles (HIOPs) and PAC onto a hollow-fiber UF membrane by feeding a concentrated slurry of particles to the membrane prior to filtration of the Lake Union water. For an equal mass of adsorbent, PAC removed more NOM than HIOPs, but a cake layer that exacerbated fouling formed in the system with PAC, and a positive correlation was observed between the PAC dose and fouling. HIOPs, by contrast, removed less NOM, but the HIOPs-NOM layer did not impose additional fouling. In this case, a strong correlation was found between the HIOPs dose and the operational time before reaching a certain TMP. Scanning electron microscope (SEM) images of the systems suggested that NOM binds PAC particles to each other and to the membrane surface, leading adsorbent particles to become part of the foulant. The HIOPs-NOM cake, on the other hand, was not bound to the membrane surface, and the cake layer had enough porosity to allow water to reach the membrane without additional resistance.

Cai (2011) investigated μ GAF with HAOPs as the adsorbent, using membranes made of different materials and with pore sizes from 0.05 to 12 μ m. He found that the bare membrane did not remove much soluble NOM, so the HAOPs layer was responsible for the majority of the NOM capture. Therefore, in the μ GAF process, it is possible to use coarse filters as adsorbent barriers instead of tight membranes. With this modification, it is possible to study the performance of the adsorbent layer in an upstream pretreatment unit for NOM removal and its effectiveness on fouling control of a downstream membrane. It also enables studying the fouling

on each unit separately. In addition to the benefits that separation of the μ GAF unit from the membrane filtration unit provides for research purposes, it is also potentially beneficial for industrial applications by reducing the required maintenance of the membrane unit, eliminating the complication of adsorbent deposition into hollow fiber membranes and reducing the adverse adsorbent-membrane interactions. Therefore, it might make it possible to use PAC as the adsorbent without unwanted NOM-PAC-membrane interactions. However, no studies have been conducted to investigate the performance of PAC pre-deposited on coarse filters instead of membranes.

2.5 Summary

Natural organic matter is the source of many problems in drinking water treatment, such as reduction of membrane permeability due to fouling and formation of disinfection by-products. Approaches for addressing these problems include modifying the flow pattern or flux control for membrane fouling mitigation, and application of alternative oxidants for DBP formation reduction. However, the most reliable approach is to capture foulants before they reach the membrane unit or remove the DBP precursors prior to the oxidation step. Therefore, NOM pretreatment processes have been developed extensively over the years.

Although some fractions of NOM are considered to be primarily responsible for these problems (the hydrophilic neutral fraction in membrane fouling, and hydrophobic acid fraction for DBP formation), recent research indicates that the adverse effects of NOM are not limited to a specific fraction. Therefore, pretreatment processes are desired to have reasonable efficiency for removing all fractions of NOM.

μ GAF integrates adsorption, granular media filtration and membrane filtration and has great

potential for water treatment. However, the understanding of the mechanisms by which this process works is limited. Prior research on the performance of μ GAF has focused on HAOPs as the adsorbent. Although PAC is able to adsorb NOM, adverse interactions between PAC particles, NOM, and membrane surfaces have been an obstacle in utilizing PAC in the μ GAF process. Using a coarse filter instead of a tight membrane as the support for the adsorbent might solve this problem. Such a finding would be important, because activated carbon is the most widely used adsorbent in the water treatment industry, and its physical and chemical characteristics as well as its adsorption mechanisms have been extensively studied. Furthermore, since PAC and HAOPs preferentially adsorb different fractions of NOM, using mixtures of these adsorbents seems a promising technique to increase the efficiency of the process.

The main component of this research is a study of the behavior of the μ GAF process with PAC as the adsorbent. PAC characteristics and operational parameters will be studied. Mixtures of HAOPs and PAC will also be examined as a potential method for improving the process performance. The performance will be evaluated in terms of membrane fouling mitigation, DBP formation potential reduction, and the capture of different fractions of NOM. Comparisons will be made with available μ GAF-HAOPs data to provide a thorough assessment of the process performance. It is expected that this research will provide a better evaluation of the potential of the μ GAF process and contribute to development of an efficient pretreatment process for the water treatment industry.

Chapter 3. Materials and methods

3.1 Materials

3.1.1 Water samples

Organic free water with a resistivity of 18.2 M Ω -cm was obtained from a Milli-Q water purification system (Millipore Milli-Q, Billerica, MA).

Freshwater was collected from the Lake Union (LU) at the Portage Bay, Seattle, WA. Water samples were stored at 4°C and were brought to room temperature prior to use. The pH of the water was 7.5 \pm 0.3 and it contained 2.1~2.5 mg/l DOC. The UV₂₅₄ of the water was 0.053~0.062 cm⁻¹. Therefore, the specific UV absorbance at 254 nm (SUVA₂₅₄) was 2.4~2.5 L/mg-m.

The pH of the water samples was adjusted to 7 \pm 0.05 with 1 M NaOH or HCl. Ionic strength was adjusted by adding 0.5 mM NaHCO₃ and 0.5 mM NaCl to all the water samples. With the added buffering capacity, pH of the water remained within \pm 0.2 throughout the experiments.

3.1.2 Adsorbents

Heated aluminum oxide particles (HAOPs) and 3 commercially available PACs were the adsorbents used in the experiments. HAOPs were synthesized by neutralizing aluminum sulfate (Al₂(SO₄)₃·18 H₂O) solution with NaOH (4 M) to pH 7.0 to generate a 10 g/L-Al solution of Al(OH)₃ precipitate. Then the solution was oven heated at 110°C for 24 hours in a closed glass bottle and then cooled to room temperature. HAOPs prepared with this method were reported to have a point of zero charge at pH 7.7 (Kim et al, 2008).

The activated carbons used in this study were WPH (Calgon, Pittsburgh PA), Norit SA UF and Norit SA SUPER (Cabot Co. Boston, MA). Excess water was removed by drying at 110°C for 24 hours. Samples were then cooled to room temperature and a 10 g/L slurry solution was made with Milli-Q water. Table 3.1 presents the characteristics of the adsorbents applied in this study.

Table 3-1 Characteristics of different adsorbents used

Properties	HAOPs	WPH	SA UF	SA SUPER
Mean Diameter (um)	7.5	5 ^a	5 ^b	15
Total Surface Area (B.E.T) (m ² /g)	35.6	903 ^a	1100 ^b	1150
Micropore (<2nm) Surface Area(m ² /g)	-	888 ^a	733 ^a	-
Mesopore (2-500nm) Surface Area (m ² /g)	-	15 ^a	379 ^a	-
Source of Carbon	-	Coal	Vegetable raw material	Vegetable raw material
Activation Method		Thermal	Steam	Steam

a) Data reported by Li et al. (2003)

b) Data reported for the mean diameter and B.E.T surface area by Li et al. are 3(um) and 1112(m²/g), respectively

3.1.3 Mesh filters and membranes

In experiments where water was passed through a layer of adsorbent, the adsorbent was deposited on paper filter (Whatman®, grade 40) with a nominal pore size of 8 µm. In many experiments, either raw water or water that had been pre-treated by passage through an adsorbent layer was applied to a flat-disk polyethersulfone (PES) UF membrane (Microdyn-Nadir, Germany) with nominal pore size of 0.05 µm. Both the paper filters and UF membranes were

pre-conditioned by soaking and rinsing in deionized water prior to the experiment. Filter sheets were cut into a disk shape with diameter of 47 mm and installed into a filter holder cartridge. An O-ring was employed to seal the cartridge. Each cartridge provided an effective surface area of 9.62 cm².

3.2 Analytical methods

3.2.1 UV₂₅₄ and DOC analysis

UV absorbance at 254 nm (UV₂₅₄) was measured by using a dual-beam Lambda-18 spectrophotometer (Perkin-Elmer GmbH., Überlingen Germany) with a 1-cm quartz cell. DOC was determined with a Siever 900 TOC analyzer (GE, Boulder, CO.).

3.2.2 NOM molecular weight distribution analysis

A high-performance liquid chromatography system (DIONEX Ultimate 3000, Thermo Scientific, Waltham, MA) with a GE Siever 900 TOC analyzer was used to measure dissolved organic carbon. A TOSOH TSKgel G3000 PWxl size exclusion chromatography (SEC) column for analyzing molecular weights up to 50,000 Da was used. A solution of 0.02 M NaH₂PO₄ at pH 6.9 was used as the mobile phase at a flow rate of 1 ml/min.

3.2.3 Three-dimensional excitation-emission matrix (EEM) fluorescence spectroscopy

Fluorescence measurements were conducted using an Aqualog – 800 spectrofluorometer (HORIBA Instruments Inc., NJ, USA) at room temperature. EEMs were generated by scanning over excitation wavelengths of 200 - 450 nm at 10 nm intervals, and emission wavelengths of 300 – 600 nm at 10 nm intervals. To eliminate Raman scattering of water and reduce other background noise, fluorescence spectra for Milli-Q water will be subtracted from all the spectra.

3.2.4 DBP formation potential

THM and HAA samples were prepared following USEPA methods 551 and 552, respectively. A Shimadzu gas chromatograph (GC) 2010 was used to analyze samples.

3.3 Experimental methods

3.3.1 Batch adsorption tests

Experiments were carried out by adding the desired amount of adsorbent to 100 ml of Lake Union water. The pH was adjusted to 7.0 ± 0.1 with 1 M NaOH or HCl. Flasks were then placed on a rotary shaker. After 2 hours of contact, the samples were passed through a $0.45 \mu\text{m}$ nylon syringe filter and stored at 4°C in glass vials until analysis.

For the mixed adsorbent tests, both simultaneous and sequential treatment were examined. In the sequential mode, one of the adsorbents was spiked to the solution and after 2 hours of mixing, it was removed by filtration through a paper filter grade 40. Then, the other adsorbent was added to the filtrate and the solution was mixed for another 2 hours. For the sequential mode, sampling was done at the end of each step.

3.3.2 Sequential pretreatment-membrane filtration

3.3.2.1 Batch adsorption-membrane filtration

A 2-liter glass beaker was used as a batch adsorption reactor. The given dose of adsorbent or adsorbents was spiked into the solution followed by mixing for 2 hours. The solution was then filtered with a paper filter to retain the adsorbent, and the filtrate was fed to a membrane filtration unit with a peristaltic pump at a fixed flow rate.

3.3.2.2 μ GAF- membrane filtration

The schema of the experimental set-up is presented in Figure 3.1. Adsorbent was deposited by injecting a concentrated adsorbent slurry into the cartridge with a syringe. The filter cartridge was shaken gently during the adsorbent injection to help form a uniform adsorbent layer on the mesh. A peristaltic pump was used to provide a constant flow of the feed water to the upstream μ GAF unit. The inlet of the filter cartridge was connected to a pressure transducer (Omega Engineering, CT, USA). The transducer was connected to a data logger which itself was linked to a desktop computer. Online data from the transducer was recorded on the desktop computer.

The permeate line was connected to a three-way pinch valve. One channel was connected to an auto-sampler for sampling and another channel led to the permeate reservoir.

The downstream membrane filtration unit was fed by the permeate from the upstream unit. This unit was similar to the upstream unit, except a bare UF membrane (i.e., with no adsorbent layer) was used instead of the filter paper.

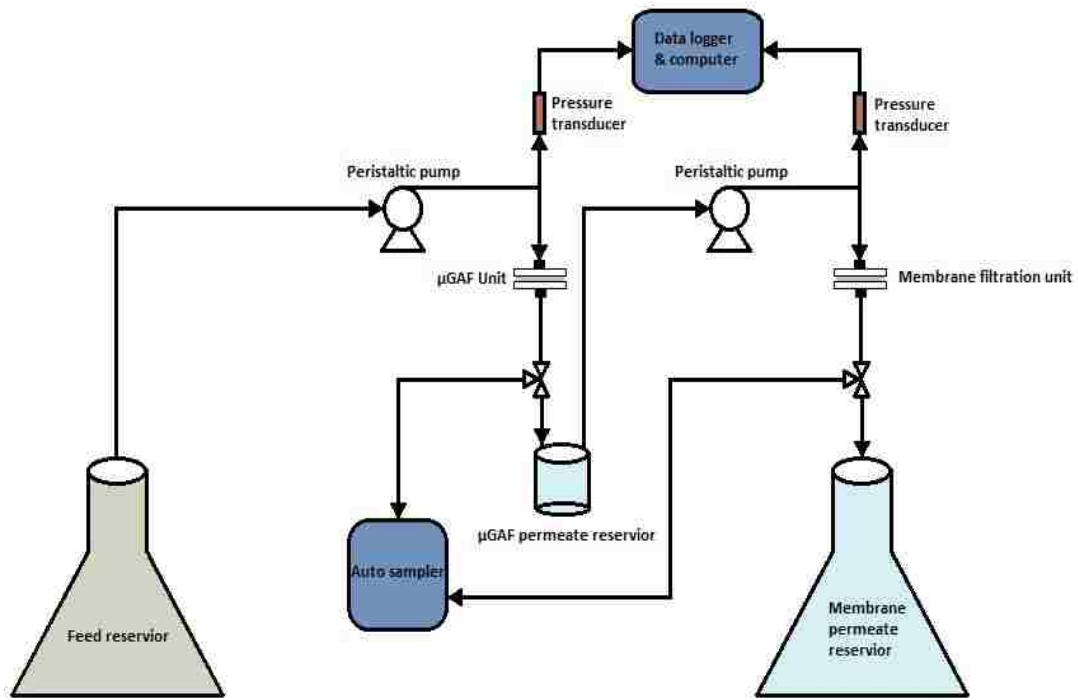


Figure 3-1 Schematic setup of sequential filtration system

Chapter 4. Results & Discussion

In this chapter, experiments and results are presented and discussed. First, NOM removal by three commercially available PACs in batch adsorption and μ GAF tests is presented to find a proper PAC for NOM pretreatment. Second, the advantages of μ GAF over batch adsorption for NOM removal and membrane fouling control are discussed and the effectiveness of mixtures of HAOPs and PAC for NOM removal is presented.

In the second part of this chapter, the effect of the μ GAF process design parameters, including adsorbent surface loading and the importance of the outer surface of the adsorbent layer, are discussed. Lastly, the effect of the applied flux on the μ GAF-PAC process is presented and compared with the corresponding effect on the μ GAF-HAOPs process.

4.1 HAOPs and PAC for NOM removal and μ GAF pretreatment

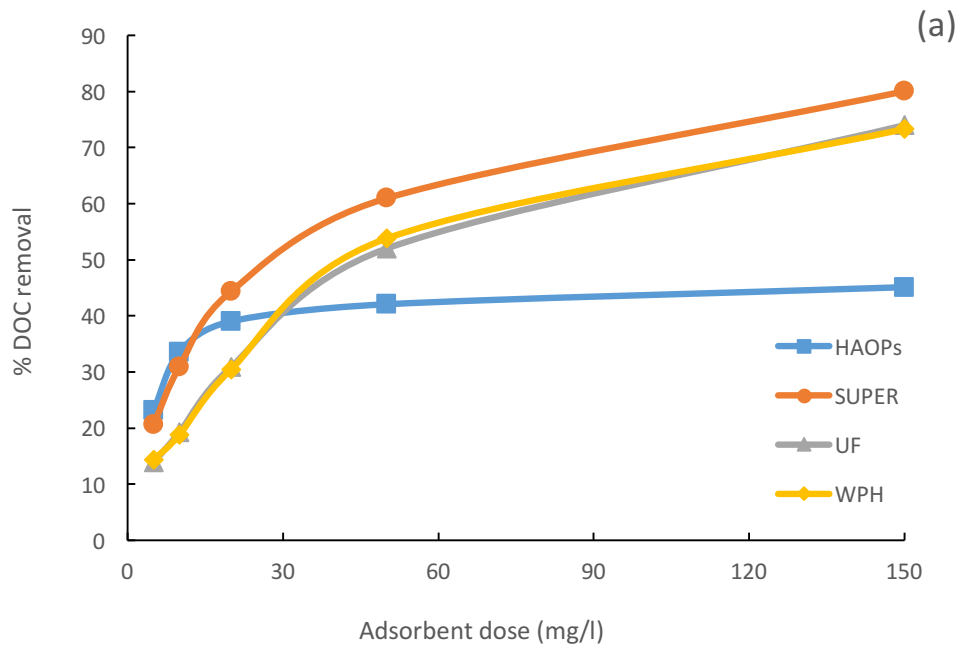
4.1.1 Batch adsorption

A previous effort by Cai (2010) to utilize PAC in μ GAF was not successful, partly because the PAC did not have a comparable NOM removal efficiency. Therefore, effort was made to find a better PAC for NOM removal.

NOM adsorption by three commercially available PACs was tested. The PACs were WPH (Calgon, Pittsburgh PA), Norit SA UF and Norit SA SUPER (Cabot Co. Boston, MA). WPH adsorbs small molecules (up to a few hundred Daltons [Li et al. 2003]) and is widely used in the US for taste and odor control in drinking water treatment. Norit SA UF and Norit SA SUPER remove larger adsorbates due to their high ratio of mesopore volume to surface area (Li et al. 2003; Haberkamp et al. 2007).

Adsorption of LU NOM onto PACs and HAOPs was first evaluated in batch experiments. As shown in Figure 4.1, NOM removal efficiency by HAOPs reaches a plateau, indicating that a fraction of the NOM is not adsorbable by HAOPs (Cai 2010). However, all three PACs achieved almost complete NOM removal at high adsorbent doses.

At low doses HAOPs and SA SUPER performed similarly in removing NOM. HAOPs, however, removed slightly more UV₂₅₄, which is indicative of its higher affinity for humic material. Both adsorbents outperformed SA UF and WPH within the common adsorbent dose range used in water treatment.



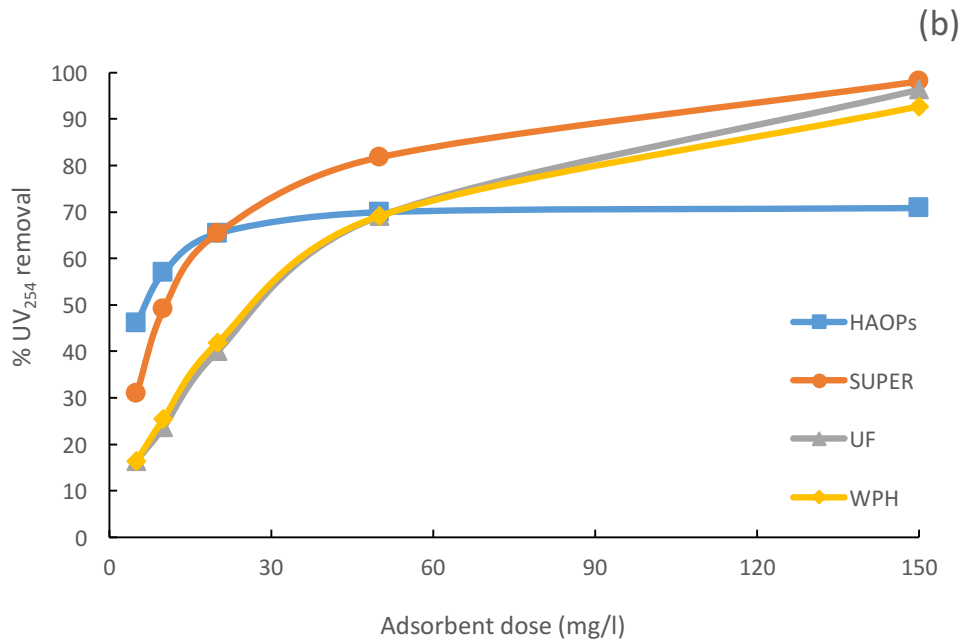


Figure 4-1 Batch adsorption of NOM from LU water by HAOPs and different PACs. a) DOC
b) UV₂₅₄

Another important characteristic for adsorbents in μ GAF applications is adsorption kinetics, since the contact time in μ GAF is on the order of only a few seconds. The kinetics of adsorption of LU NOM onto HAOPs and three PACs are presented in Figure 4.2. HAOPs and SA SUPER have significantly higher adsorption rates than SA UF and WPH. Within the first minute of contact, adsorption of DOC by either HAOPs or SA SUPER was 85% of the ultimate equilibrium value, whereas the corresponding fractions for SA UF and WPH were 56% and 50%, respectively, although as mentioned in section 3.1.2 SA UF and WPH have smaller mean particle sizes (Figure 4.2a). A similar pattern was observed for the removal of UV₂₅₄ by these adsorbents (Figure 4.2 b). HAOPs equilibrated with the UV₂₅₄-absorbing NOM almost instantaneously (97% of the equilibrium value within the first minute), whereas SA SUPER, SA UF and WPH removed 90%, 47%, and 50% of their equilibrium amounts, respectively, within the first minute of contact.

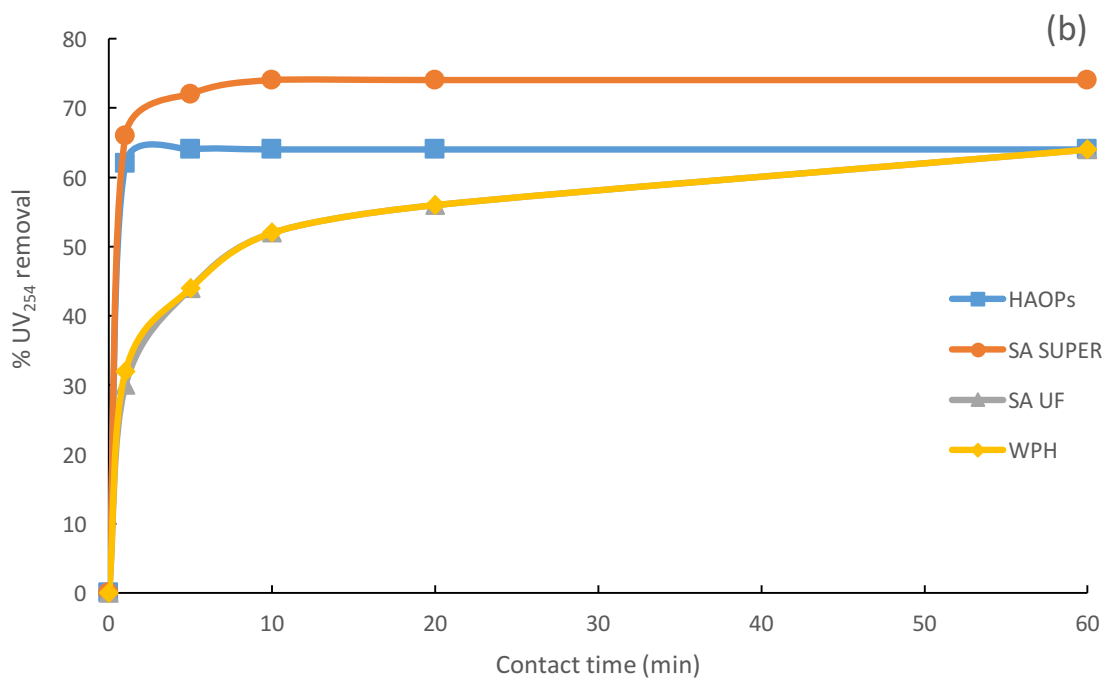
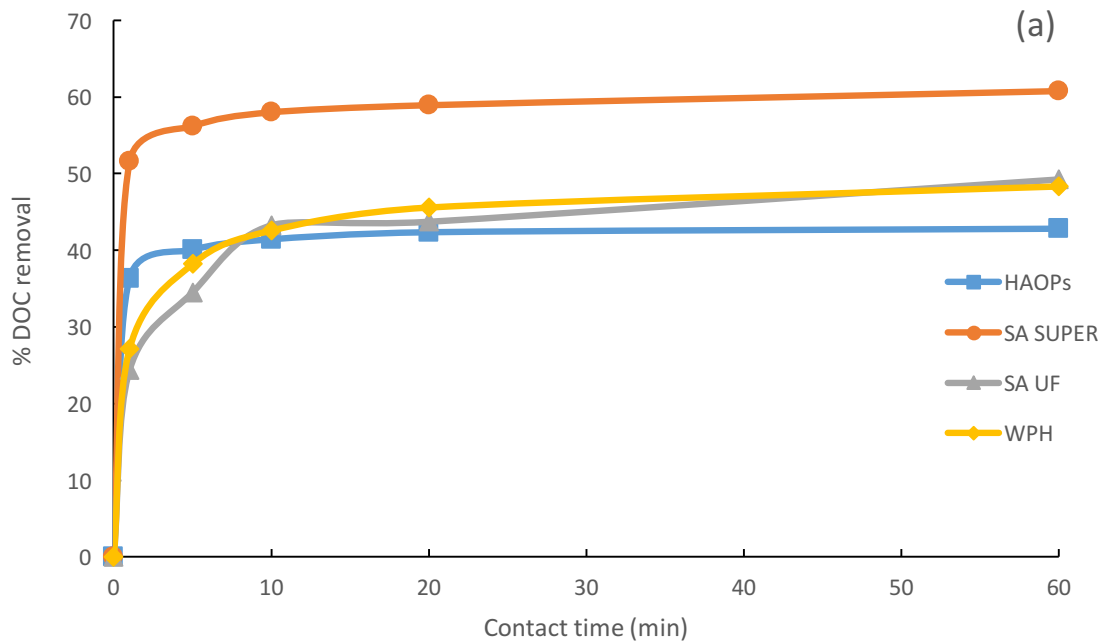
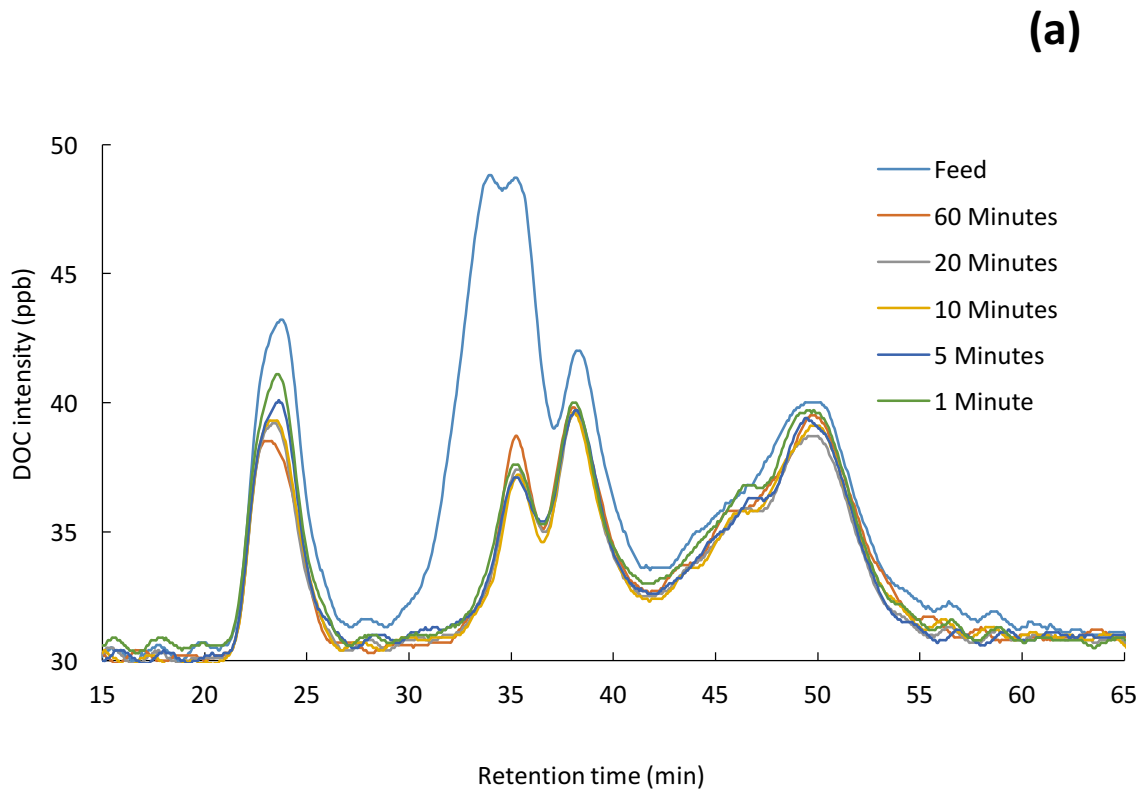


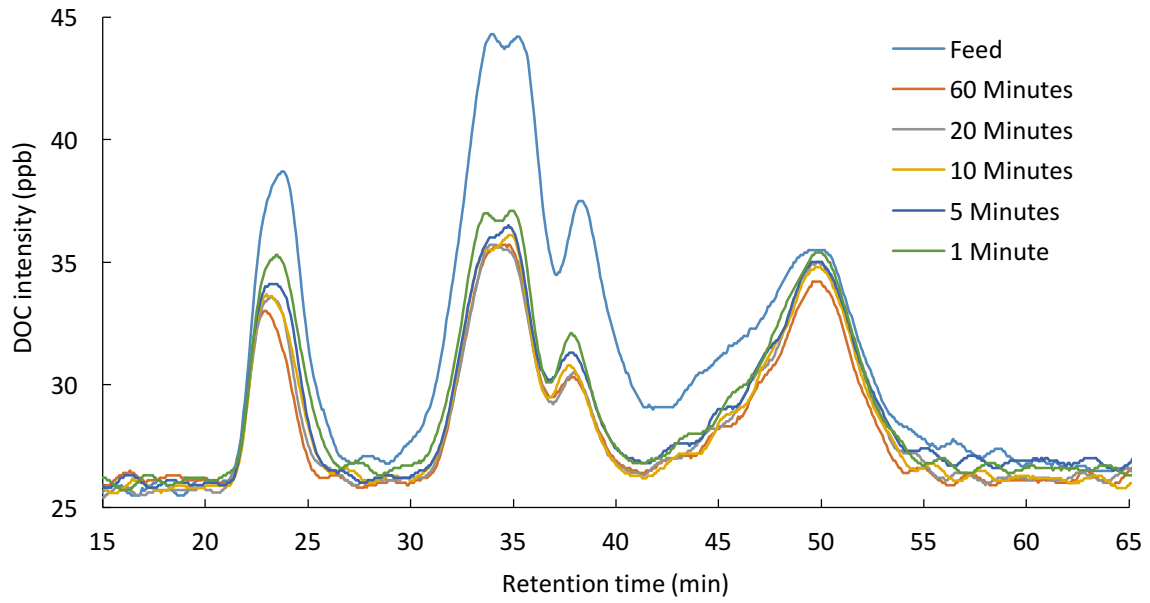
Figure 4-2 NOM adsorption kinetics of HAOPs and three PACs at an adsorbent dose of 50 mg/l. a) DOC b) UV₂₅₄

SEC analysis provided insight into the adsorption kinetics of different NOM fractions by the adsorbents (Figure 4.3). HAOPs removed humic substances and building blocks almost instantaneously, consistent with the rapid adsorption kinetics of UV₂₅₄-absorbing NOM presented above. This result can be explained by the negligible internal porosity of HAOPs particles (Cai 2010), so that adsorption occurs mainly on the outer surface of the particles.

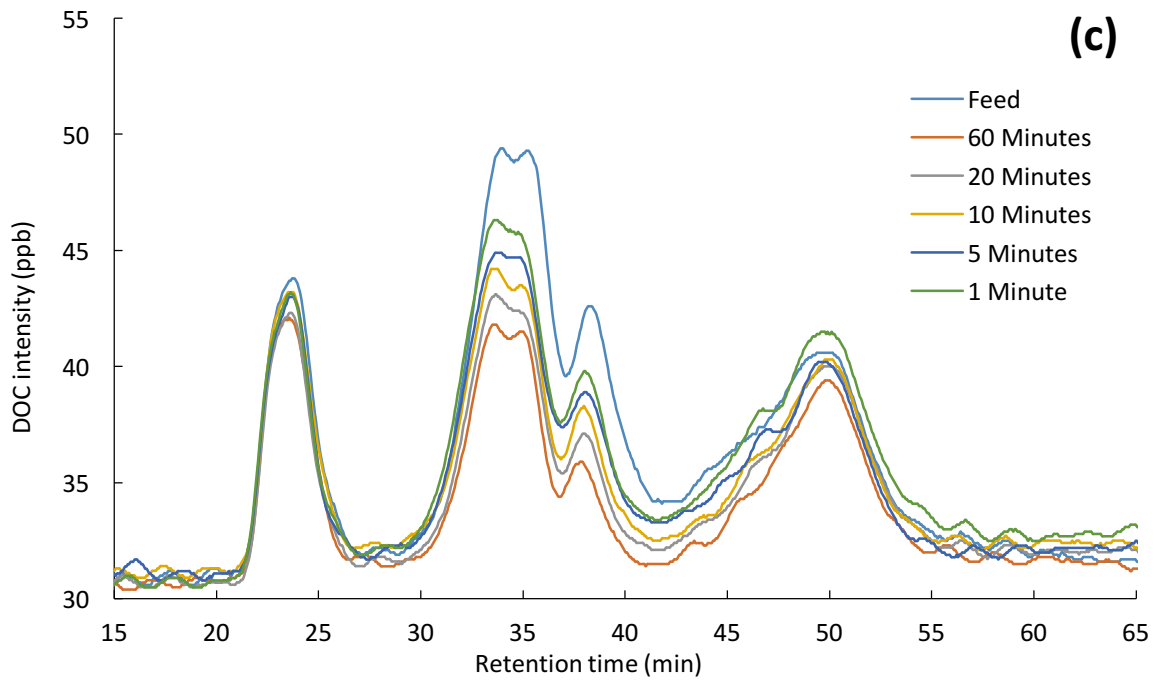
The rate of adsorption for the high molecular weight biopolymer fraction was not as high as for the humics. The gradual increase in the DOC removal by HAOPs, observed in kinetics tests, could be mostly attributed to the gradual adsorption of this fraction.



(b)



(c)



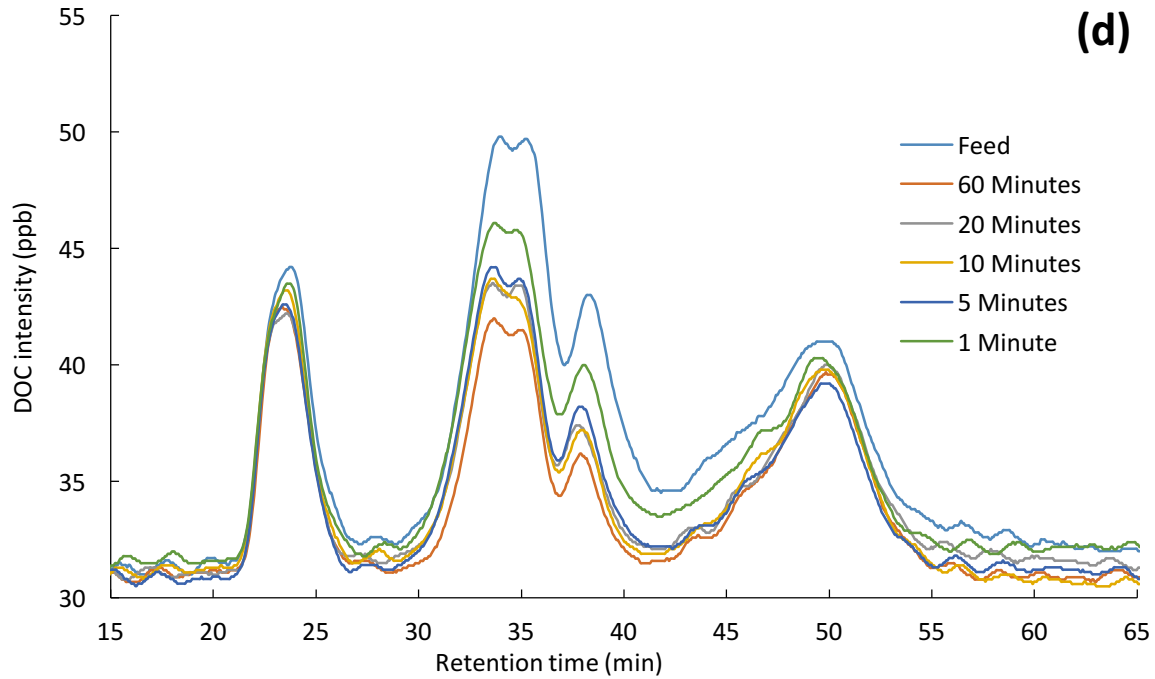


Figure 4-3 SEC chromatograms showing adsorption kinetics of various NOM fractions onto (a) HAOPs; (b) SA SUPER; (c) SA UF; and (d) WPH at an adsorbent dose of 50 mg/l.

SA SUPER behaved similarly to HAOPs, gradually removing the biopolymer fraction and rapidly removing the rest of the NOM fractions. This similarity might be due to the high ratio of mesopore volume to surface area for this adsorbent, making the adsorption sites more accessible to NOM molecules (Haberkamp et al. 2007). SA UF and WPH, on the other hand, gradually adsorbed all the NOM fractions, which can be attributed to their high microporosity.

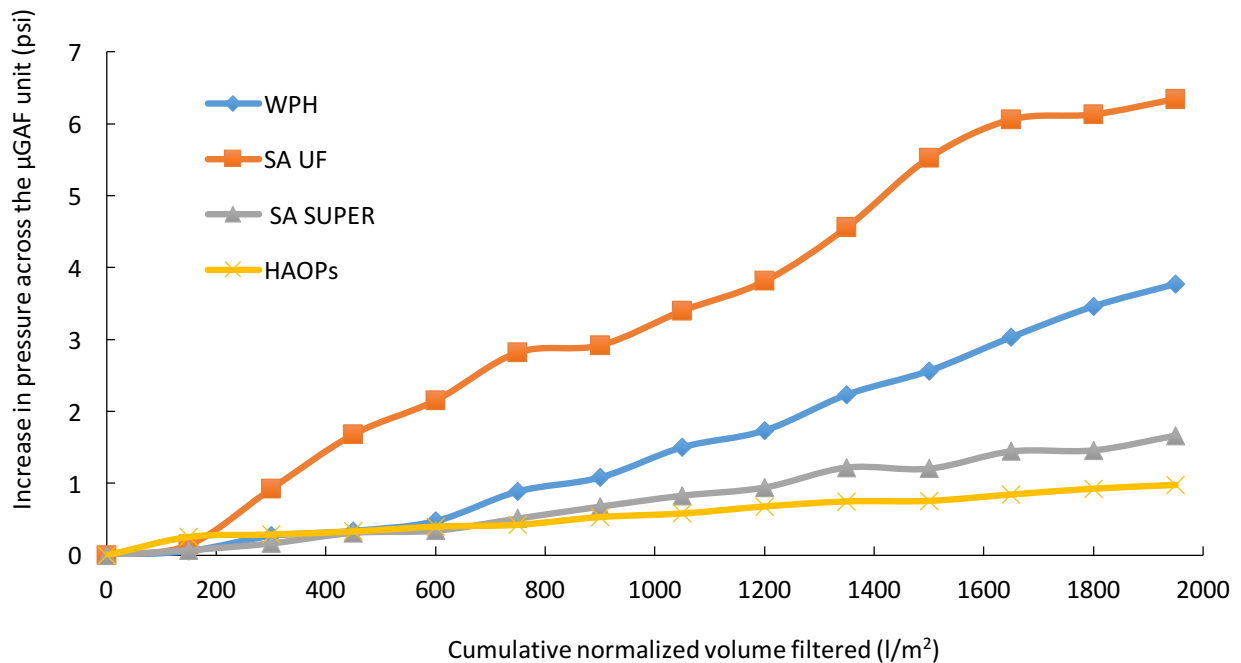
4.1.2 Sequential adsorption and membrane filtration

Experiments were carried out to compare the performance of the PACs with that of HAOPs in a sequential μ GAF-membrane filtration process. Lake Union water was used as the feed. The adsorbent surface loading in the μ GAF unit was 30 g/m^2 , and a flat-sheet $0.05\text{-}\mu\text{m}$ PES membrane was used in the downstream unit. Filter paper was used to hold the adsorbent in the

μ GAF unit. The pressure required to pass water through the bare filter paper (without a layer of adsorbent) did not increase during a control run, indicating that the large openings in the filter were not blocked by the feed water. Therefore, any pressure increase across the μ GAF unit indicated fouling of the adsorbent layer.

Results for the sequential filtration tests are shown in Figure 4.4. The performance of SA SUPER was similar to that of HAOPs, and both of those adsorbents outperformed the other two PACs in terms of UV_{254} removal in the upstream unit and fouling control in the downstream unit. UV_{254} removal by SA SUPER was higher than that by HAOPs at the beginning of the run, but it decreased more rapidly. During the whole run, SA SUPER and HAOPs removed 63% and 72% of the UV_{254} , respectively.

(a)



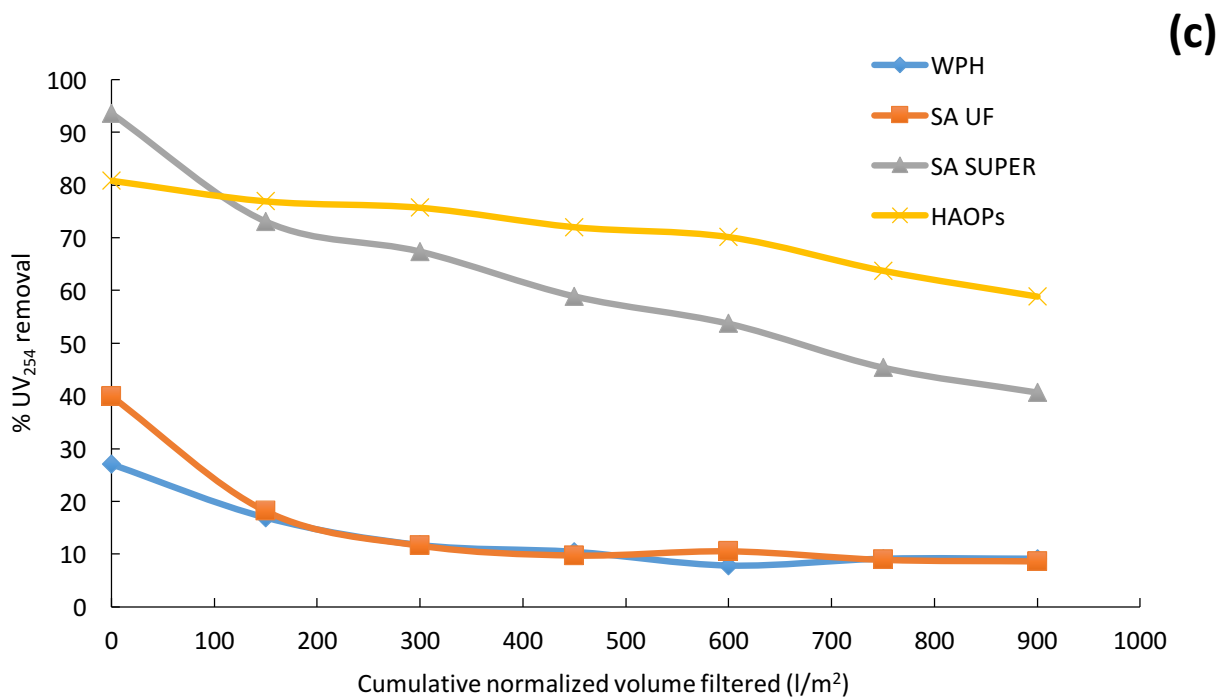
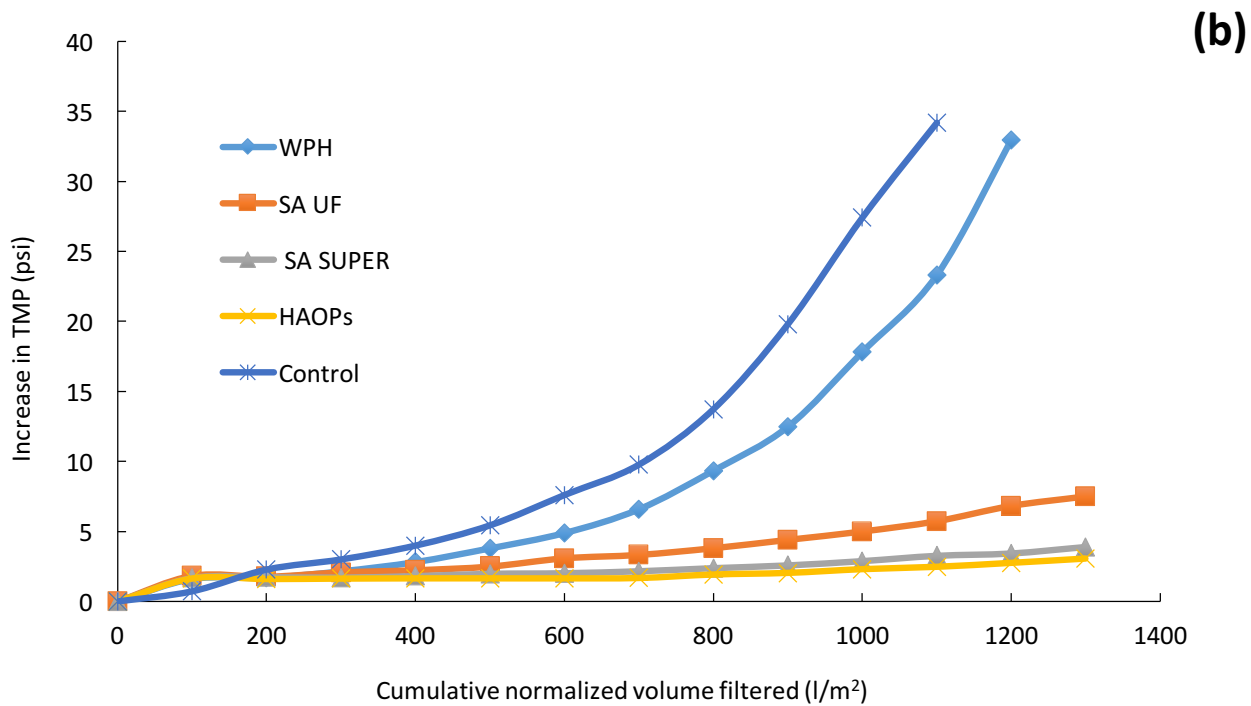


Figure 4-4 Performance of μ GAF-membrane systems with various adsorbents. (a) TMP in upstream μ GAF. Flux=150 LMH, adsorbent surface loading=30 g/m²; (b) TMP profiles of downstream membrane. Flux=100 LMH; and (c)percentage UV₂₅₄ removal in μ GAF systems shown in part (a).

Although SA UF and WPH removed UV_{254} almost identically in batch adsorption and sequential filtration tests, the pressure increase in the μ GAF unit was larger when SA UF was used, and that adsorbent mitigated fouling of the downstream membrane better than WPH did.

Different PACs are made from different carbon sources and are activated in different ways, yielding different pore size distributions and surface functional groups. As a result, each PAC has a unique adsorption performance for NOM (as well as other adsorbates). Even two PACs with similar adsorption efficiencies in batch adsorption tests (such as SA UF and WPH) can perform differently when applied in the μ GAF process. Therefore, one cannot generalize whether any particular PAC will be an efficient adsorbent for NOM or for use in the μ GAF process. Based on the preceding results, SA SUPER was chosen as the activated carbon to use in subsequent tests.

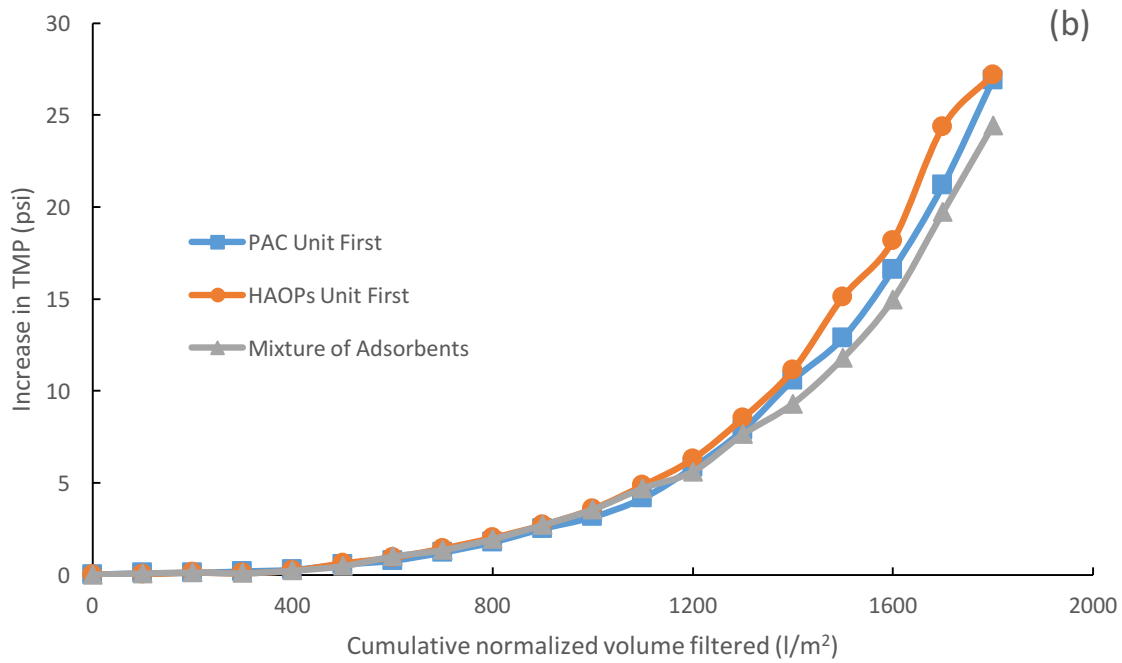
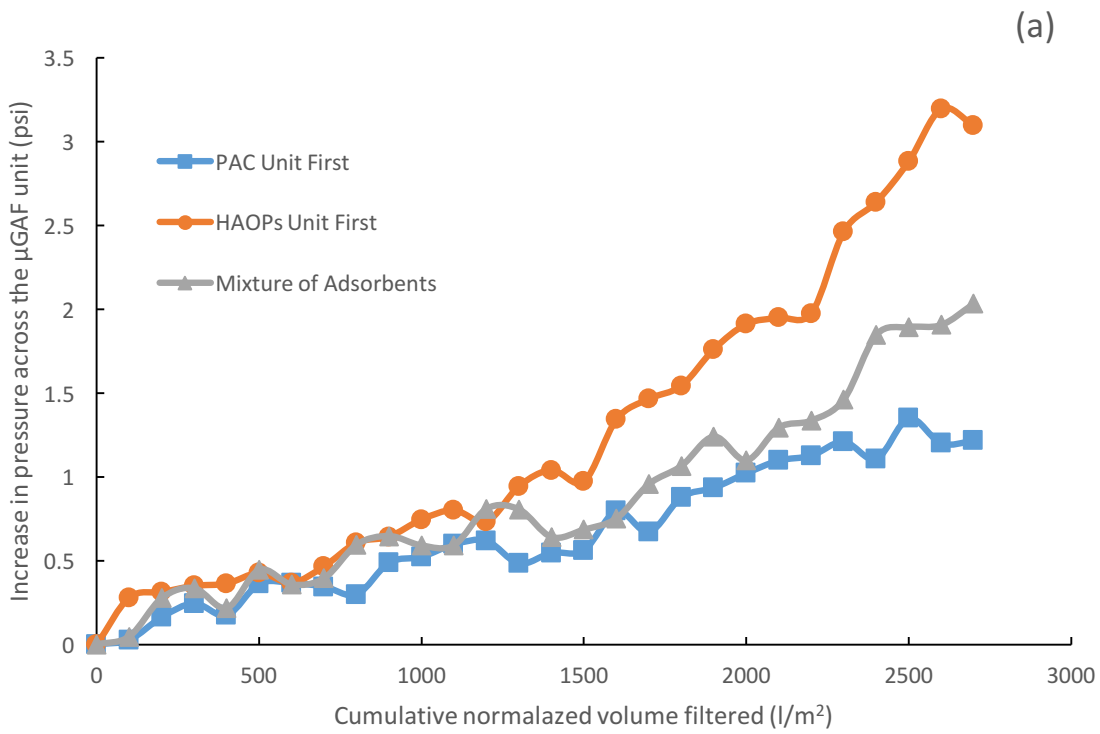
4.2 Effect of sequential vs simultaneous contact on NOM removal by PAC and HAOPs combination

Three batch adsorption tests were next conducted to see if adding the adsorbents simultaneously versus sequentially would affect the adsorption process. In one test, the adsorbents were spiked into LU water simultaneously, and the suspension was mixed for 2 hours. In the other two tests, one of the adsorbents was added to the water, and the suspension was mixed for 2 hours prior to removing the adsorbent by filtering through filter paper. The other adsorbent was then added to the water, followed by another 2 hours of mixing. As illustrated in Table 4.1, no difference in NOM removal efficiency was observed among these three systems.

Table 4-1 NOM removal by 10 mg/l HAOPs and 10 mg/l SA SUPER, added simultaneously or sequentially to the LU water

% Removal	Simultaneous	Sequential	
		HAOPs Added First	PAC Added First
DOC	49.9	49.6	50.4
UV ₂₅₄	75.9	75.3	76.5

Analogous tests were conducted in μ GAF systems. In one case, the adsorbents were mixed prior to deposition onto the μ GAF unit (simultaneous contact). In the other cases, two μ GAF units were used in series, with one unit containing only HAOPs and other unit containing only PAC. A membrane filtration unit was placed downstream of each of the pretreatment processes. Figure 4.5a shows the pressure drop across the μ GAF units. When two units were used in series, the pressure drop shown is the sum of the pressure drops across both units. As presented in Figure 4.5b, fouling of the downstream membrane was essentially identical regardless of whether the water was treated sequentially or with the mixture of adsorbents. Also, similar to the batch adsorption tests, all three configurations resulted in similar NOM removal efficiencies (Figure 4.5c). Therefore, for the rest of the experiments, and for the ease of operation, simultaneous contact was applied for batch and μ GAF tests.



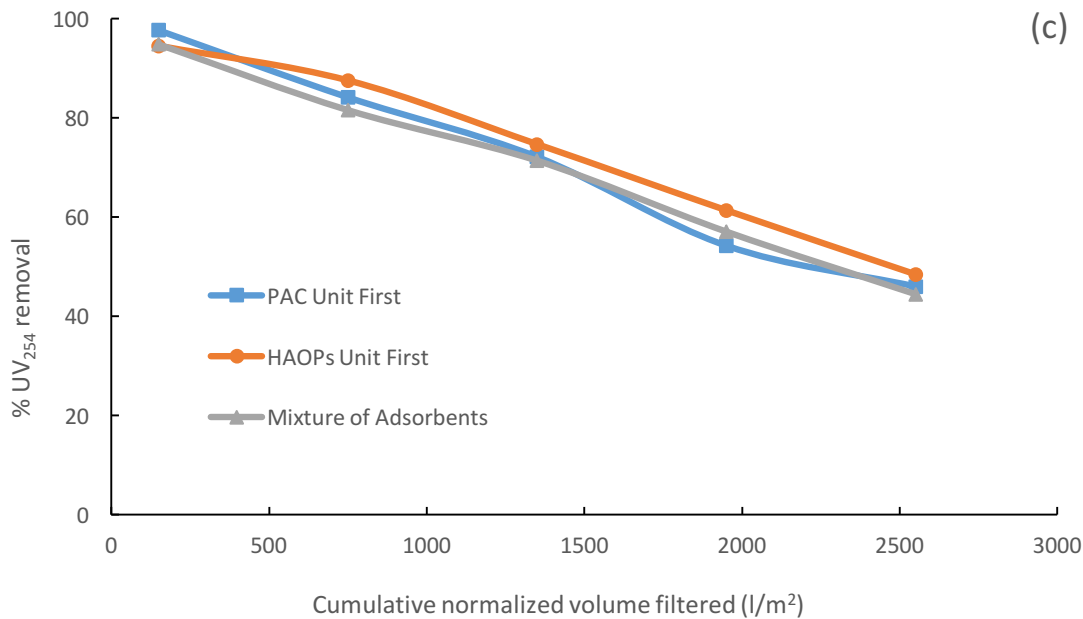


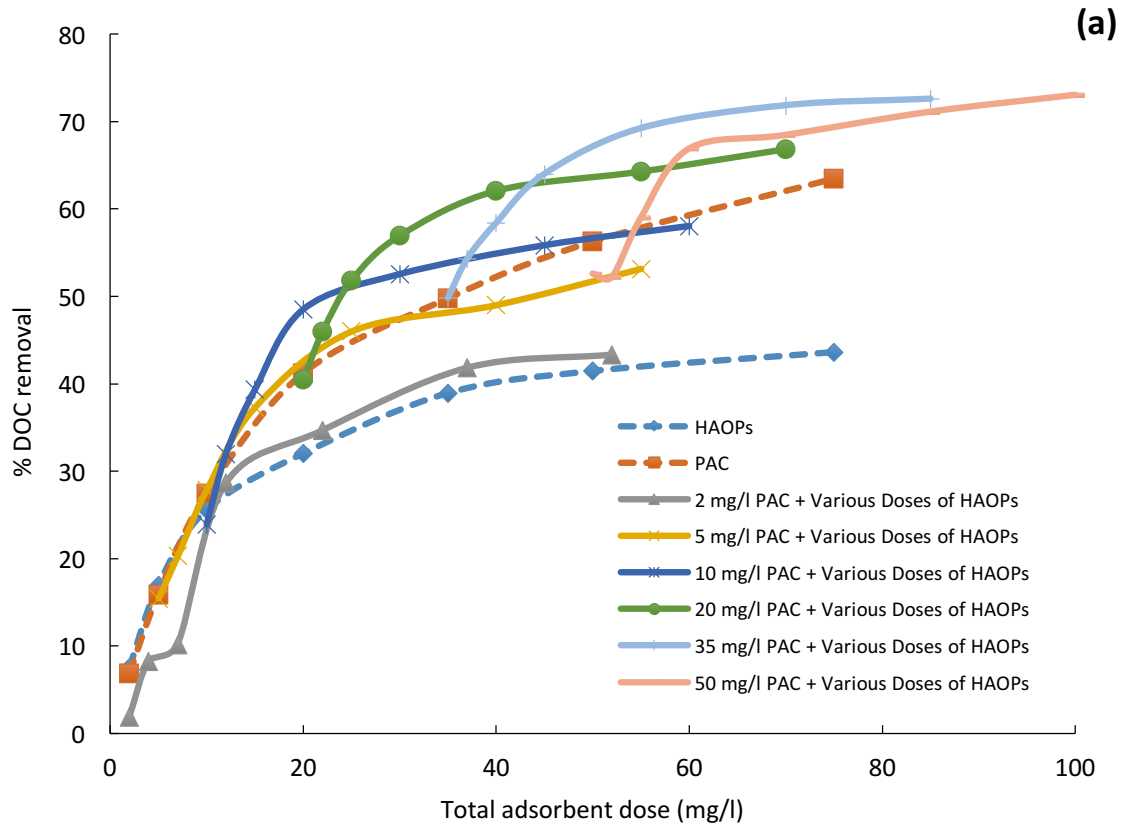
Figure 4-5 Effect of the application of the adsorbents in sequential μ GAF units versus mixture of adsorbents. (a) Total pressure increase in upstream μ GAF system(s). Flux=150 LMH, adsorbent surface loading 20 g/m² for each adsorbent; (b) TMP profiles of downstream membrane systems. Flux=100 LMH; and (c) UV₂₅₄ removal in upstream μ GAF systems

4.3 Batch adsorption of NOM by combinations of PAC and HAOPs

4.3.1 NOM removal efficiency

Batch adsorption tests were performed with HAOPs and SA SUPER to investigate the effect of adsorbent dose on NOM removal. Results are presented in Figure 4.6, where each curve represents the percentage of NOM removal (DOC or UV₂₅₄) at a fixed dose of PAC and various doses of HAOPs. At low doses of PAC, addition of HAOPs enhanced the removal significantly. However, as the dose of PAC increased, the effect of HAOPs addition declined. As mentioned before, HAOPs remove only a fraction of the NOM (for LU water NOM, at most around 45% and 70% of the DOC and UV₂₅₄, respectively). It seems that as the dose of PAC increased, the

PAC removed more of the NOM that is also adsorbable by HAOPs, so there was less organic material for HAOPs to adsorb.



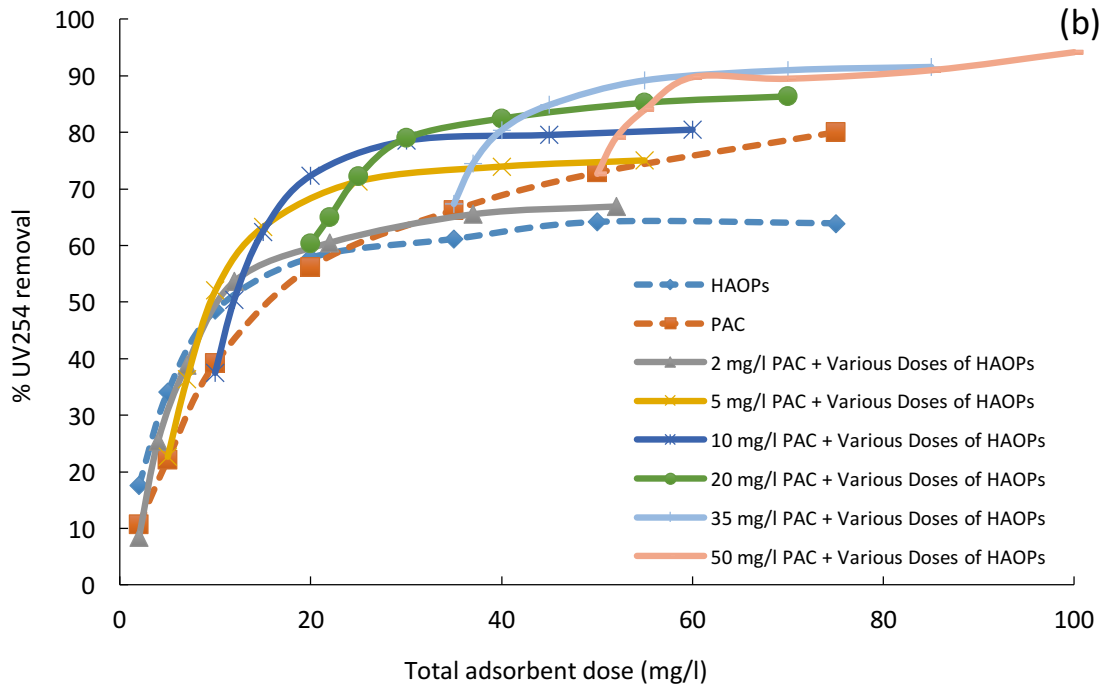
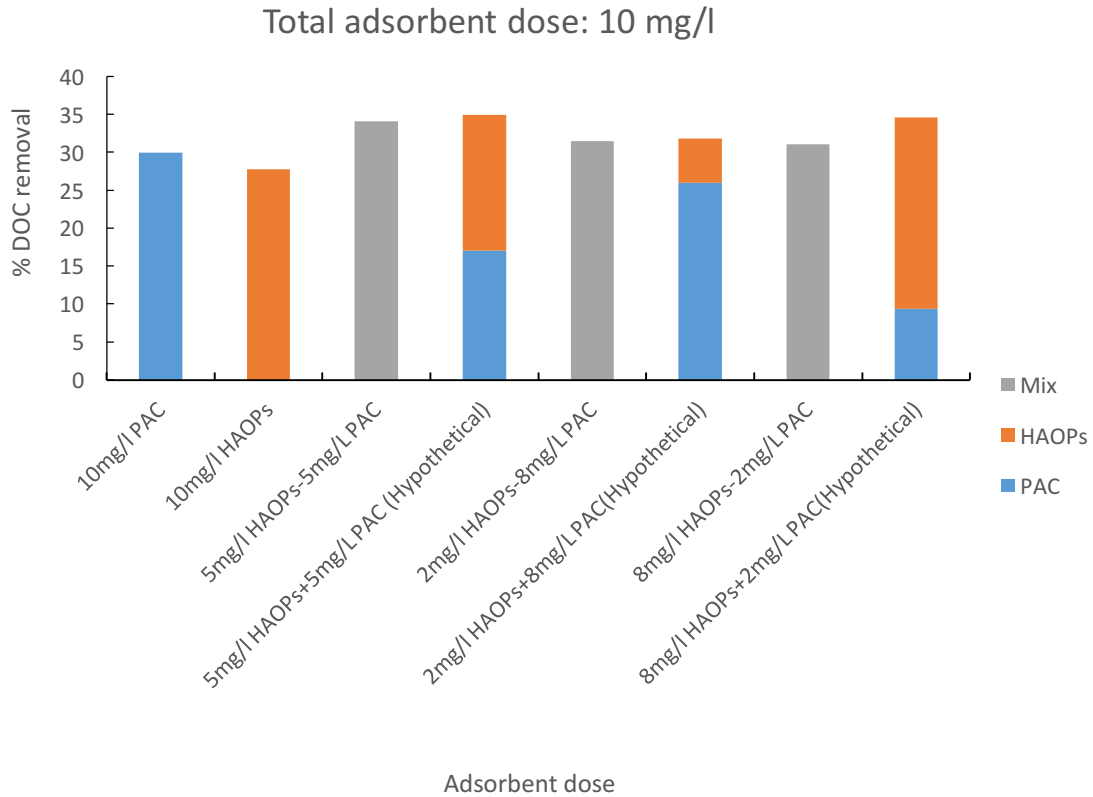


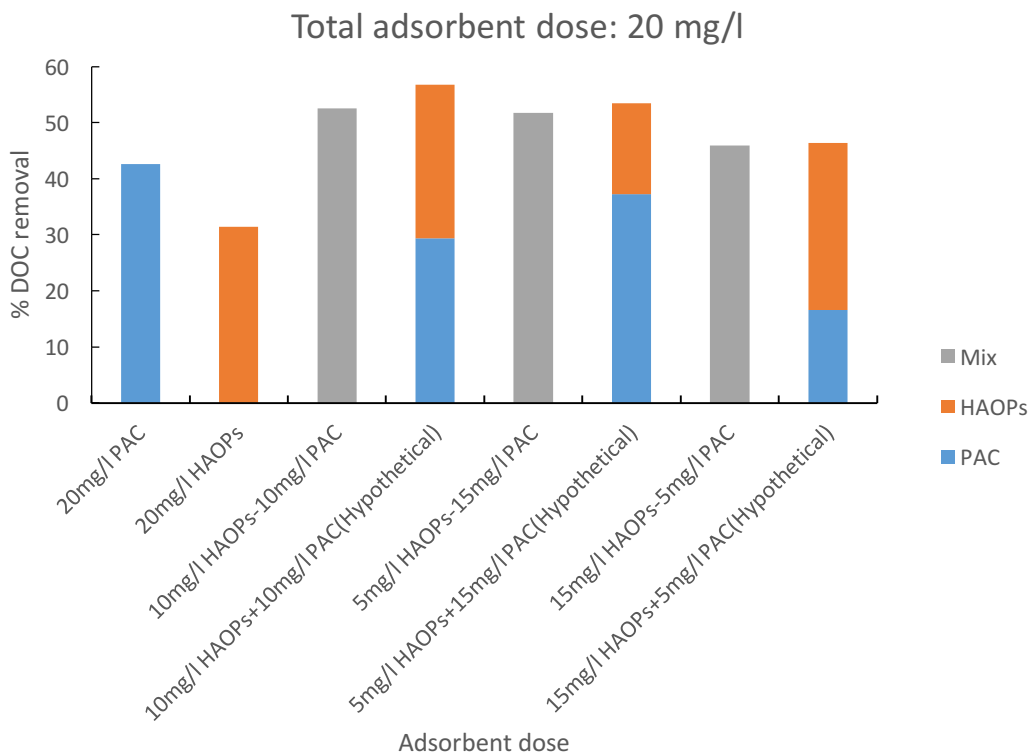
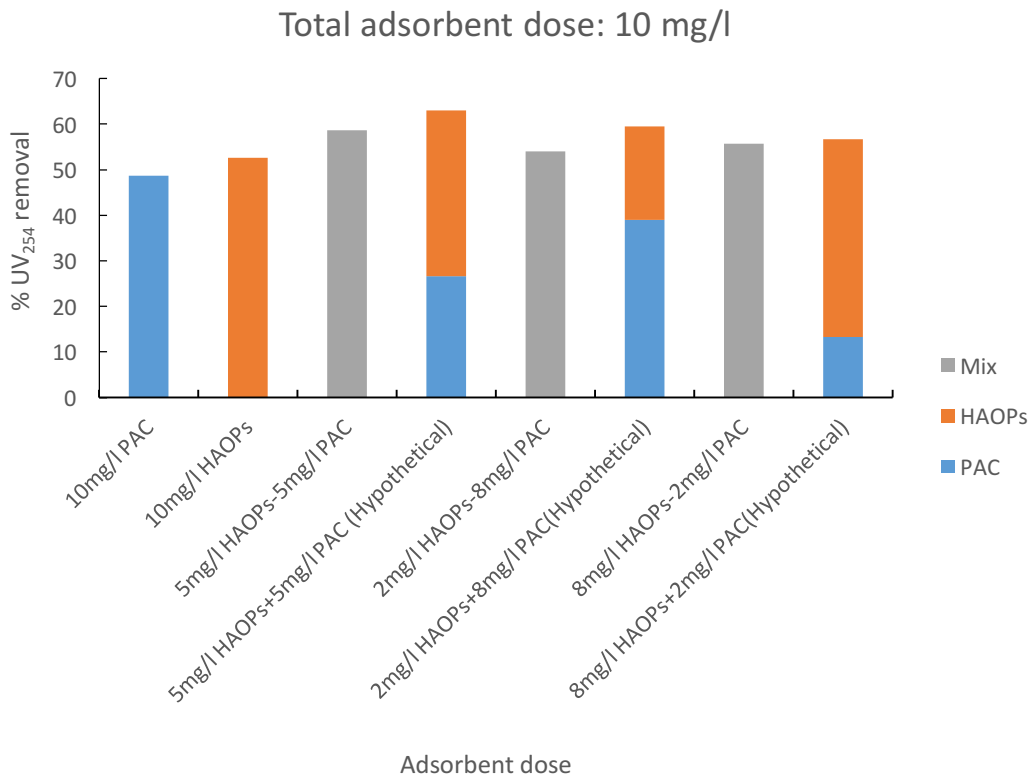
Figure 4-6 LU water NOM removal by fixed doses of PAC and various doses of HAOPs (a) DOC removal; (b) UV₂₅₄ Removal

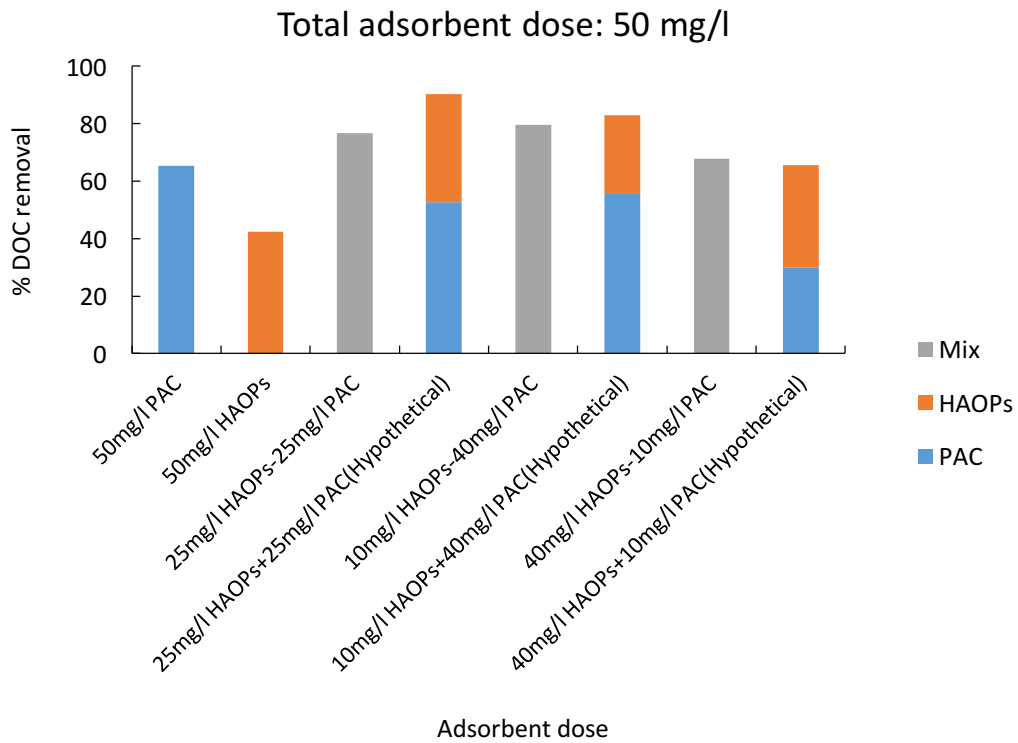
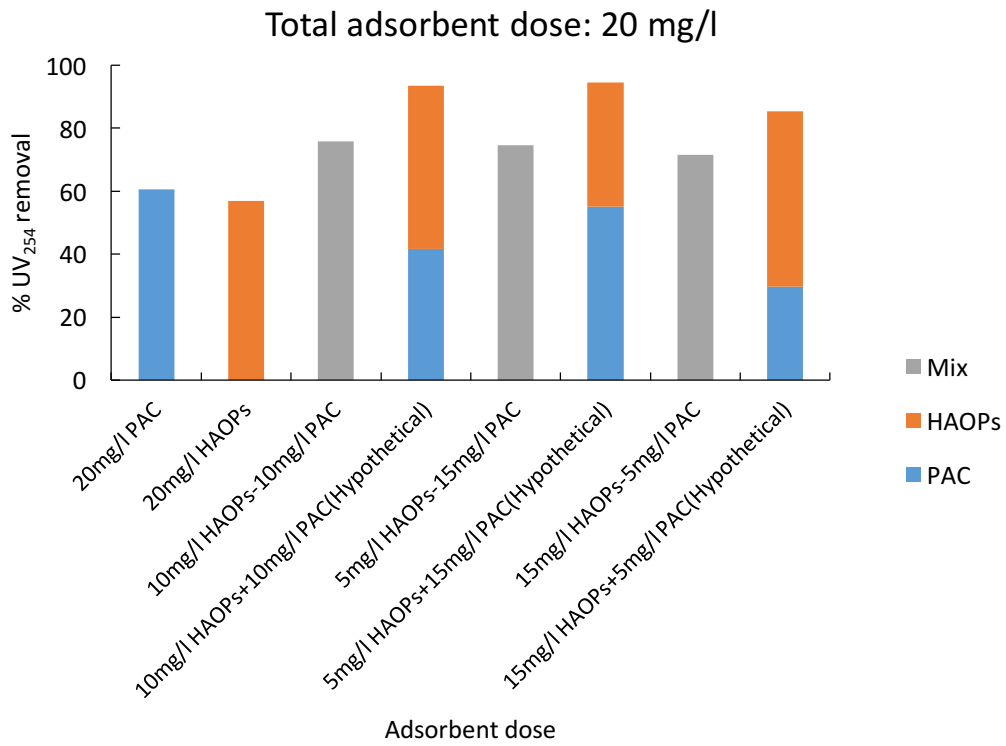
Next, the adsorption of LU NOM by mixtures of HAOPs and PAC was investigated at three fixed total adsorbent doses of 10, 20, and 50 mg/l (Figure 4.7). Results were compared to hypothetical situations in which the removal of NOM equaled the summation of the removals by each of the adsorbents alone at the given dose. In all cases, mixtures of adsorbents removed more NOM than when either of the adsorbents was used alone. At the lowest total adsorbent dose, the difference between the removal of NOM with a mixture of adsorbents and the corresponding hypothetical removal was insignificant.

Each adsorbent preferentially collects adsorbates for which it has higher affinity. Therefore, if HAOPs and PAC preferentially remove different fractions of NOM, their combined removal efficiency would equal the sum of the removals by each adsorbent separately. Also, at low doses, if there is an overlap between the fractions that each adsorbent removes, there is enough NOM available for both adsorbents to collect.

The difference between the removal of NOM with a mixture of adsorbents and the corresponding hypothetical removal based on non-overlapping adsorbate populations grew as the total adsorption dose increased. This difference was more pronounced for UV₂₅₄ than DOC, as both adsorbents have high affinity for the UV₂₅₄-adsorbing fraction of NOM.







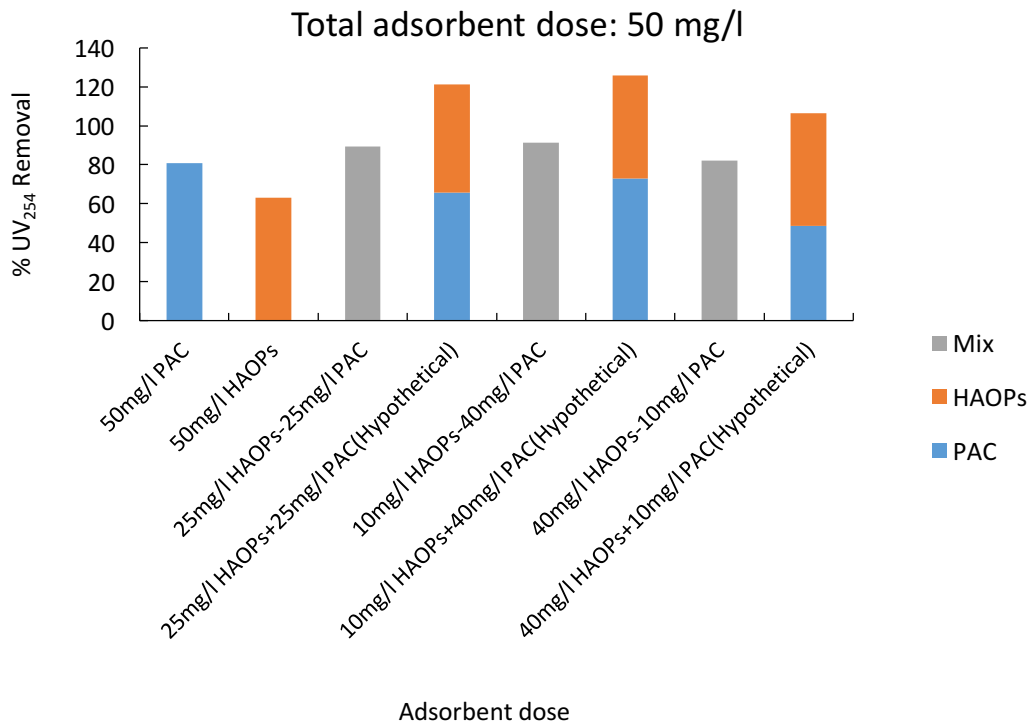


Figure 4-7 NOM removal from LU water by different mixtures of HAOPs and PAC at various fixed total adsorbent doses (a) DOC removal at total adsorbent dose of 10 mg/l; (b) UV₂₅₄ DOC removal at total adsorbent dose of 10 mg/l; (c) DOC removal at total adsorbent dose of 20 mg/l; (d) UV₂₅₄ DOC removal at total adsorbent dose of 20 mg/l; (e) DOC removal at total adsorbent dose of 50 mg/l; (f) UV₂₅₄ DOC removal at total adsorbent dose of 50 mg/l.

4.3.2 Effect on membrane fouling of batch pretreatment with HAOPs and/or SA SUPER

In the next tests, LU water was treated by batch adsorption with HAOPs, PAC, or a mixture of both, at a total adsorbent dose of 20 mg/l. The treated water was then fed to a UF membrane at a flux of 100 LMH. A control test was conducted by filtering LU water through a membrane without pretreatment. Figure 4.8 illustrates the TMP profiles in these tests. In all cases, batch adsorption pretreatment significantly reduced the fouling of the downstream membrane. Changing the adsorbent in the pretreatment step from 20 mg/l HAOPs to 20 mg/l SA SUPER PAC reduced fouling of the downstream membrane. Pretreatment with 15 mg/l SA SUPER and 5

mg/l HAOPs resulted in a similar TMP buildup to pretreatment with 20 mg/l PAC, but the water pretreated with the mixture of adsorbents contained 9% less DOC and absorbed 14% less UV₂₅₄.

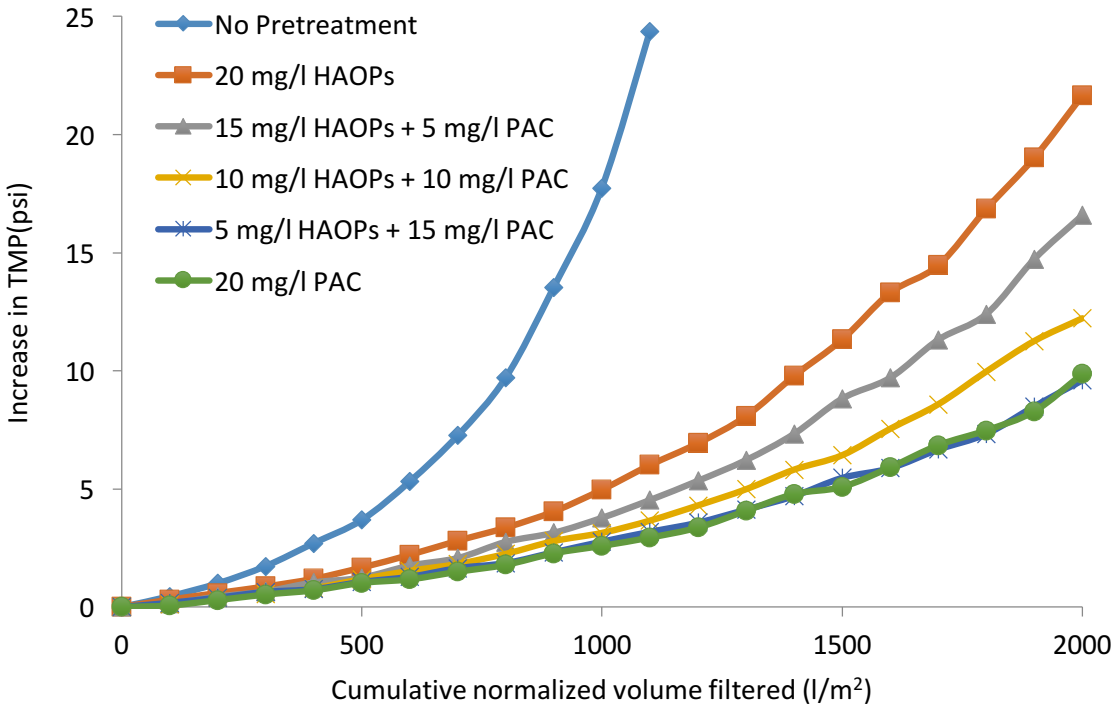


Figure 4-8 TMP profiles for membranes fed LU water pretreated by batch adsorption with mixtures of HAOPs and SA SUPER. Total adsorbent dose = 20 mg/l, Flux=100 LMH.

4.3.3 Changes in NOM fractions caused by adsorption

4.3.3.1 Size exclusion chromatography

An SEC chromatogram of LU water is presented in Figure 4.9. The fractions of NOM identifiable in LU water, from highest to lowest apparent molecular weight, are biopolymers, humic substances, building blocks, LMW acids and LMW neutrals, respectively.

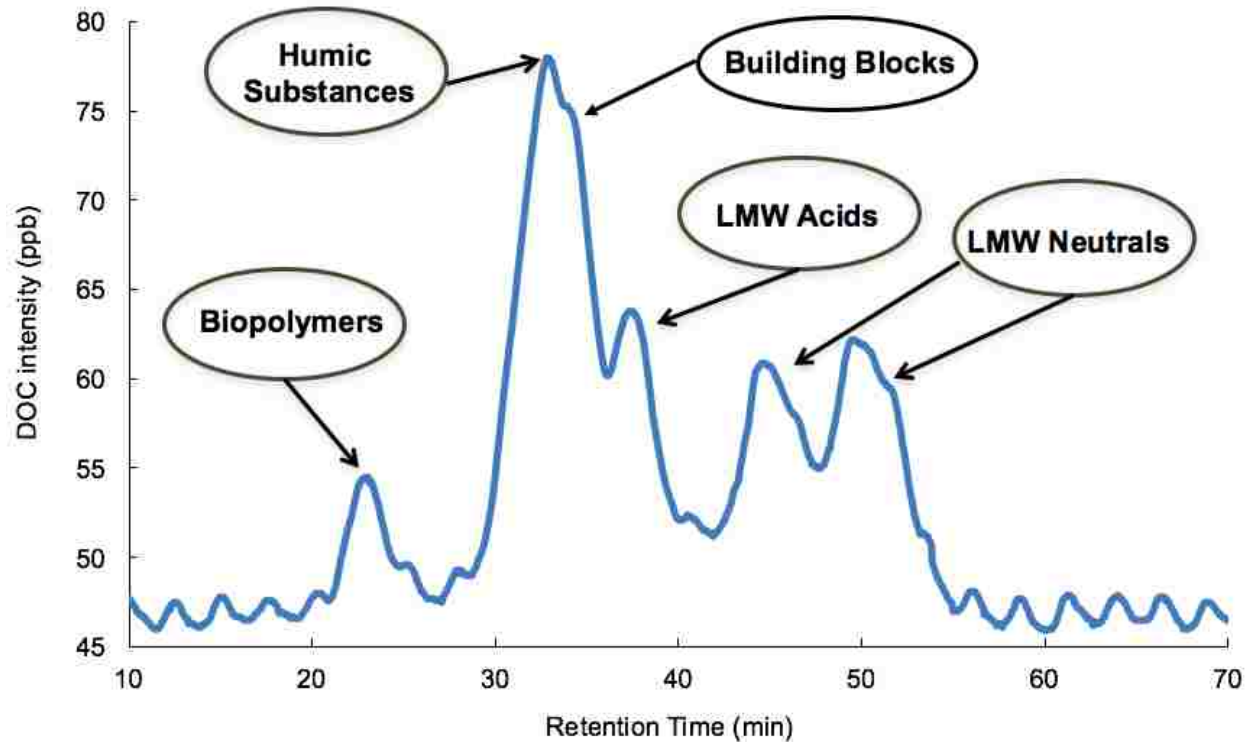


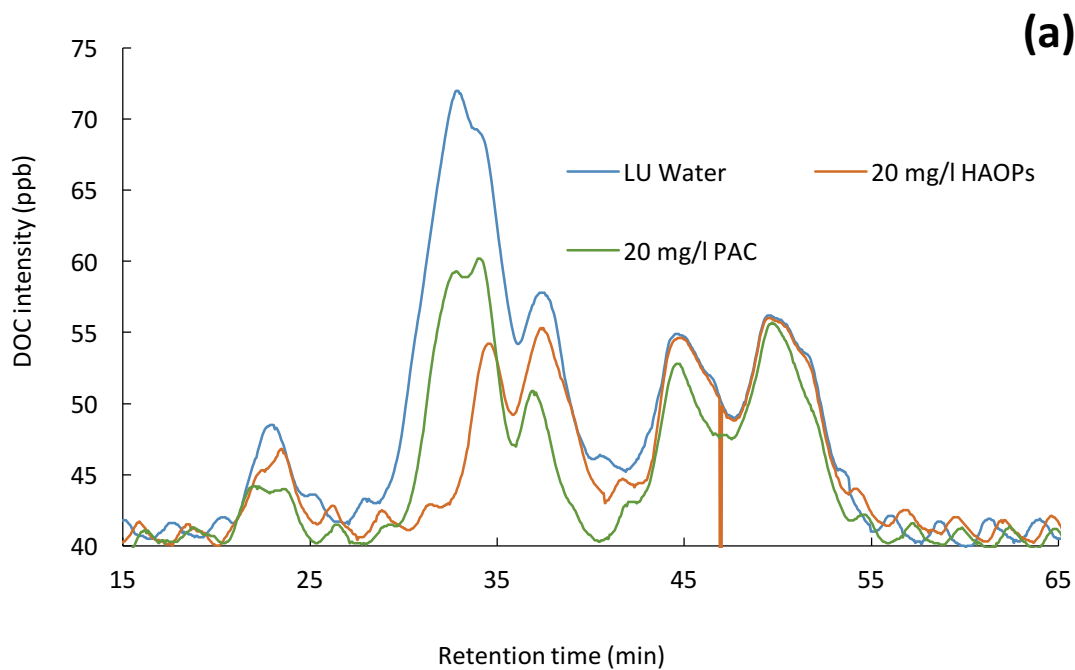
Figure 4-9 SEC chromatogram of LU water

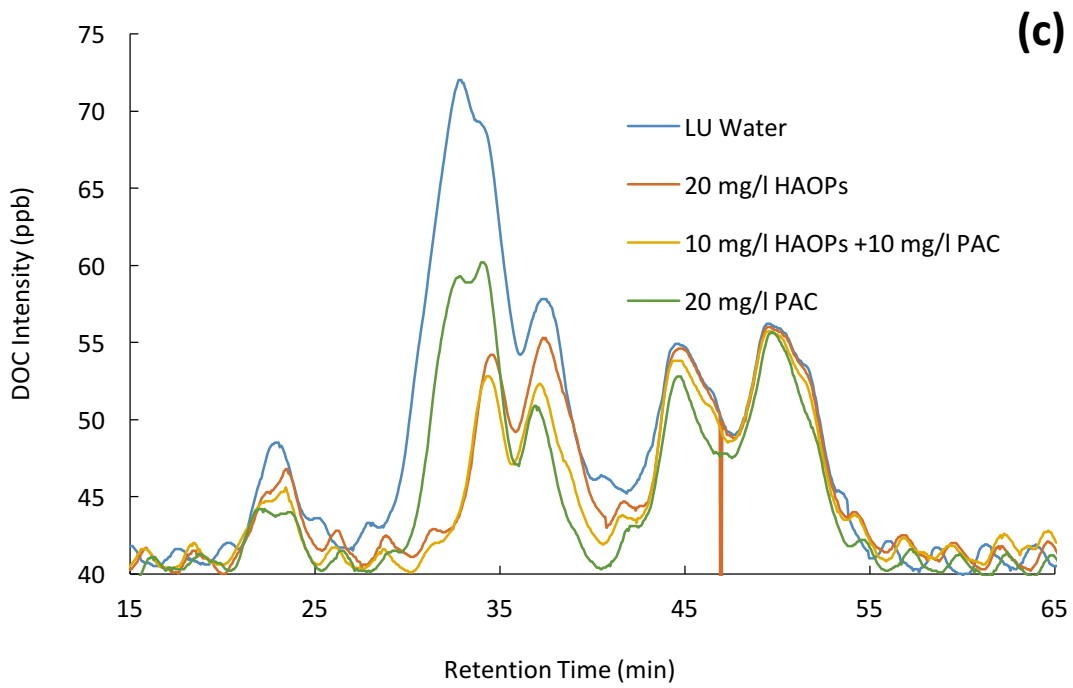
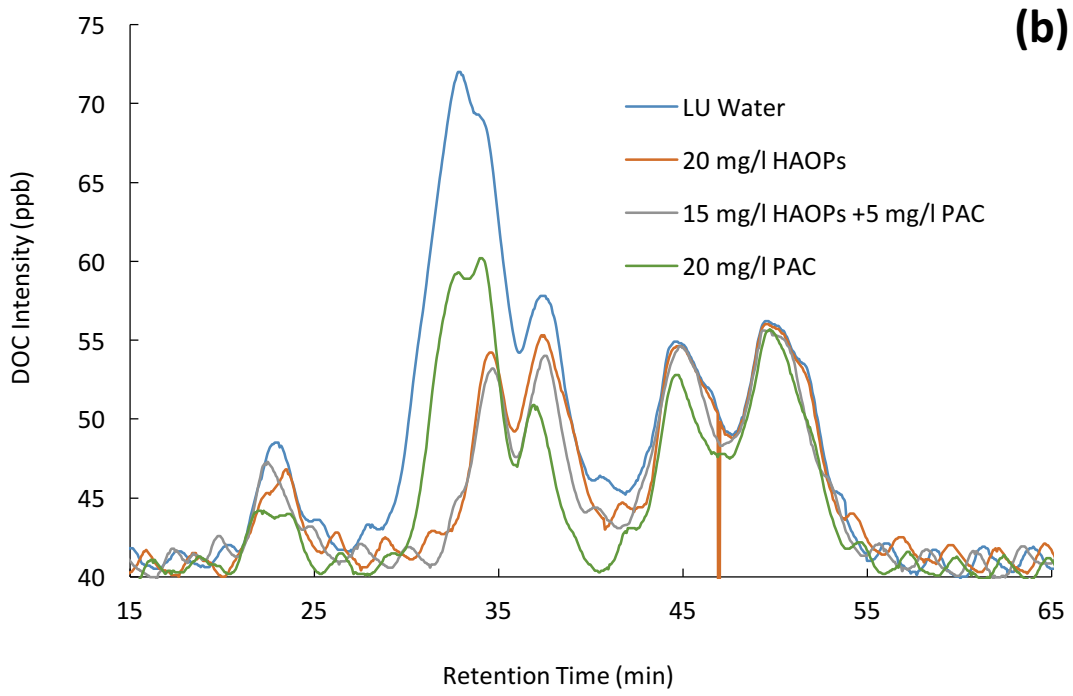
Chromatograms for LU water treated with a total adsorbent dose of 20 mg/l are presented in Figure 4.10. At this dose, both adsorbents collected some of every NOM fraction, except that the LMW neutrals were untouched by HAOPs. HAOPs had higher affinity toward humic substances and building blocks, whereas SA SUPER adsorbed more of the LMW acids and the biopolymer fraction. When a mixture of HAOPs and SA SUPER was applied, the intensity of each peak was usually close to or lower than for treatment with either adsorbent alone. As a result, overall removal was higher than the removal achieved by HAOPs or PAC alone, consistent with the higher removals of DOC and UV_{254} presented earlier.

Fouling of the membranes in these systems seemed to correlate with the intensity of the biopolymer peak. Increasing the contribution of SA SUPER improved the removal of the biopolymer NOM and lowered the TMP buildup on the downstream membrane. This is in

agreement with previous reports, as mentioned in section 2.2, that the removal of high molecular weight biopolymers is crucial for fouling reduction.

Treatment with a mixture of 5 mg/l HAOPs and 15 mg/l SA SUPER achieved the highest removal of low-MW NOM. Although PAC is generally a good adsorbent for low-MW NOM due to its high micropore volume, adsorption of these molecules can be hindered due to pore blockage by larger NOM molecules. It seems that at these doses of the adsorbents, enough HAOPs are present to remove some of the large NOM molecules that cause this hindrance, and enough PAC is available to adsorb many of the small molecules.





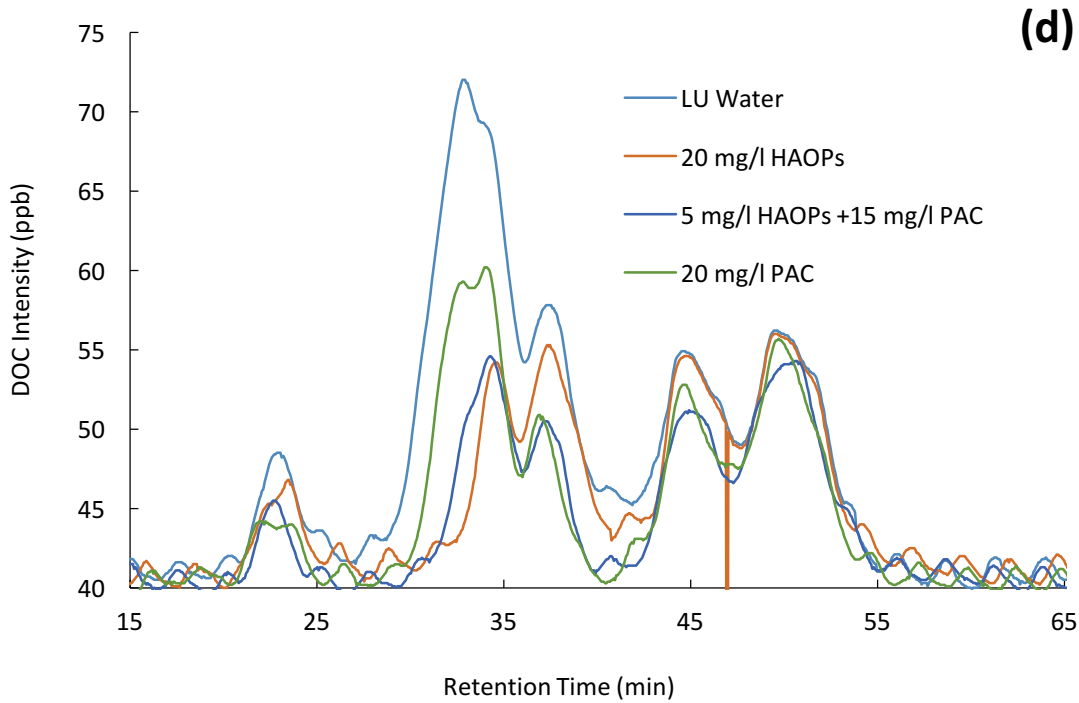


Figure 4-10 SEC chromatogram of LU water treated in batch adsorption mode with mixtures of HAOPs and SA SUPER. Total adsorbent dose = 20 mg/l.

4.3.3.2 Excitation-emission matrix fluorescence spectrometry

Three classes of molecules were identified in Lake Union raw water based on EEM spectra (Figure 4.11): proteinaceous compounds (at excitation wavelengths <250 nm and emission wavelengths <380 nm), fulvic acid-like materials (at excitation wavelengths <250 nm and emission wavelengths >380 nm), and humic acid-like materials (at excitation wavelengths >250 nm and emission wavelengths > 350 nm). In general, soluble microbial by-product-like material can also be characterized by EEM spectra. However, Figure 4.11 suggests that this group of organic material is negligible in LU water.

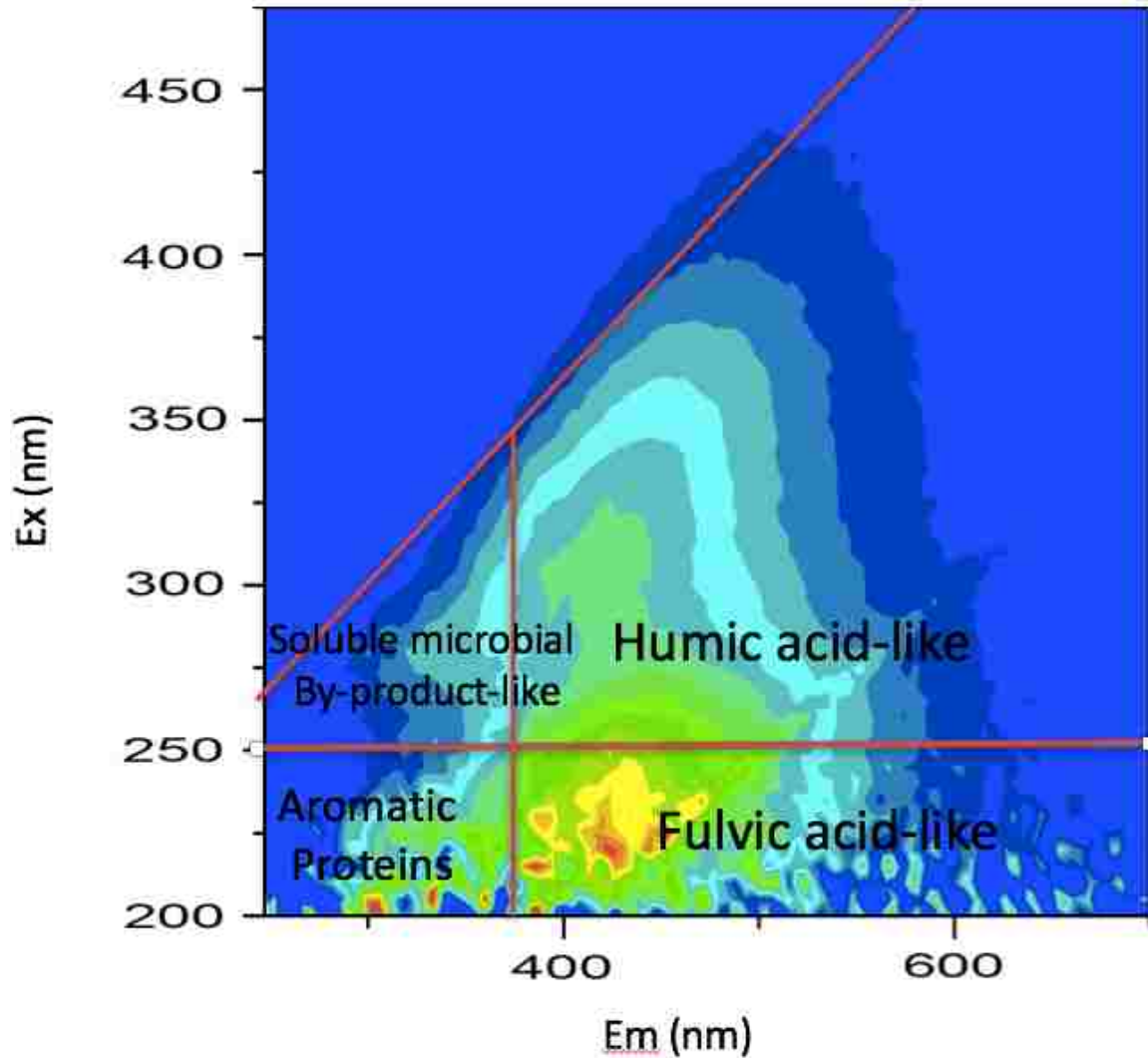
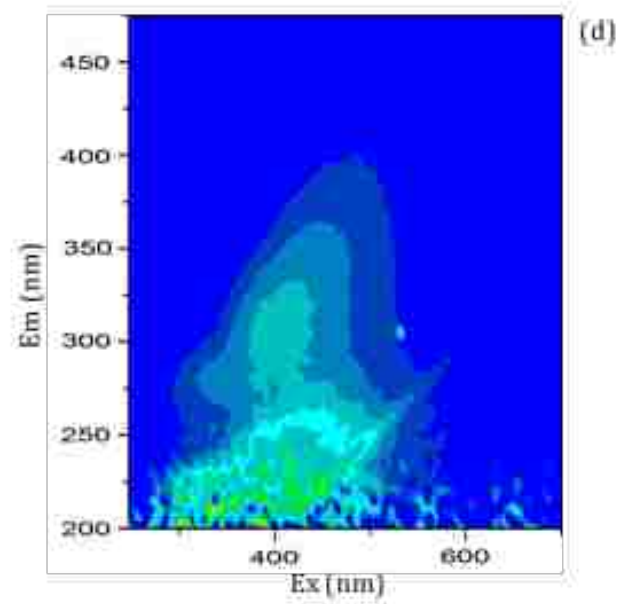
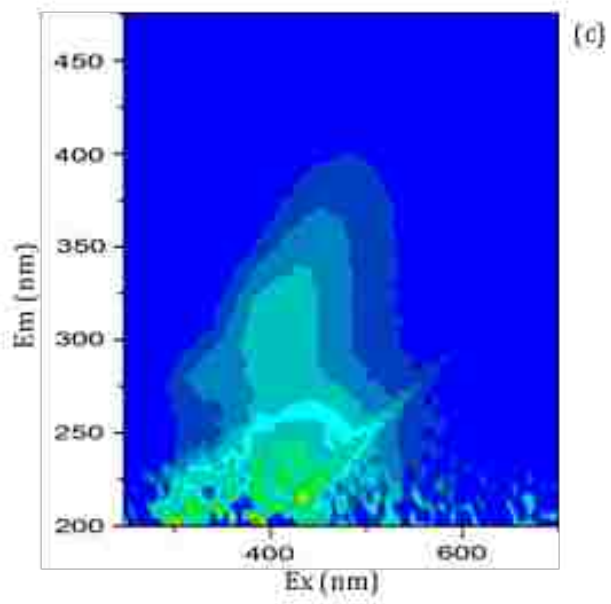
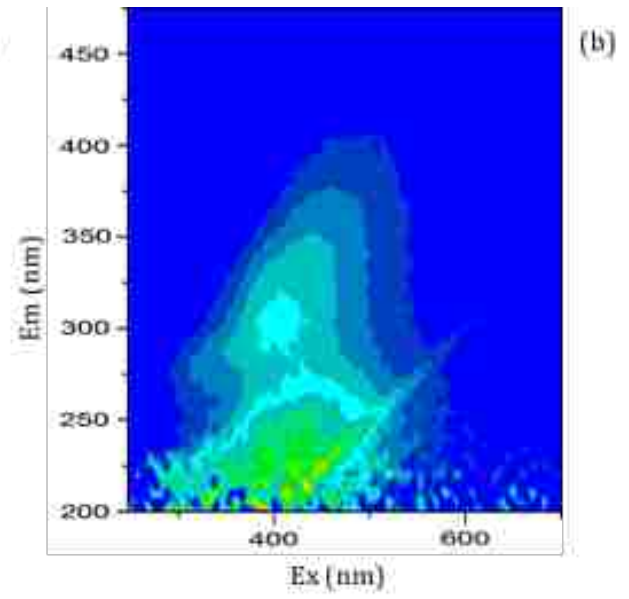
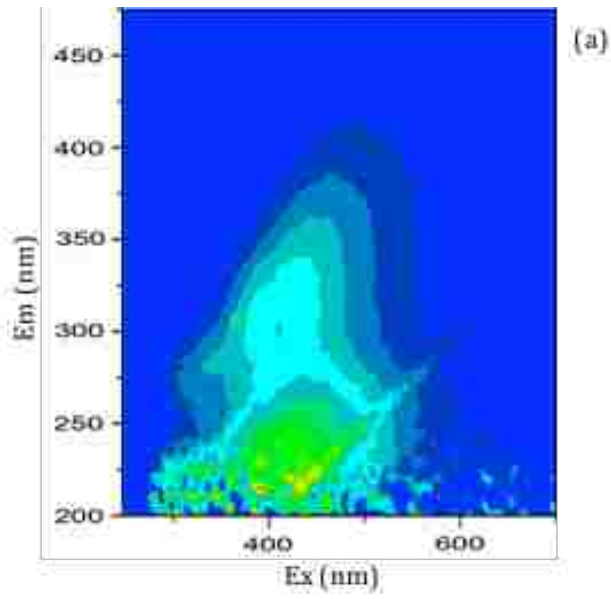
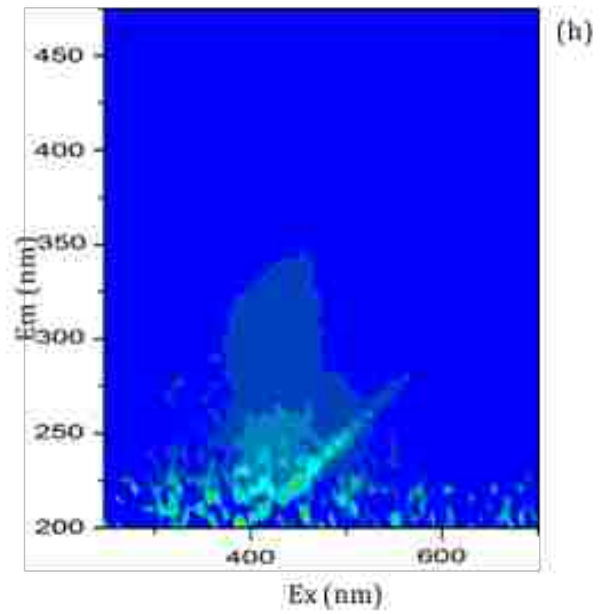
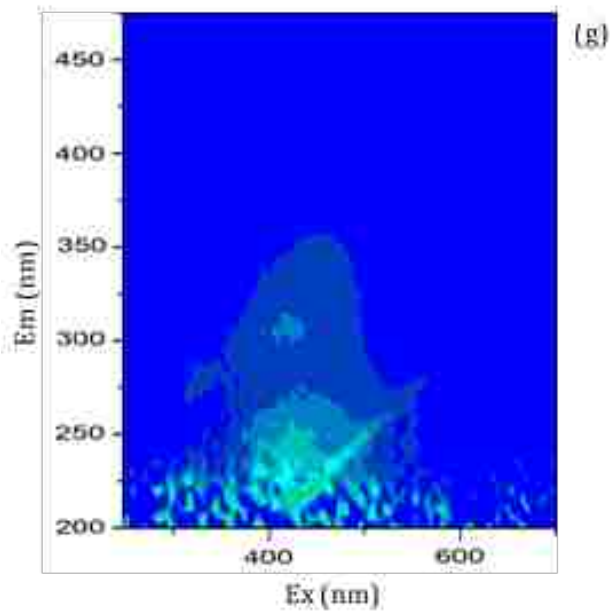
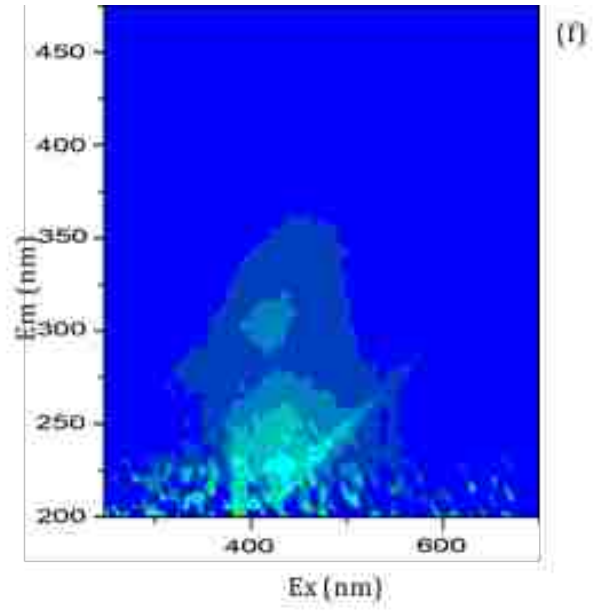
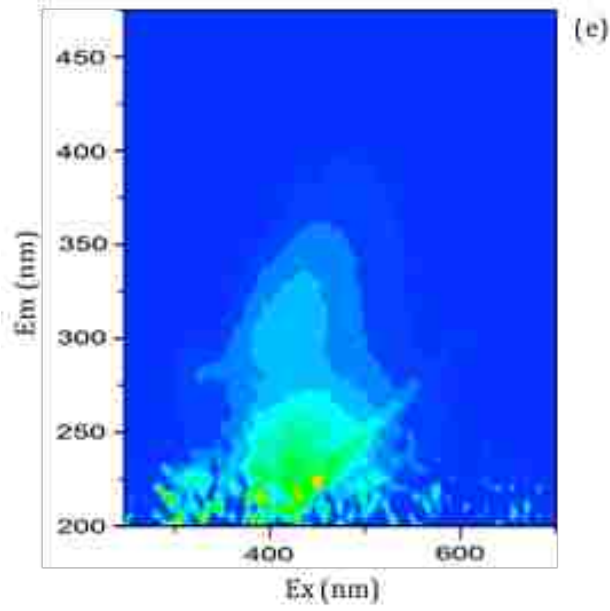


Figure 4-11 3D EEM spectra of LU water and its identifiable classes of organic material.

Both adsorbents removed portions of all three NOM fractions, as shown in Figure 4.12. However, SA SUPER removed the fluorescent NOM better than HAOPs did. The combination of SA SUPER and HAOPs at a total adsorbent dose of 20 mg/l significantly more fluorescent NOM than either of the adsorbents alone at this dose. Since SA SUPER was more effective in adsorbing the fluorescent NOM, increasing its proportion in the HAOPs-PAC mixture increased the removal of the fluorescent NOM.





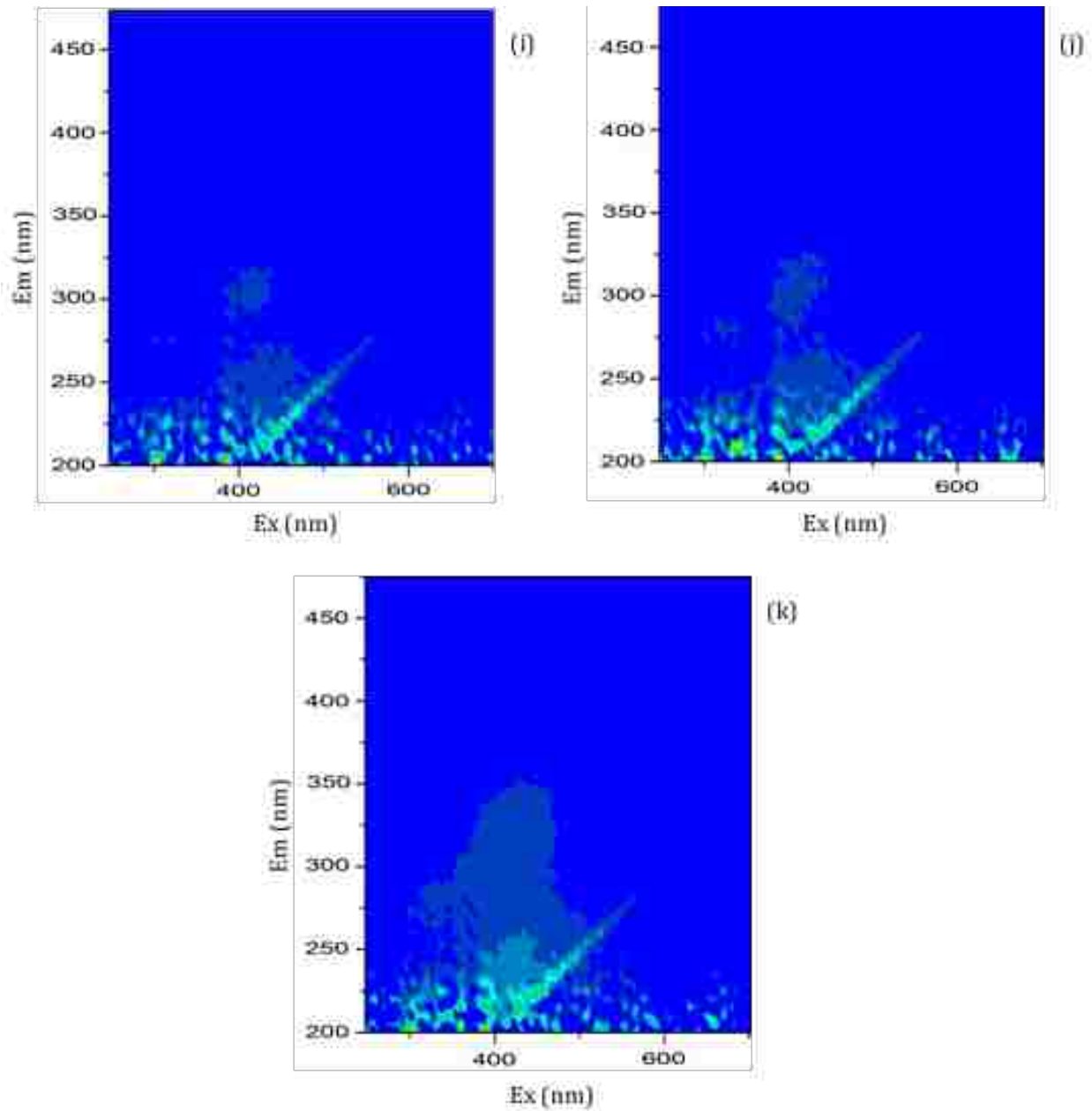


Figure 4-12 EEM spectra of LU water after batch adsorption treatment with various doses of HAOPs and SA SUPER. (a) 5mg/l HAOPs; (b) 10mg/l HAOPs; (c) 15mg/l HAOPs; (d) 20mg/l HAOPs; (e) 5mg/l PAC; (f) 10mg/l PAC; (g) 15mg/l PAC; (h) 20mg/l PAC; (i) 5mg/l HAOPs + 15mg/l PAC; (j) 10mg/l HAOPs + 10mg/l PAC; (k) 15mg/l HAOPs + 5mg/l PAC

A strong correlation has been reported between the intensity of the NOM fluorescence, especially the proteinaceous compounds, and membrane fouling (Peldszus et al. 2011, Kimura et

al. 2014a, Shao et al. 2014). It seems that such a correlation could exist here, too, since SA SUPER removed more fluorescence, including the proteinaceous material, and also mitigated membrane fouling more than HAOPs did.

4.4 μ GAF pretreatment of NOM by combinations of PAC and HAOPs

In the next experiments, LU water was used as the feed water in μ GAF pretreatment tests with HAOPs and/or SA SUPER. The total adsorbent surface loading was 40 g/m², and 2000 l/m² of water was pretreated to achieve an effective adsorbent dose of 20 mg/l. Hence, the final total effective adsorbent dose equaled the dose used in the previous batch pretreatment experiments.

4.4.1 NOM removal efficiency

Figure 4.13 shows the removal of NOM in these tests. Similar to the result in the batch pretreatment tests, application of a mixture of the adsorbents enhanced the NOM removal efficiency. For equal doses of adsorbent(s), μ GAF pretreatment removed more NOM than batch pretreatment did. This enhancement was most pronounced when HAOPs were used alone and was attenuated with a decreasing proportion of HAOPs. However, even when only SA SUPER was used, the NOM removal was still slightly improved in the μ GAF system (2% increase in DOC removal and 6% increase in UV₂₅₄ removal).

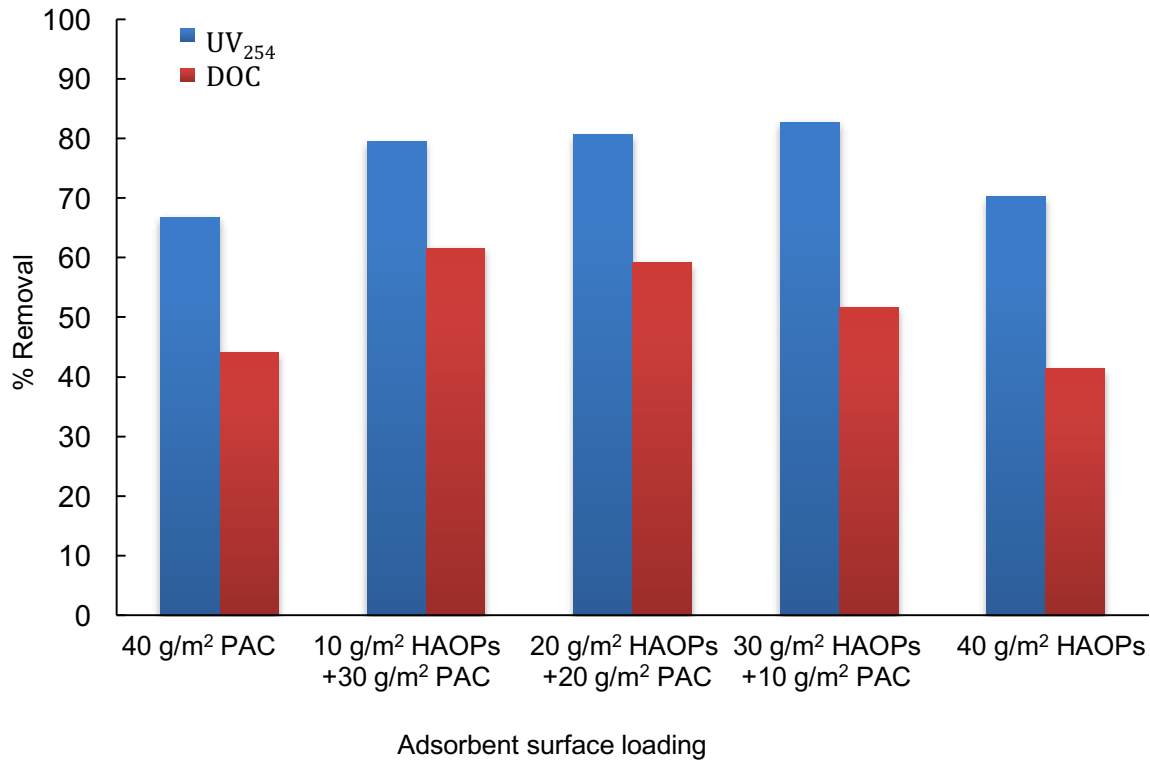
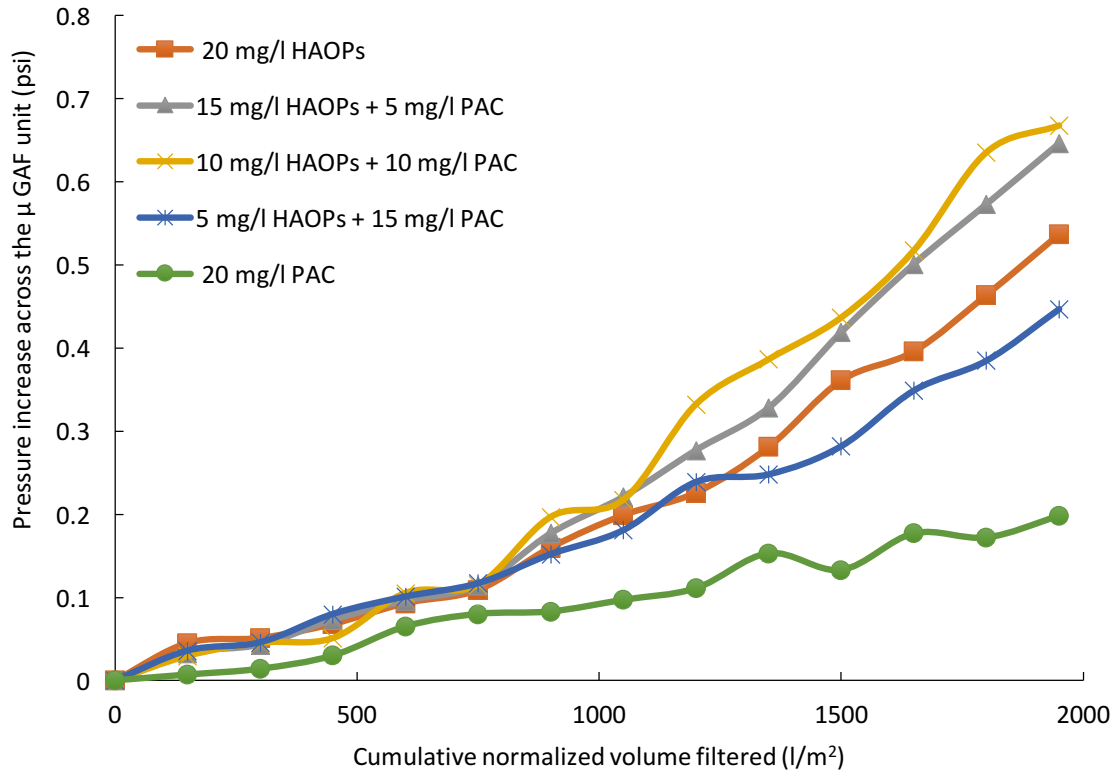


Figure 4-13 NOM removal from LU water by μ GAF pretreatment using mixtures of HAOPs and PAC at a fixed total effective adsorbent dose of 20 mg/l (surface loading of 40 g/m² applied to V_{sp} of 2000 l/m²)

4.4.2 Fouling in sequential μ GAF-membrane filtration

Figure 4.14 illustrates the fouling patterns in sequential μ GAF-membrane systems, using fluxes of 150 and 100 LMH for the μ GAF and membrane units, respectively. Application of SA SUPER alone resulted in the least fouling of the μ GAF unit, but in all cases the pressure increase was less than 1 psi (Figure 4.14a). Fouling profiles of the downstream membrane filtration units are presented in Figure 4.14b. Similar to experiments using batch pretreatment, μ GAF pretreatment significantly reduced fouling of the membrane. Changing the adsorbent in the pretreatment step from 40 g/m² SA SUPER PAC to 40 g/m² HAOPs improved protection of the

membrane. Pretreatment with 30 g/m² HAOPs + 10 g/m² SA SUPER resulted in a similar TMP buildup to pretreatment with 40 g/m² of HAOPs, but the water pretreated with the mixture of adsorbents contained 10% less DOC and absorbed 12% less UV₂₅₄.



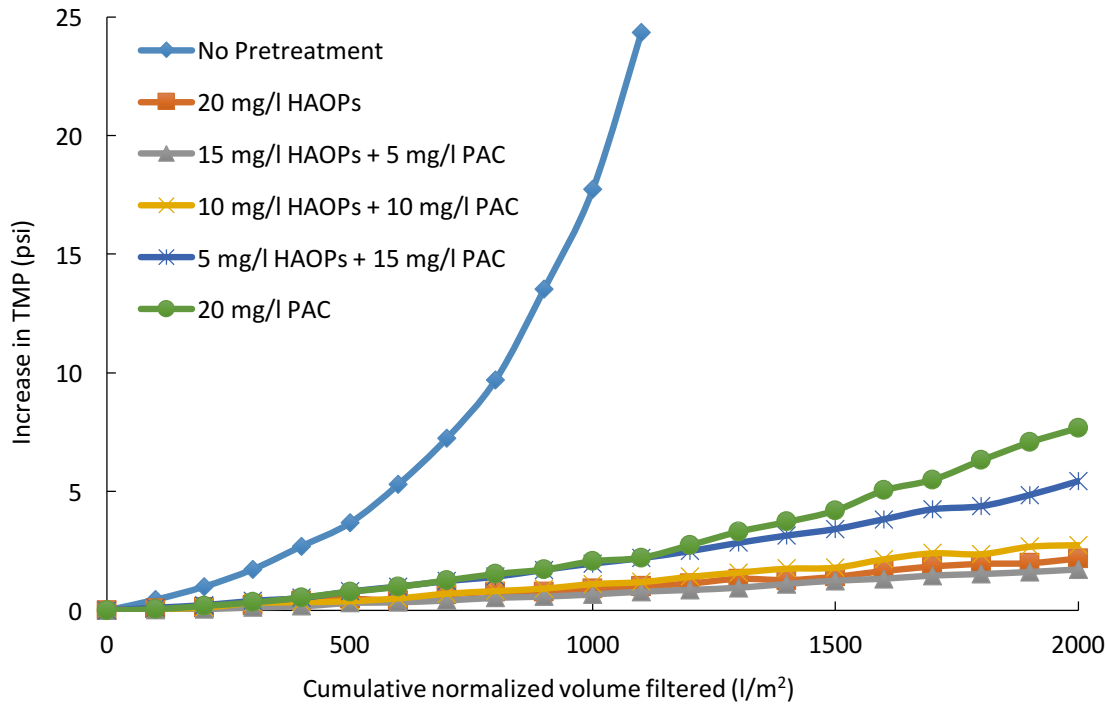


Figure 4-14 (a) Pressure increase across the upstream μ GAF units with different proportions of HAOPs and SA SUPER (b) TMP increase profiles of downstream membrane units when fed with composite permeate collected from corresponding upstream μ GAF units

4.4.3 Effectiveness of μ GAF compared to batch adsorption for reduction of membrane fouling

As mentioned earlier, the adsorbent surface loading and the volume of water treated in the μ GAF pretreatment tests yielded an effective adsorbent dose equal to the actual dose used in batch pretreatment tests. Figure 4.15 presents the total headloss at the end of the filtration process. For batch pretreatment experiments, this value is the TMP of the downstream membrane unit when V_{sp} was 2000 l/m². For the μ GAF-membrane process, the value includes the headloss across both the μ GAF unit and the downstream membrane.

In all cases, μ GAF pretreatment led to dramatically less headloss than batch pretreatment did. Increasing the proportion of HAOPs in the HAOPs-SA SUPER mixture increased the

difference between the two pretreatment processes. Apparently, μ GAF increased the ability of HAOPs to capture membrane foulants. On the other hand, process performance using SA SUPER in μ GAF was only slightly better than in batch pretreatment, suggesting that SA SUPER captured almost the same material in the two treatment modes.

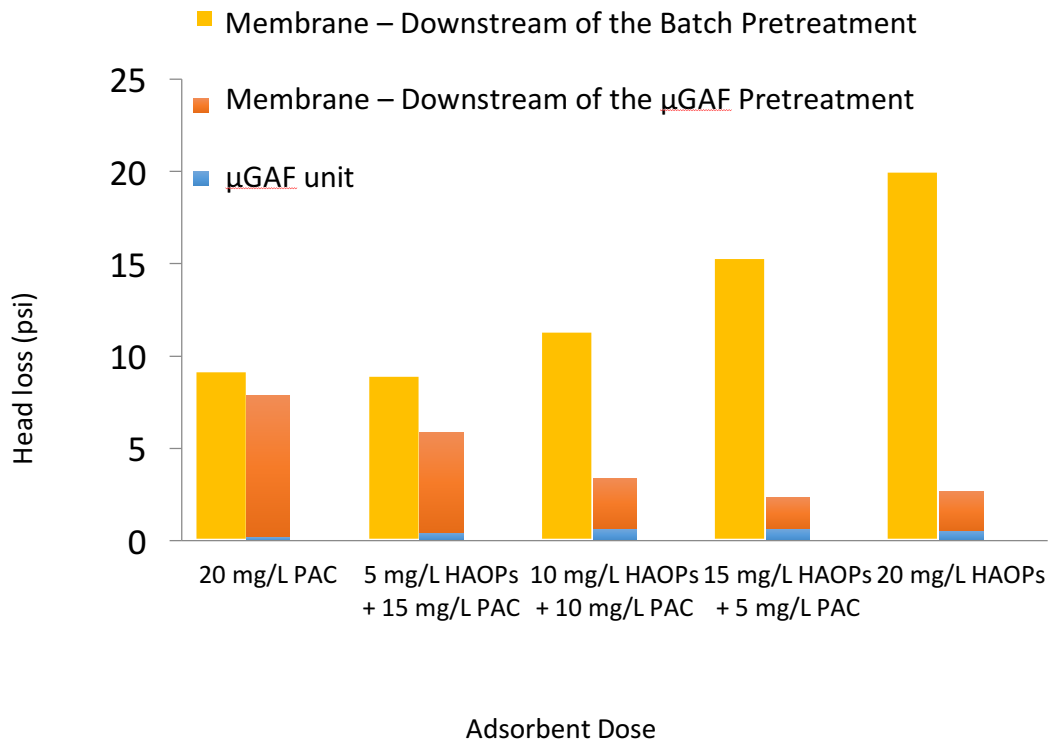
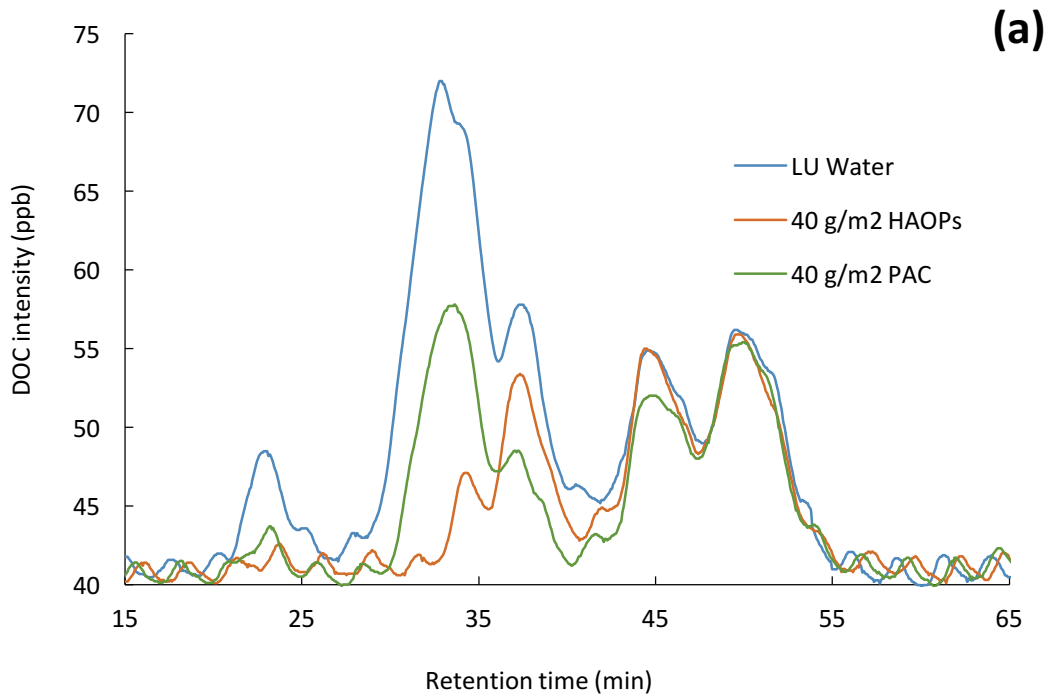


Figure 4-15 Final head loss at the end of the filtration V_{sp} of 2000 l/m^2 for batch pretreatment-membrane filtration tests and their corresponding μ GAF pretreatment-membrane filtration experiments.

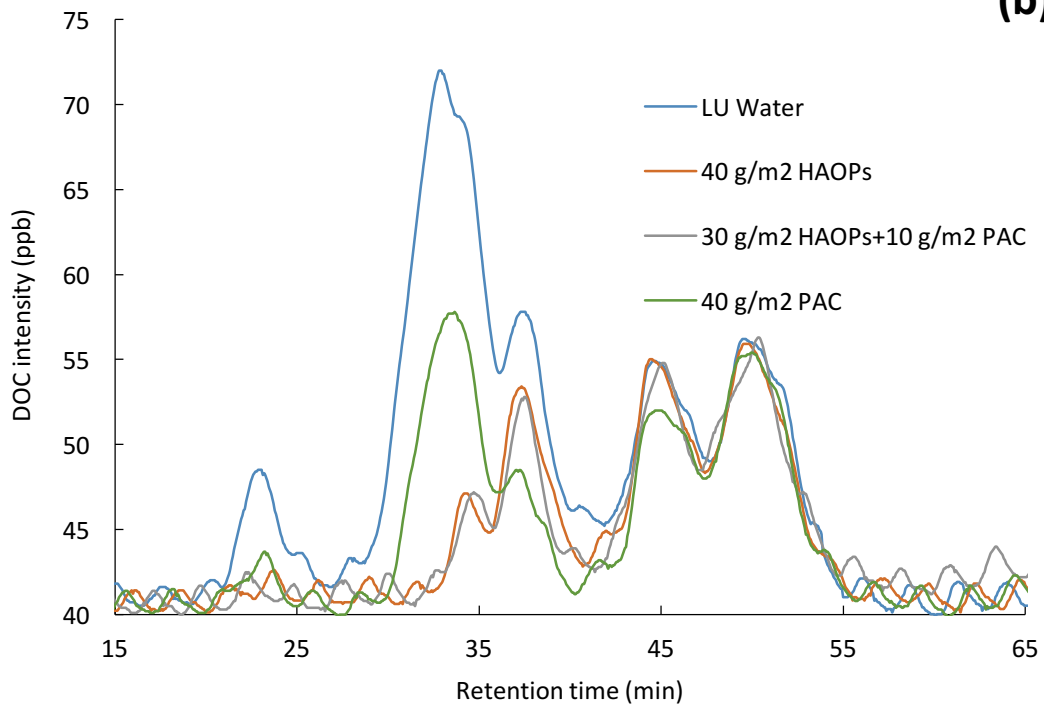
4.4.4 Characterization of the adsorbed NOM fraction by μ GAF pretreatment

4.4.4.1 Size exclusion chromatography

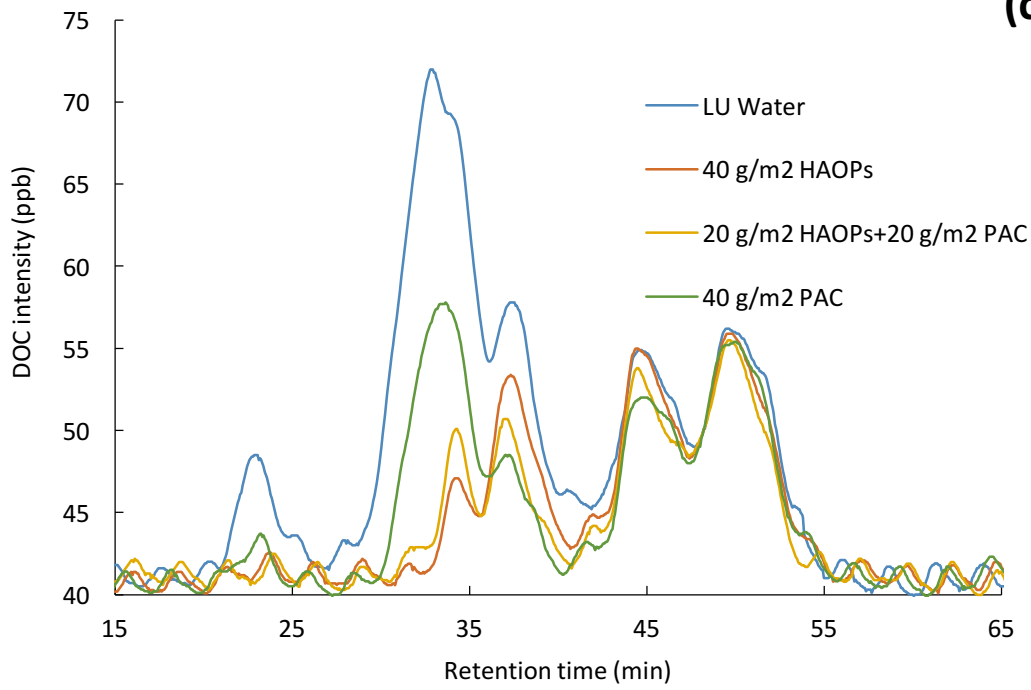
Size exclusion chromatograms of LU water samples treated by μ GAF with mixtures of HAOPs and SA SUPER are shown in Figure 4.16. Similar to the case for batch pretreatment, SA SUPER was more effective at capturing LMW NOM, HAOPs were more efficient at removing HMW NOM, and when a mixture of adsorbents was used, NOM with a broad range of molecular sizes was removed.



(b)



(c)



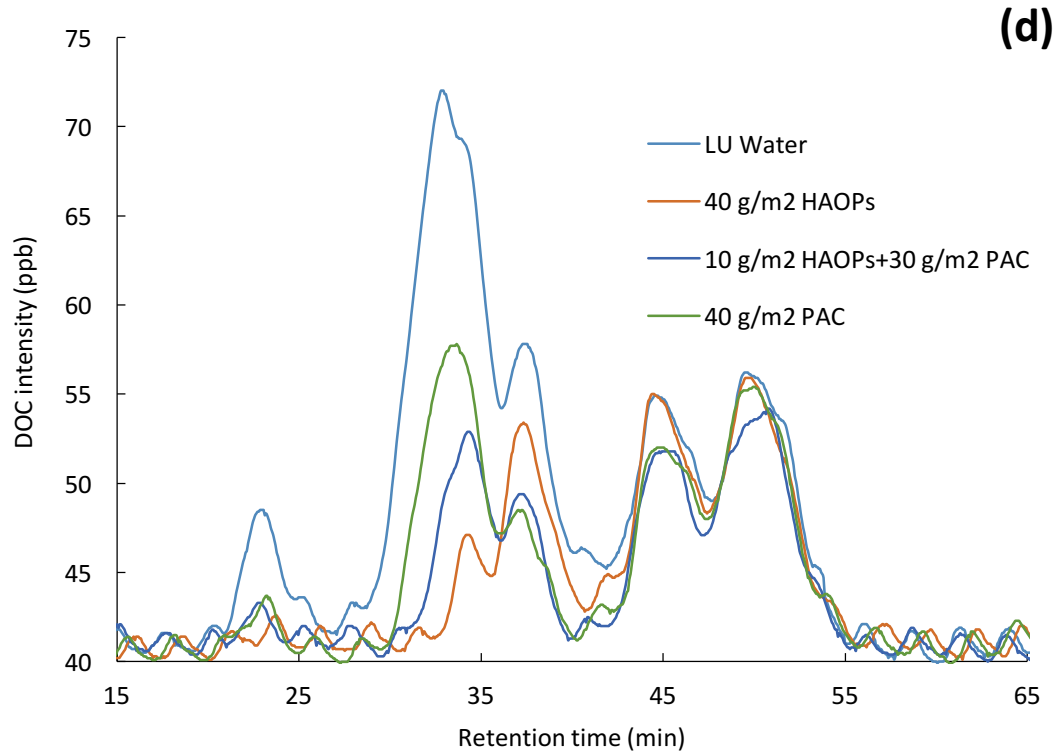
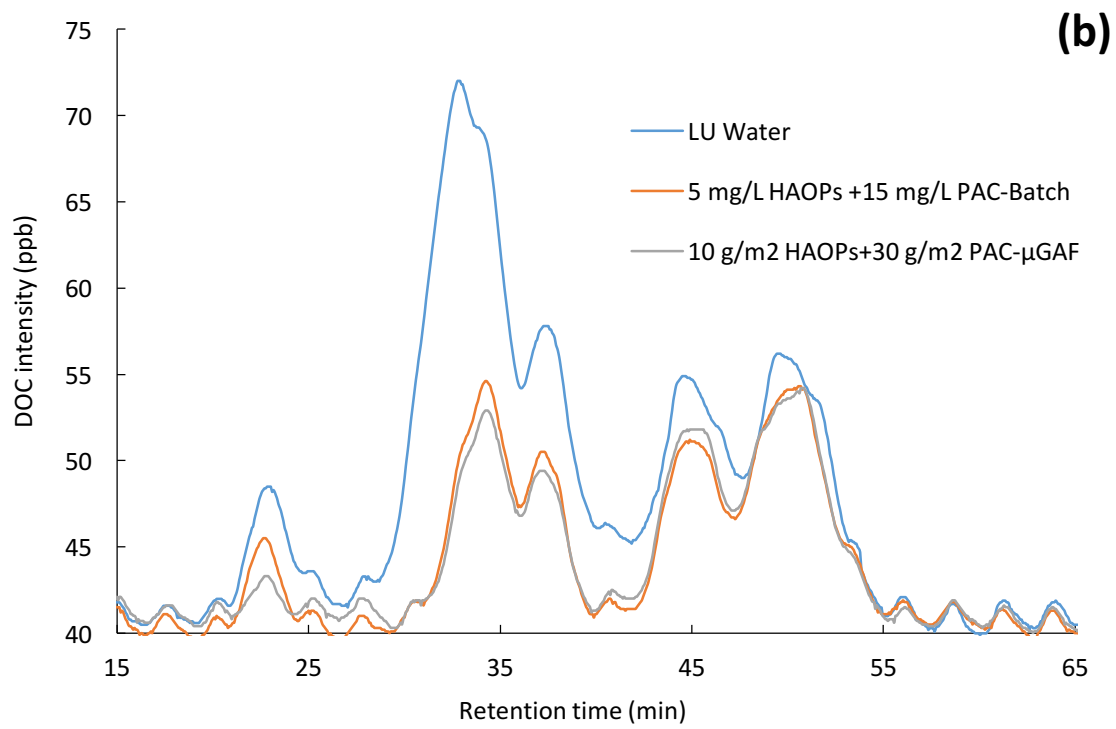
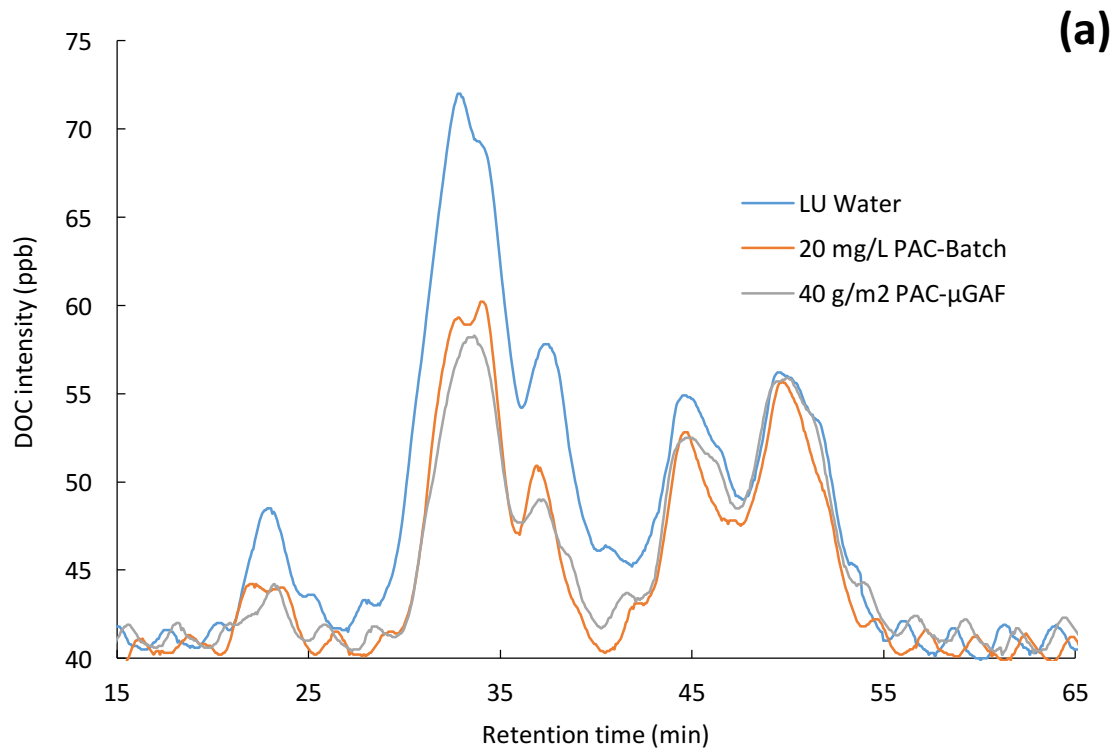
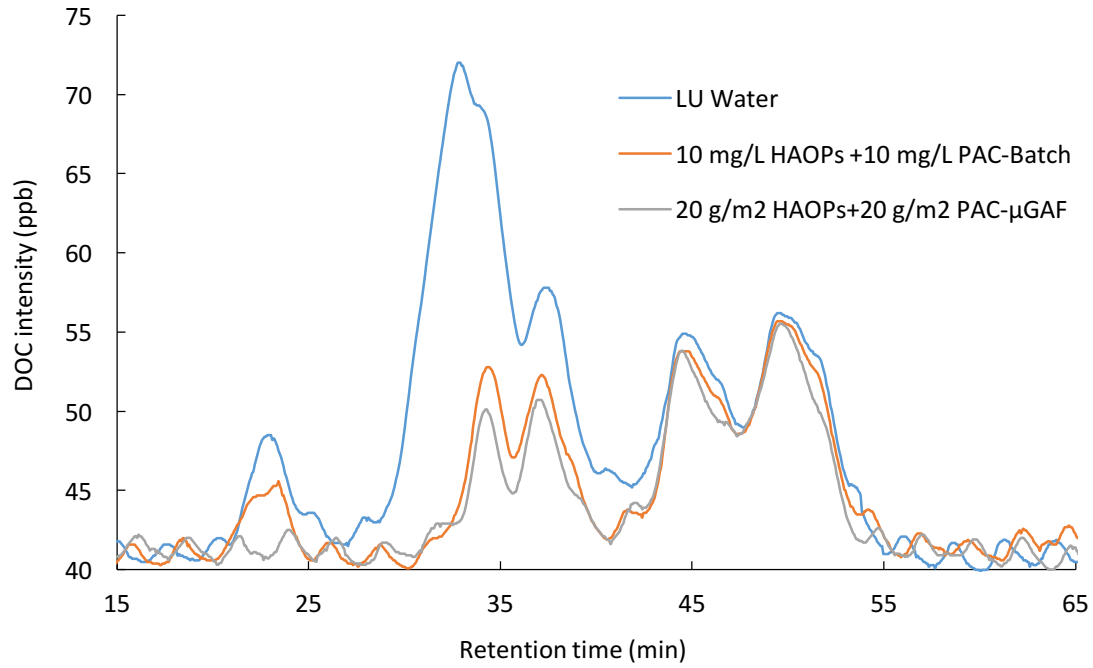


Figure 4-16 SEC chromatograms of LU water treated by batch adsorption with HAOPs and/or SA SUPER. Total adsorbent surface loading = 40 mg/l, $V_{sp} = 2000 \text{ l/m}^2$ (total effective adsorbent dose = 20 mg/l)

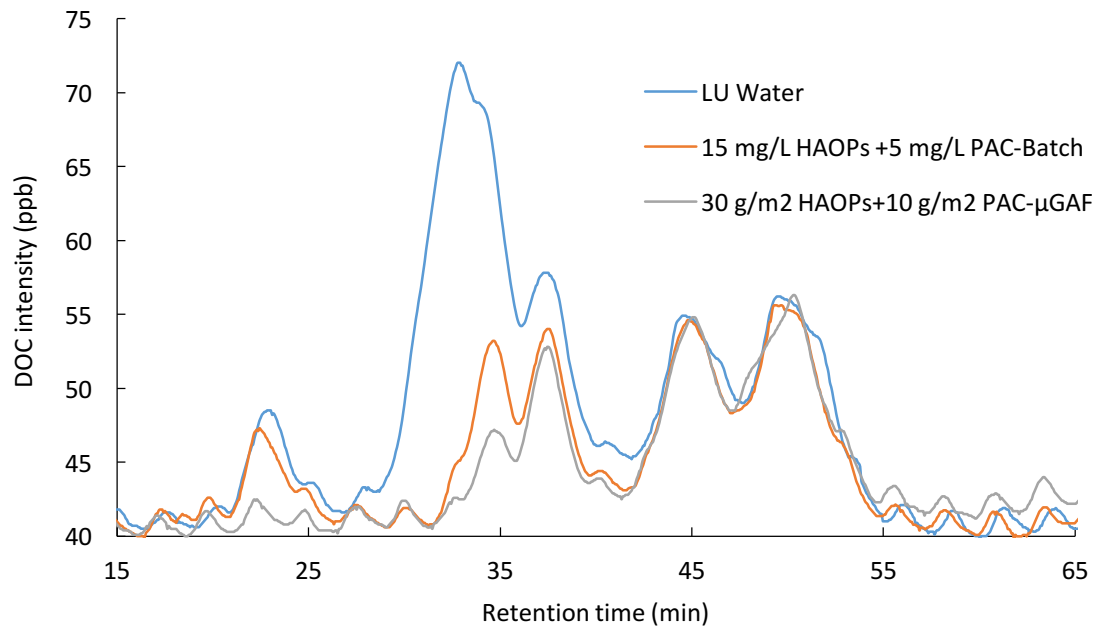
SEC chromatograms of LU water pretreated with each adsorbent or mixture of adsorbents in batch adsorption are compared to the corresponding chromatograms for μGAF pretreatment in Figure 4.17. In all cases, μGAF removed more of the high-MW NOM, including the biopolymer and humics fractions, than batch adsorption did. This observation could explain the reduced fouling of the membranes downstream of μGAF pretreatment. Also, this phenomenon was more significant for pretreatment by HAOPs than by SA SUPER, which is consistent with the lower final headloss with increasing the proportion of HAOPs in the HAOPs-SA SUPER mixture, as presented in Figure 4.15.



(c)



(d)



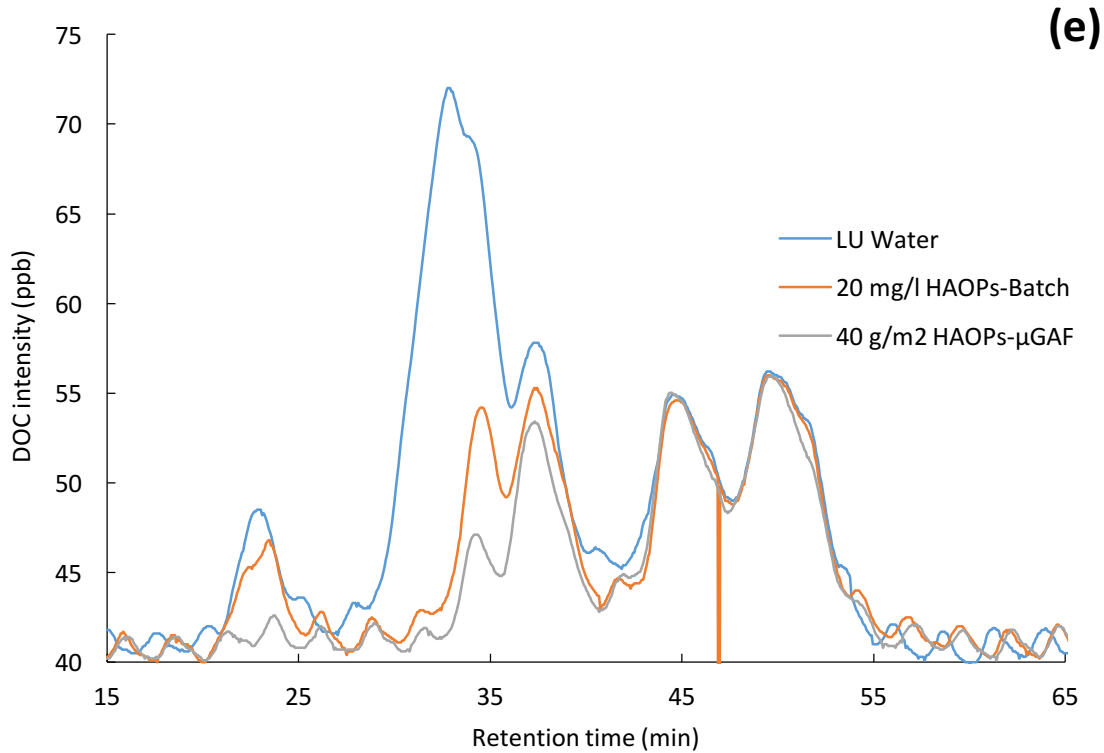


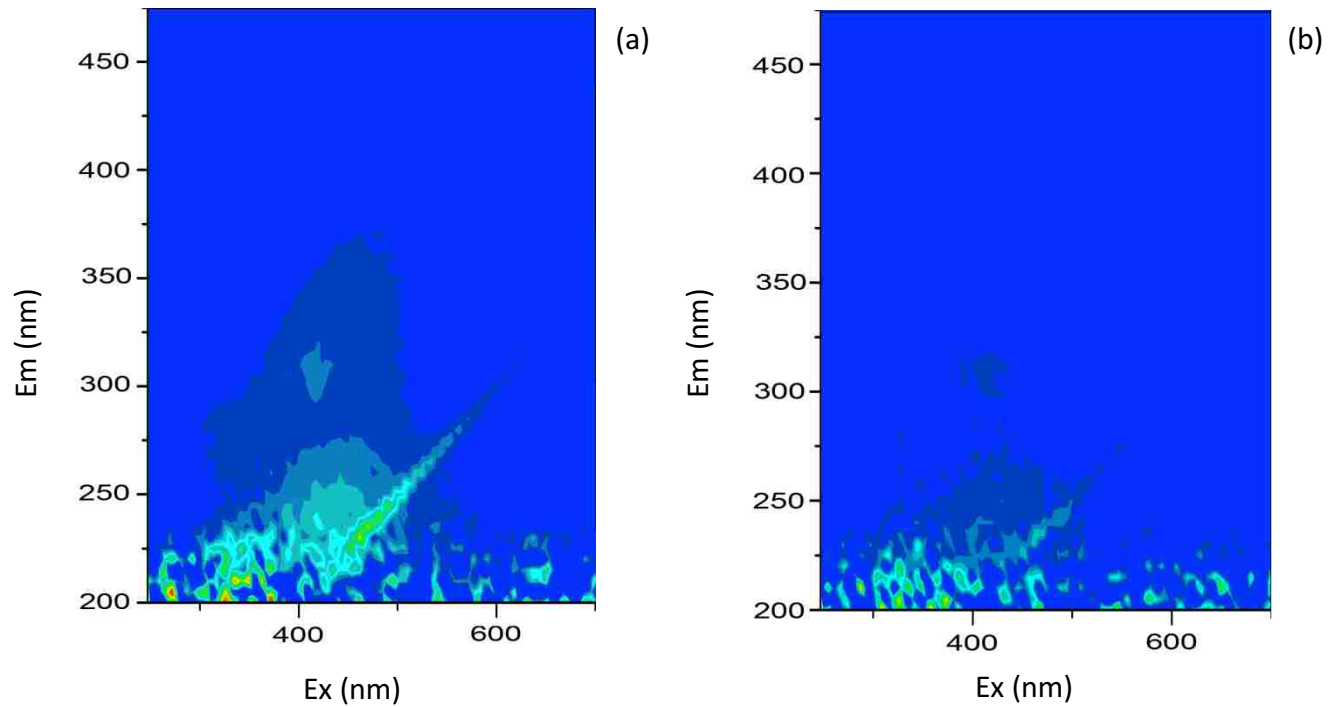
Figure 4-17 SEC chromatograms of LU water pretreated with μ GAF versus batch adsorption. a) 20mg/l PAC vs 40g/m² PAC; b) 15 mg/l PAC + 5 mg/l HAOPS vs 30 g/m² PAC + 10 g/m² HAOPS; c) 10 mg/l PAC + 10 mg/l HAOPS vs 20 g/m² PAC + 20 g/m² HAOPS; d) 5 mg/l PAC + 15 mg/l HAOPS vs 10 g/m² PAC + 30 g/m² HAOPS; e) 20mg/l HAOPS vs 40g/m² HAOPS

4.4.4.2 3-dimensional excitation-emission matrix fluorescence spectrometry

3-D EEM spectra of LU water pretreated with μ GAF followed the same trend as for pretreatment by batch adsorption (Figure 4.18). SA SUPER was more effective in removing fluorescent NOM, and increasing the proportion of SA SUPER in the adsorbent mixture increased the fluorescent NOM removal efficiency.

As mentioned earlier, in recent years, several investigators (Peldszus et al. 2011, Kimura et al. 2014a, Shao et al. 2014) have reported a direct correlation between the removal of fluorescent NOM and a reduction in membrane fouling. However, unlike the results from the batch

adsorption tests, 3-D EEM spectra of the water after μ GAF pretreatment did not follow this trend. Although pretreatment with HOAPs removed significantly less fluorescent NOM than SA SUPER, it was considerably more effective in reducing membrane fouling.



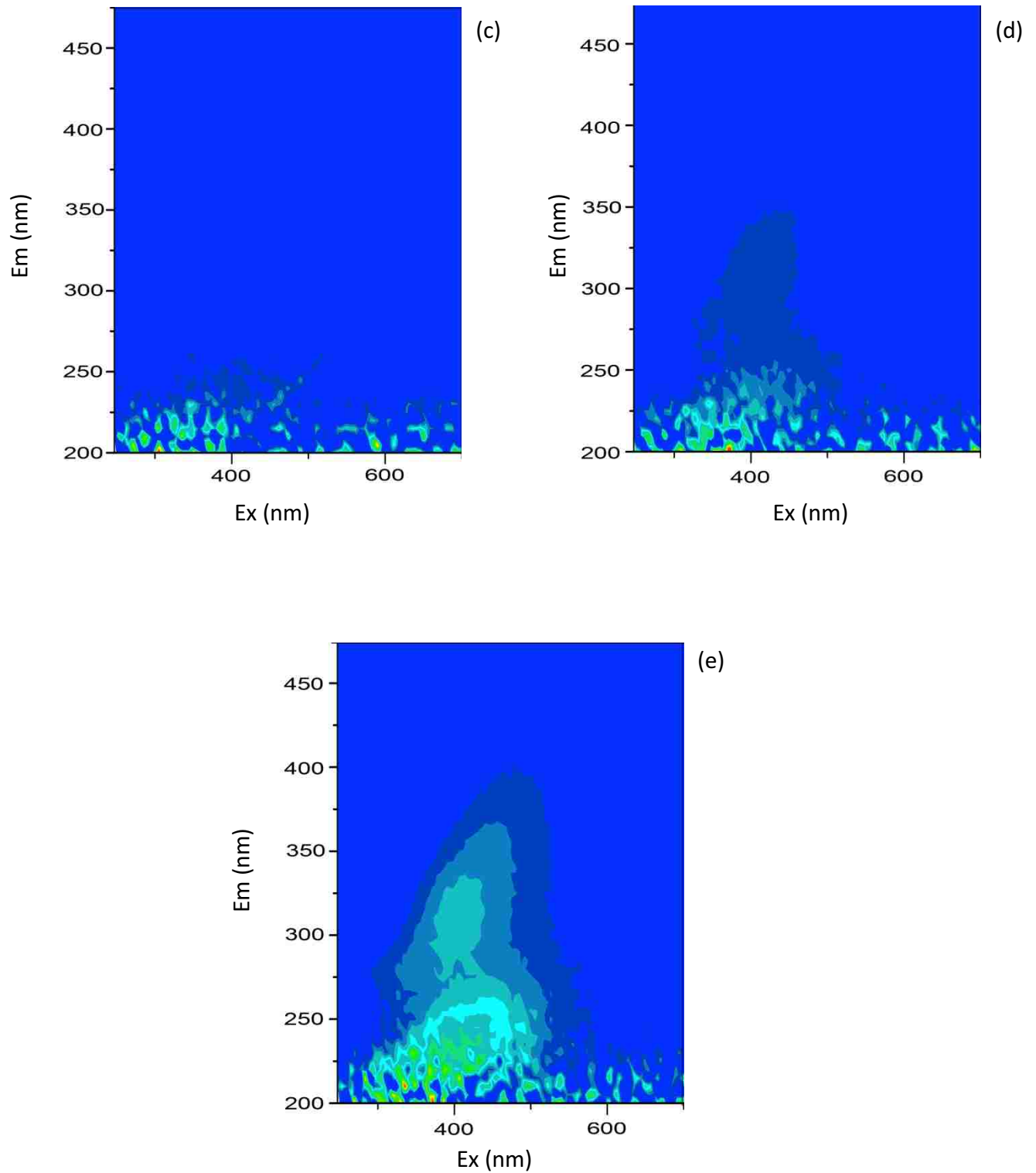


Figure 4-18 EEM spectra of LU water after μ GAF treatment with HAOPs and/or SA SUPER. (a) 40 g/m^2 PAC; (b) 30 g/m^2 PAC + 10 g/m^2 HAOPs; (c) 20 g/m^2 PAC + 20 g/m^2 HAOPs; (d) 10 g/m^2 PAC + 30 g/m^2 HAOPs; (e) 40 g/m^2 HAOPs.

4.4.5 Removal of DBP precursors by μ GAF pretreatment with mixture of HAOPs and SA SUPER

NOM removal tests using both batch adsorption and μ GAF showed that, for a given total adsorbent dose, mixtures of the adsorbents removed significantly more NOM than the individual adsorbents did. Therefore, DBP formation potential tests were conducted to investigate whether this enhanced NOM removal was correlated with better removal of DBP precursors. LU water pretreated in μ GAF systems with HAOPs or SA SUPER alone, and with a mixture of 50% HAOPs + 50% SA SUPER, were chlorinated, and formation of HAAs and THMs was measured (Table 4.2).

Table 4-2 Removal of DBP formation precursors by HAOPs or SA SUPER alone or a mixture of the 2 adsorbents. Total adsorbent surface loading 40 g/m². V_{sp} of 2000 l/m²

Water Sample	HAA Formation Potential (μ g/l)	% Removal	THM Formation Potential (μ g/l)	% Removal
LU Water	60.9		103.1	
40 g/m ² SA SUPER	19.7	67.6	37.4	63.7
40 g/m ² HAOPs	12.6	79.3	38.6	62.6
20 g/m ² HAOPs + 20 g/m ² SA SUPER	9.0	85.3	21.4	79.2

At an effective adsorbent dose of 20 mg/l (adsorbent surface loading of 40 g/m² and V_{sp} of 2000 l/m²), the pretreatment significantly reduced the DBP formation potential in all three systems. HAOPs was more efficient than SA SUPER in removing UV_{254} and HAA precursors, and the two “pure” adsorbents removed about equal amounts of THM precursors. However, the mixture of HAOPs and SA SUPER reduced the DBP formation potential of the water considerably, especially for THMs. Thus, by using a mixture of HAOPs and SA SUPER, it is

possible to reach a given DBP formation potential in the treated water with a lower total amount of adsorbents used.

4.5 Effect of operational parameters on μ GAF performance

Operational parameters including adsorbent surface loading, adsorbent layer outer surface and operational flux are crucial for designing the μ GAF process. In the second part of this study, the effects of these parameters on the NOM removal and membrane fouling control of μ GAF-PAC system were investigated. Results are compared with the corresponding effects on the μ GAF-HAOPs process.

4.5.1 Effect of the adsorbent layer surface on μ GAF performance

4.5.1.1 Effect of the HAOPs layer surface on capturing NOM in μ GAF

Cai (2010) suggested that although the discoloration of the HAOPs layer in μ GAF occurs mainly at the surface of the adsorbent layer, the depth of the layer is as effective as the surface in capturing soluble NOM and membrane foulants. However, the preceding results could indicate that the surface of the adsorbent layer might be more effective than particles deeper in the layer for capturing the foulants. Therefore, the effect of the surface of the adsorbent layer in μ GAF on the quality of the filtered water was investigated.

LP water with 50% dilution was used as the feed water and was treated by μ GAF with 96 g/m² of adsorbent surface loading. In one test, all the adsorbent was deposited in one μ GAF unit, but in another, three μ GAF units were used in series, each containing one-third of the adsorbent, providing three locations where the water contacted the surface of an adsorbent layer. The final filtrate from each test was collected and fed to a membrane unit downstream.

Figure 4.19 shows an image of the surface of the HAOPs layers in the μ GAF units. The color intensity decreased from dark to light brown from the first to the third unit in the system with three cartridges in series. Considering the HAOPs layers as microscale packed bed reactors, the difference in the color intensity shows the movement of the mass transfer zone through the bed. However, as reported by Cai (2010), the discoloration of the HAOPs layer is more pronounced on the top surface than in the depth of the layer. Hence, for a fixed total adsorbent dose, increasing the surface of the HAOPs layer might increase the removal of colored NOM.

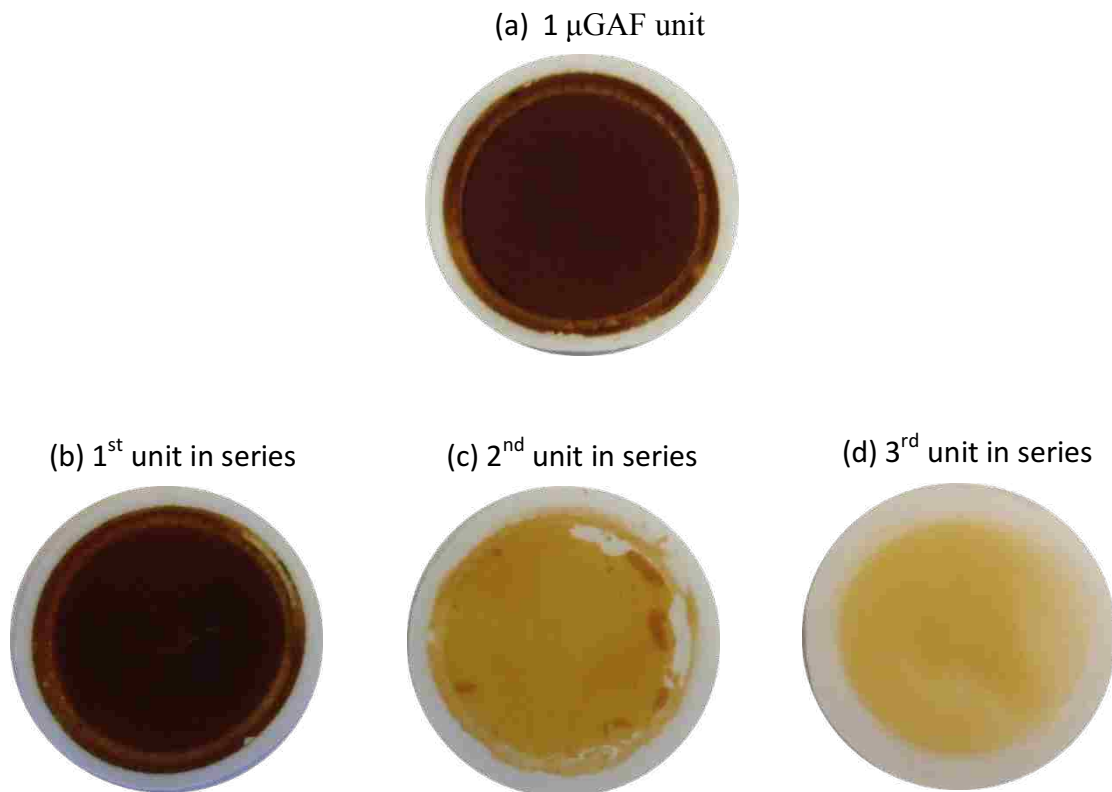
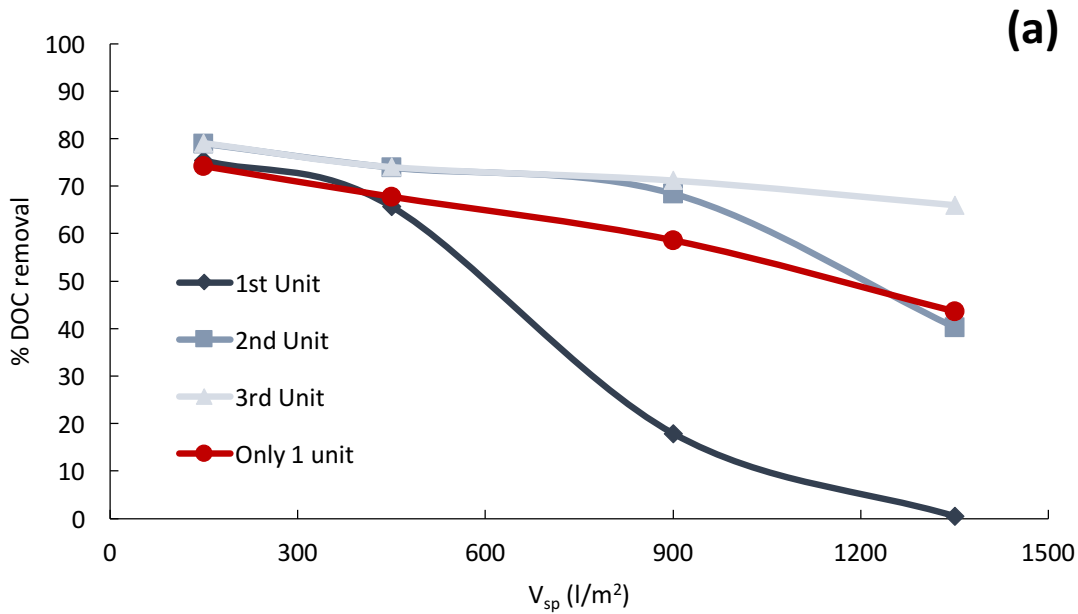


Figure 4-19 Images of the surface of the HAOPs layer at a V_{sp} of 1600 l/m^2 when one or three μ GAF units were used. In the latter case, each unit contained one-third of the total adsorbent surface loading of 96 g/m^2 . Flux= 150 LMH

NOM removal by each μ GAF unit in the sequential filtration process is illustrated in Figure 4.20. As the run proceeded, the difference between the quality of the water treated in the two systems increased. Using only one μ GAF unit resulted in 63.7% and 81.8% overall removal of DOC and UV_{254} , respectively, whereas overall DOC and UV_{254} increased to 68.4% and 90.3%, respectively, for μ GAF units in series.

The first unit in the series system removed almost no DOC at V_{sp} of 1350 l/m^2 , while still removing about 30% of UV_{254} . This could be due to competitive adsorption of different fractions of NOM on HAOPs. As the run proceeded, some of the NOM molecules with less affinity for HAOPs were released, providing adsorption sites for other NOM molecules that had higher affinity (and higher UV_{254} absorbance).



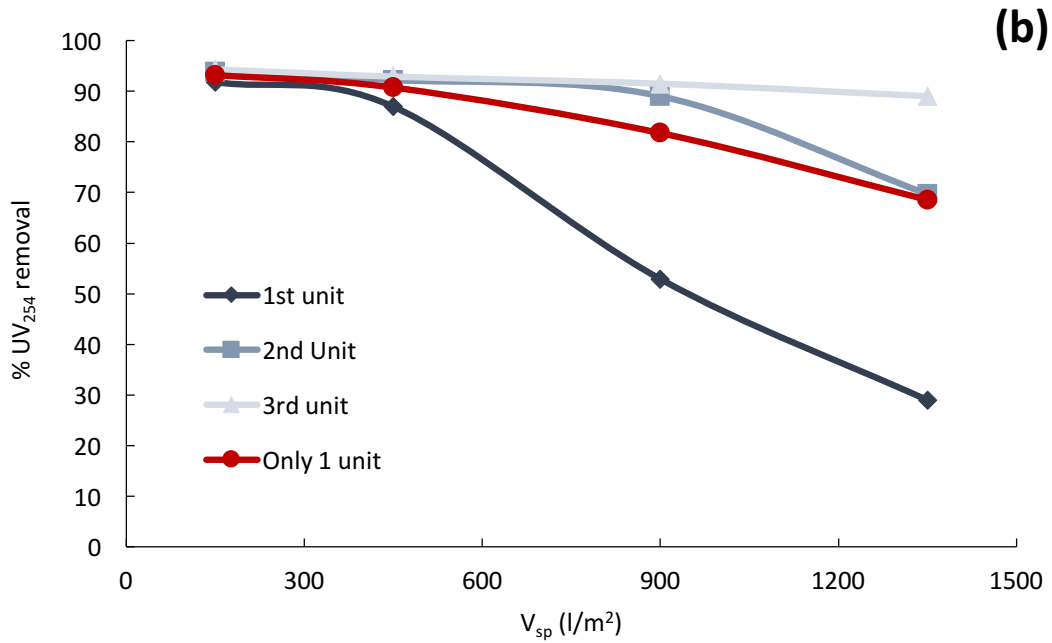


Figure 4-20 NOM removal from 50% LP water by HAOPs- μ GAF unit(s), when 1 unit with a surface loading of 32 g/m² was used compared to using 3 units in series, each with a surface loading of 32 g/m². a) DOC removal; b) UV₂₅₄

SEC chromatograms of the composite filtrates are shown in Figure 4.21, confirming the higher removal of humic substances and building blocks in the cartridges-in-series system.

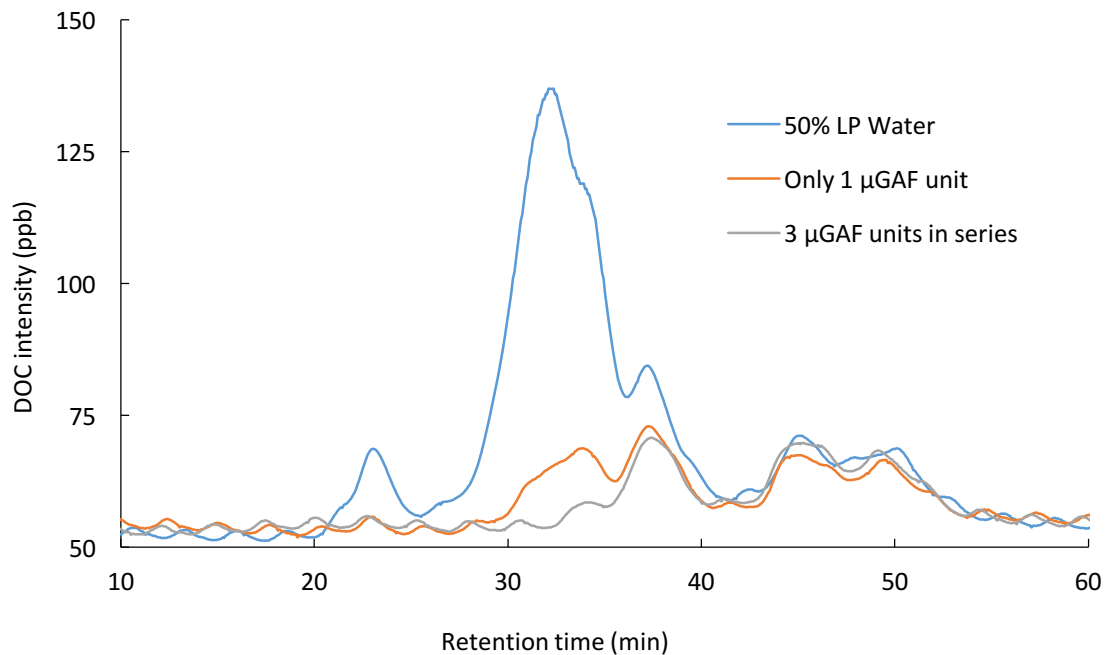


Figure 4-21 SEC chromatogram of 50% LP water treated with only 1 μ GAF unit or 3 μ GAF units in series each containing 1/3 of the total adsorbent surface loading

The increased removal of humic substances suggests that a fraction of the colored NOM that broke through the first layer surface was captured by the second layer surface and a fraction of what broke through the second layer was captured on the surface of the third layer, resulting in a higher removal efficiency for the colored NOM (mostly humic substances) in the μ GAF units in series than when an equal amount of adsorbent was used in only one unit.

SEC analysis of the filtrate of the first unit in the series, presented in Figure 4.22, illustrates the adsorption/desorption of different fractions of NOM as the adsorption capacity of the HAOPs layer is consumed during the filtration test. At early stages of filtration, almost all of the biopolymers, humic substances and building blocks are adsorbed by HAOPs. However, as filtration proceeds to around V_{sp} of 900 l/m^2 , some of the adsorbed building blocks and low-MW acids are released from the HAOPs and instead humic substances are adsorbed. At a V_{sp} of 1350

l/m², the mass of the carbon adsorbed is almost equal to the mass of the carbon desorbed, resulting in no net DOC removal. However, the adsorbed NOM at this stage is humic substances, which have high UV₂₅₄ absorbance.

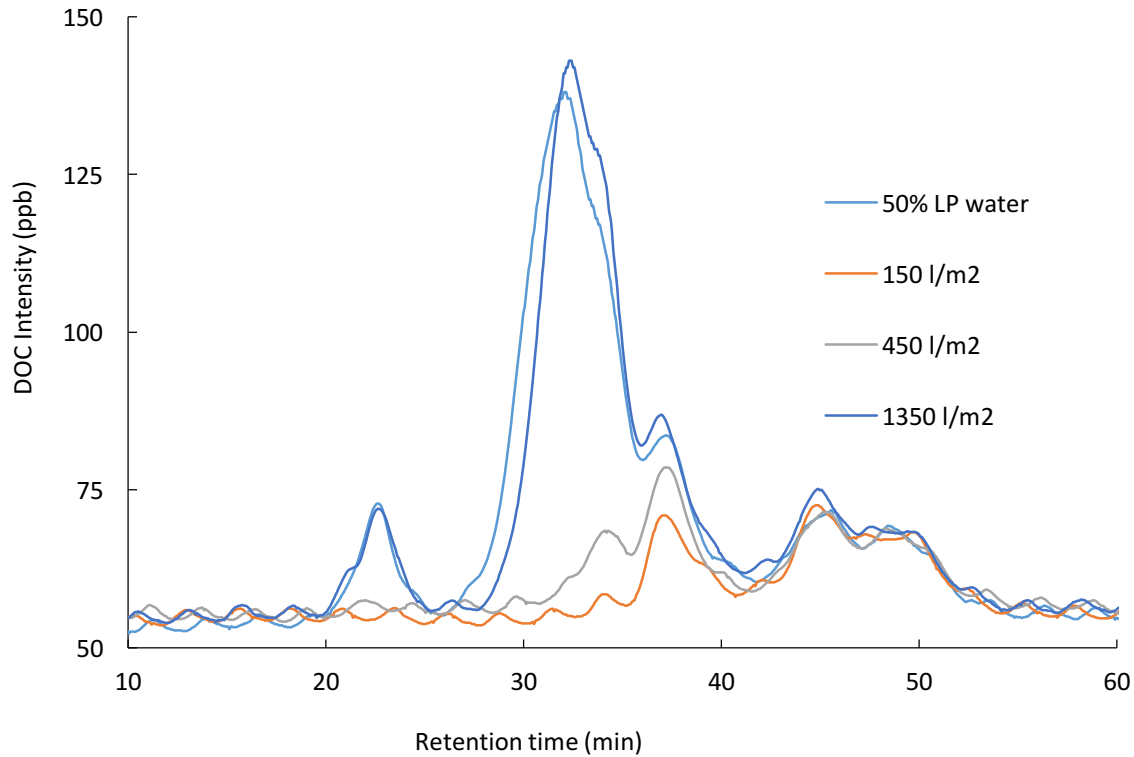


Figure 4-22 SEC chromatogram of the filtrate of the 1st μ GAF unit in a series of 3 μ GAF units during the treatment of 50% LP water

The pressure increase across the μ GAF unit(s) in these tests is illustrated in Figure 4.23. The pressure increase across the first μ GAF unit in the series was similar to that when only one unit was used, and there was no buildup of pressure across the second and third units. Liu (2015) reported that particulate and colloidal material are the main foulants of the HAOPs layer. He suggested that foulant particles can block the empty spaces between the HAOPs particles and can accumulate on top of each other. The pressure profiles suggest that the material that fouls the

HAOPs layer was entirely captured by the first unit and did not reach the second or third unit. Even when the NOM adsorption capacity of the first layer was exhausted at late stages of the filtration run, it was still capturing foulants and preventing them from reaching the subsequent layers.

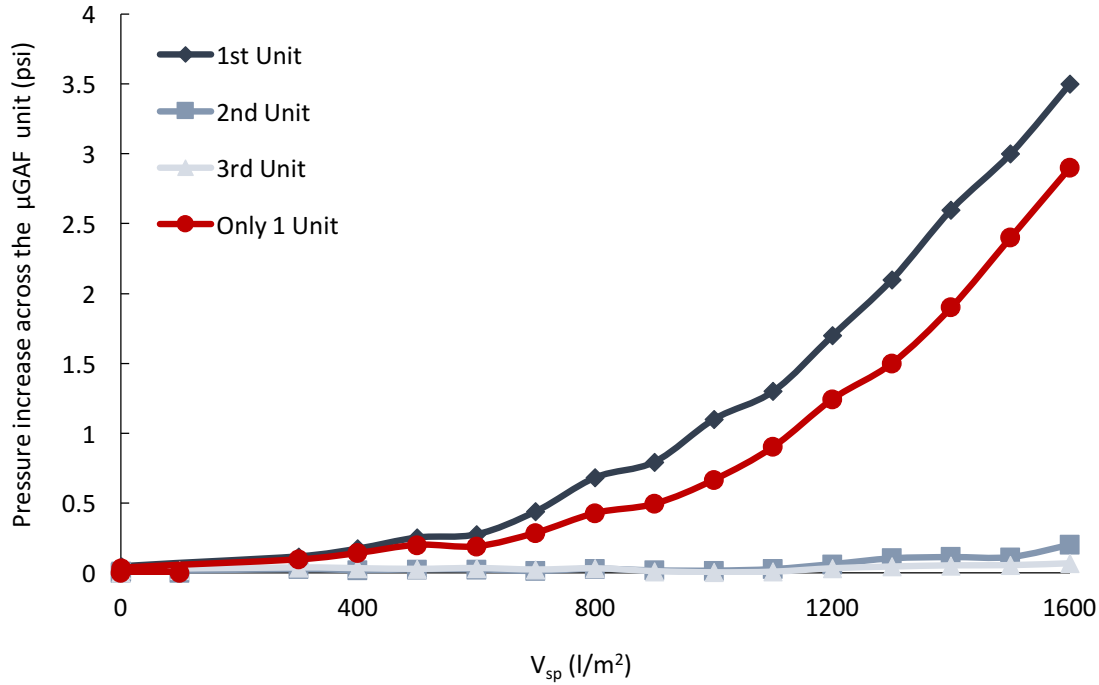


Figure 4-23 Pressure increase across the HAOPs layer for 1 μ GAF unit with an adsorbent surface loading of 96 g/m² HAOPs and 3 units in series with an adsorbent surface loading of 32 g/m² for each. Flux =150 LMH

Fouling of the downstream membranes fed with the composite filtrates of the two pretreatment processes is characterized in Figure 4.24. Although both pretreatment processes substantially reduced fouling of the downstream membrane, splitting the HAOPs into three layers significantly improved the process performance.

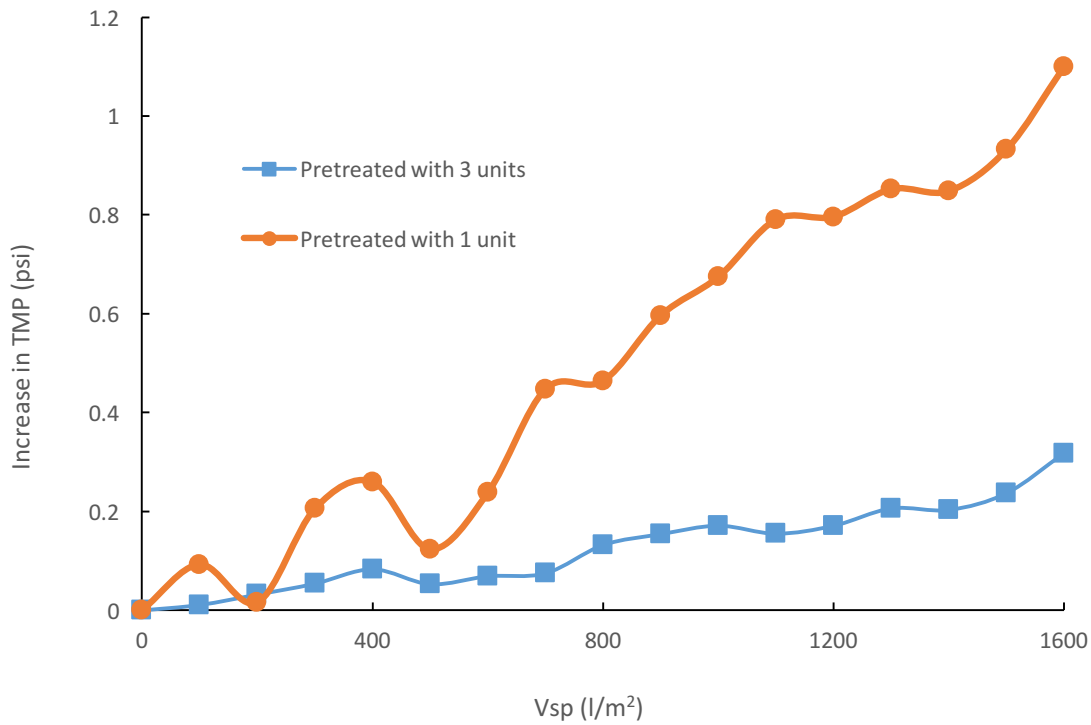


Figure 4-24 TMP profiles of membranes fed with composite filtrate of three HAOPs μ GAF units in series and a single μ GAF unit containing a HAOPs surface loading equal to the sum of the HAOPs surface loadings of the three units.

Images of the surfaces of the membranes, shown in Figure 4.25, showed a slight discoloration of the membrane downstream of the single μ GAF unit, whereas no discoloration could be observed on the surface of the membrane downstream of the three- μ GAF system.

(a) Downstream of only 1 μ GAF unit



(b) Downstream of 3 μ GAF units in series



Figure 4-25 Images of the surface of the membranes fed with the filtrate of different pretreatment process configurations.

4.5.1.2 Effect of the SA SUPER layer surface μ GAF performance

Experiments analogous to those described above were conducted with SA SUPER. NOM removal in the individual units is presented in Figure 4.26. Early in the run, when the effective dose of adsorbent is high (640 mg/l at a V_{sp} of 150 l/m²), almost 100% of the DOC was removed. In the tests with HAOPs, at this early stage, only 80% of the DOC was captured. As presented in section 4.1.1, a fraction of the NOM does not adsorb to HAOPs even at high adsorbent doses, whereas SA SUPER could reach 100% removal of DOC at high doses.

Unlike the result for HAOPs, exposing the water to SA SUPER in three sequential μ GAF units led to a deterioration in NOM removal (overall DOC and UV₂₅₄ removal of 66.7% and 79.5%, respectively, by one unit, versus 60.2% and 72.1% by three sequential units).

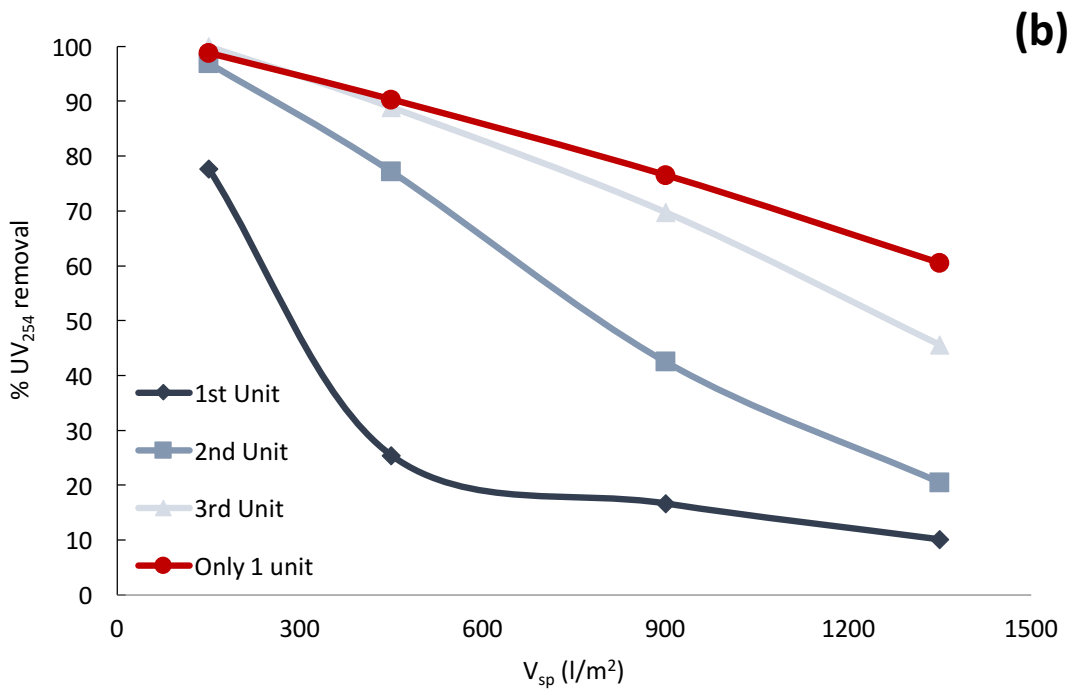
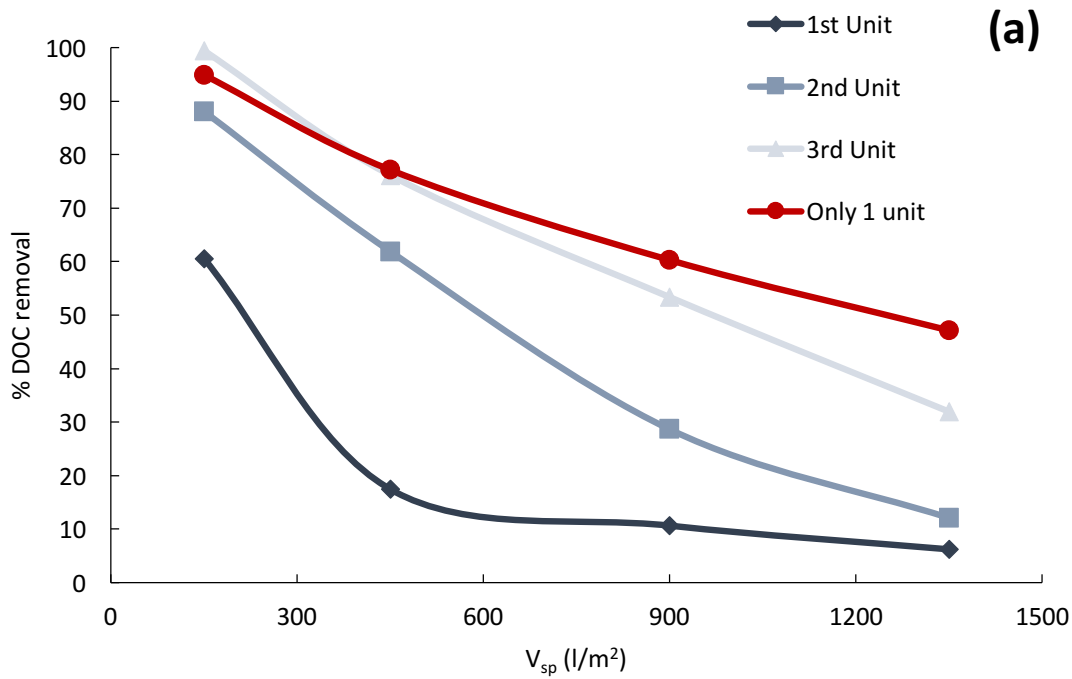


Figure 4-26 NOM removal from 50% LP water by SA SUPER- μ GAF, when one unit with a surface loading of 96 g/m² was used compared to using three units in series, each with a surface loading of 32 g/m². a) DOC; b) UV₂₅₄

SEC analysis of the composite filtrates from the two pretreatment systems indicated that the removal of NOM from all the fractions was slightly reduced when three units were used (Figure 4.27).

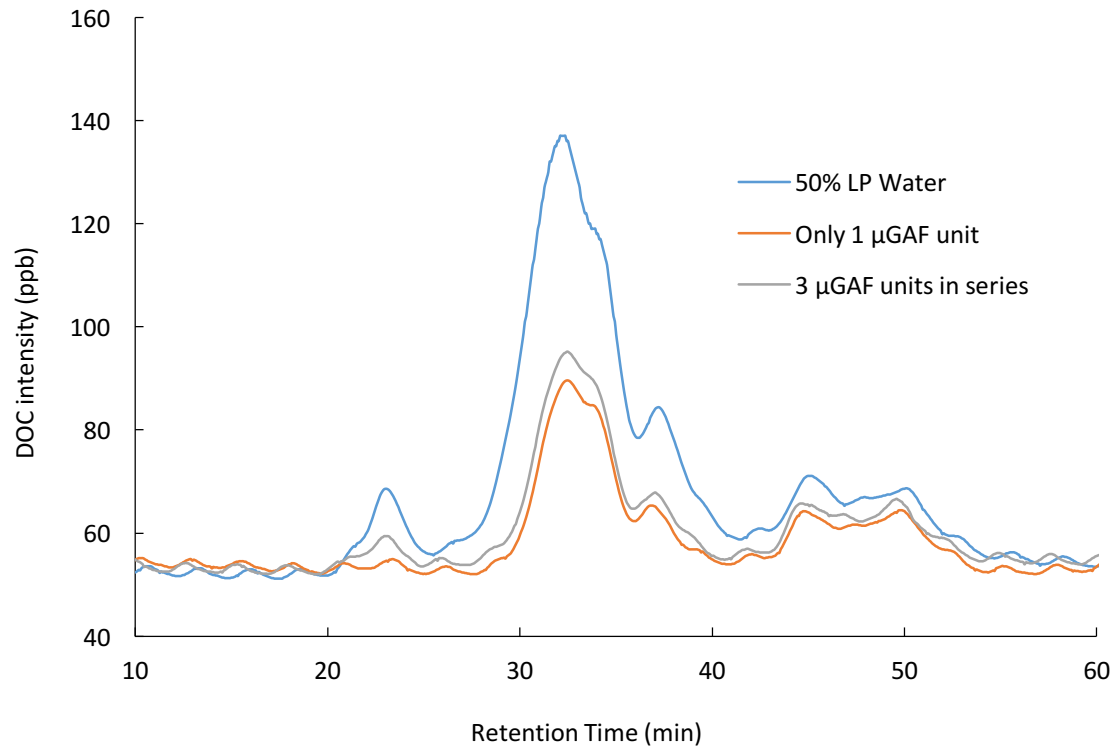


Figure 4-27 SEC chromatogram of 50% LP water treated with only 1 μ GAF unit or 3 μ GAF units in series each containing 1/3 of the total adsorbent surface loading.

The headloss across the first μ GAF unit in the 3-unit system increased significantly faster than that across the unit in the single-cartridge system (Figure 4.28). Headloss also built up slightly across the second unit during the run. These results suggest that, unlike when HAOPs was used, some of the material that could foul SA SUPER passed through the first unit and fouled the second unit. The higher rate of headloss buildup in the first unit compared to that in the single-cartridge system can be explained by adverse interactions among NOM, PAC and the surface of the filter. As reported in section 4.4 and also by other researchers (Cai 2010, Kim

2008), adhesion of PAC particles to the surface of a membrane (or, in this case, filter paper) by NOM can exacerbate fouling. Since less adsorbent was available to remove NOM in the first unit of the cartridges-in-series system, more NOM reached the interface between the filter paper and the PAC particles, causing more adhesion and more resistance to water flow.

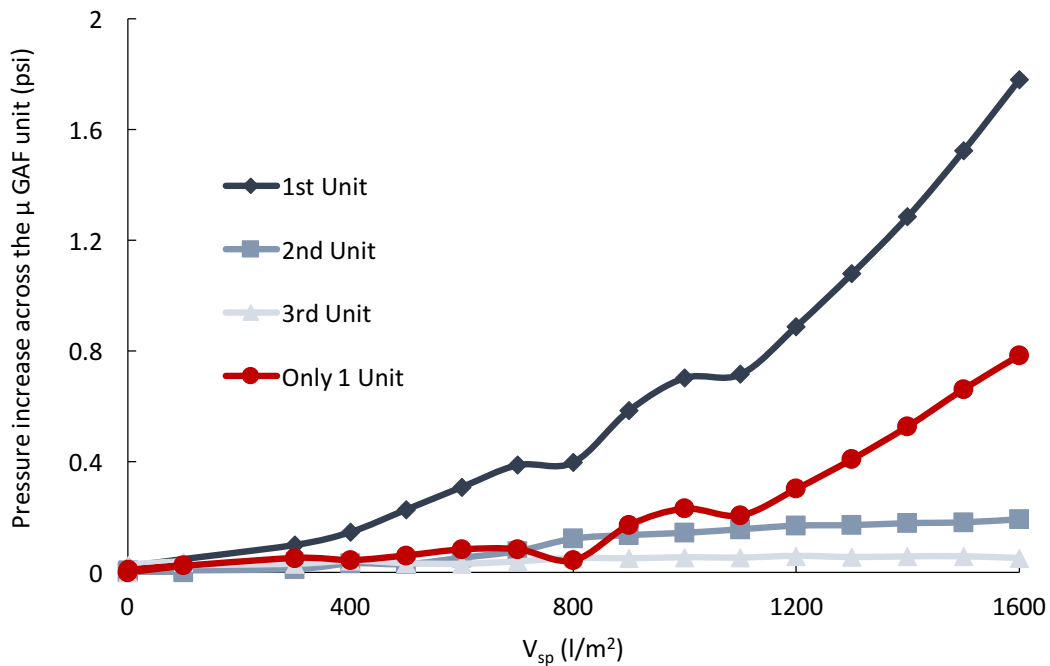


Figure 4-28 Pressure increase across the PAC layer for 1 μ GAF unit with an adsorbent surface loading of 96 g/m² PAC and 3 units in series with an adsorbent surface loading of 32 g/m² for each. Flux =150 LMH

Fouling of membranes that were fed with the composite filtrates of the two pretreatment processes is presented in Figure 4.29. Consistent with its higher NOM removal, and in contrast to the case in the systems with HAOPs, the single μ GAF unit protected the membrane better than the three units in series did.

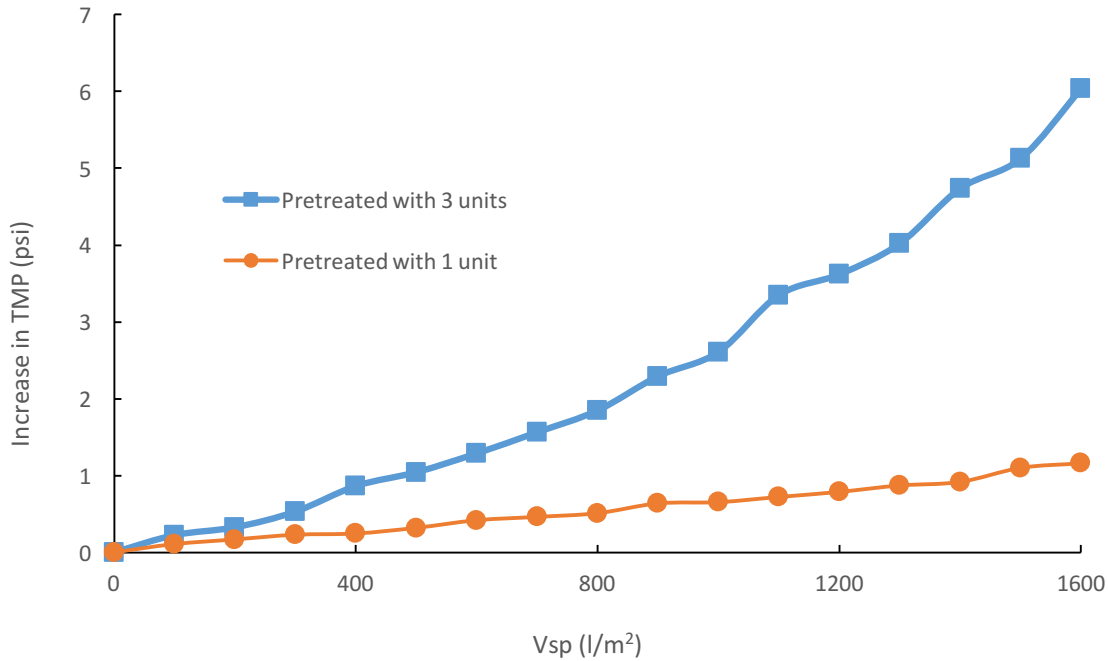


Figure 4-29 TMP profiles of membranes fed with composite filtrate of 3 PAC μ GAF units in series and only 1 μ GAF unit containing a PAC surface loading equal to the sum of the PAC surface loading of the 3 units.

At the end of the test (V_{sp} of 1600 l/m²), the membrane that received water pretreated in the series of μ GAF units was more discolored than the membrane downstream of the single unit (Figure 4.30).

(a) Downstream of only 1 μ GAF unit



(b) Downstream of 3 μ GAF units in series



Figure 4-30 Surfaces of membranes fed the filtrate from different pretreatment process configurations.

4.5.2 Effect of adsorbent surface loading

The effect of adsorbent surface loading on μ GAF performance using both HAOPs and SA SUPER as adsorbents was investigated using Lake Pleasant water with 50% dilution as feed, a flux of 150 LMH, and adsorbent surface loadings of 30, 60, and 120 g/m^2 . The effective dose of adsorbent was kept the same in all tests by adjusting the total volume of treated water. The composite filtrate from the upstream μ GAF unit was collected and fed to the downstream membrane unit at a fixed flux of 100 LMH.

4.5.2.1 Effect of HAOPs surface loading on μ GAF process performance

Cai (2010) reported that NOM removal and membrane fouling control in μ GAF-HAOPs systems was proportional to the HAOPs surface loading. However, as discussed in section 4.4.1, increasing the interfacial area between the HAOPs layer and the feed solution enhances the process performance.

In the current experiments, the total volume of treated water was varied in proportion to the adsorbent surface loading while the surface area of the adsorbent layer was constant. As a result, the ratio of the adsorbent layer surface area to the total volume of water treated increased as the adsorbent surface loading decreased.

Figure 4.31 indicates that the rates of pressure increase at three surface loadings were very similar. However, the pressure increase at the end of the run increased with increasing surface loading, which is reasonable in light of the higher total volume of water treated and therefore larger amount of foulant captured at higher loadings.

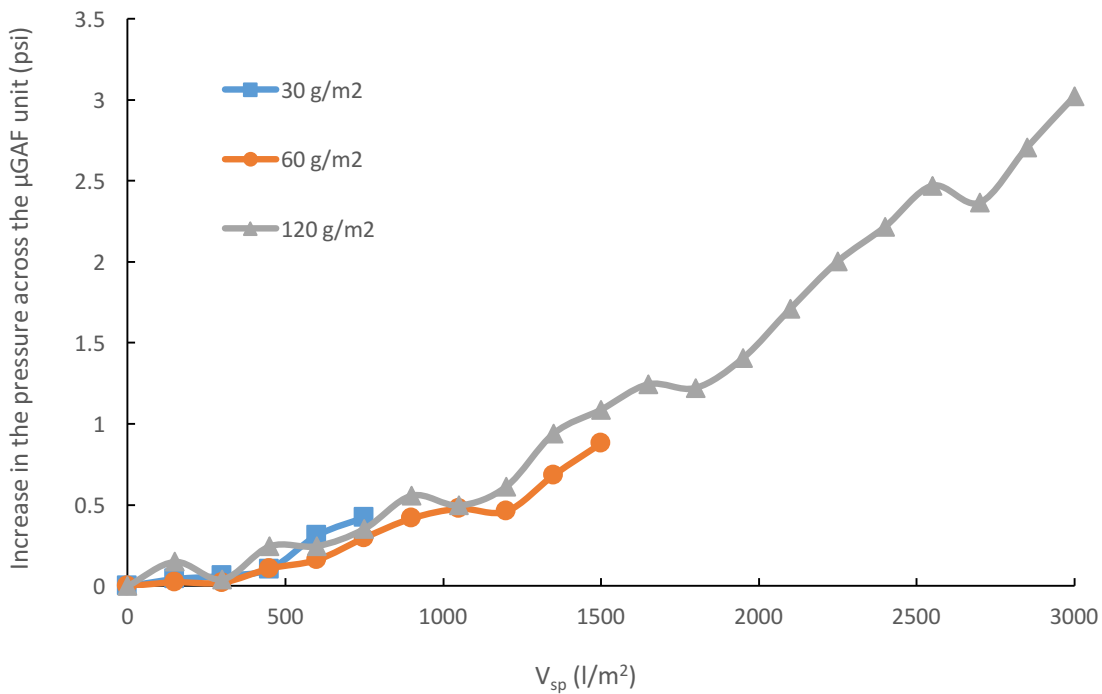


Figure 4-31 Pressure increase profiles of HAOPs-μGAF units with different adsorbent surface loadings and proportionally different total volumes of water treated at a fixed adsorbent effective dose of 40 mg/l.

The effect of the HAOPs surface loading on NOM removal is presented in Figure 4.32. Increasing the surface loading led to a slight decrease in NOM removal.

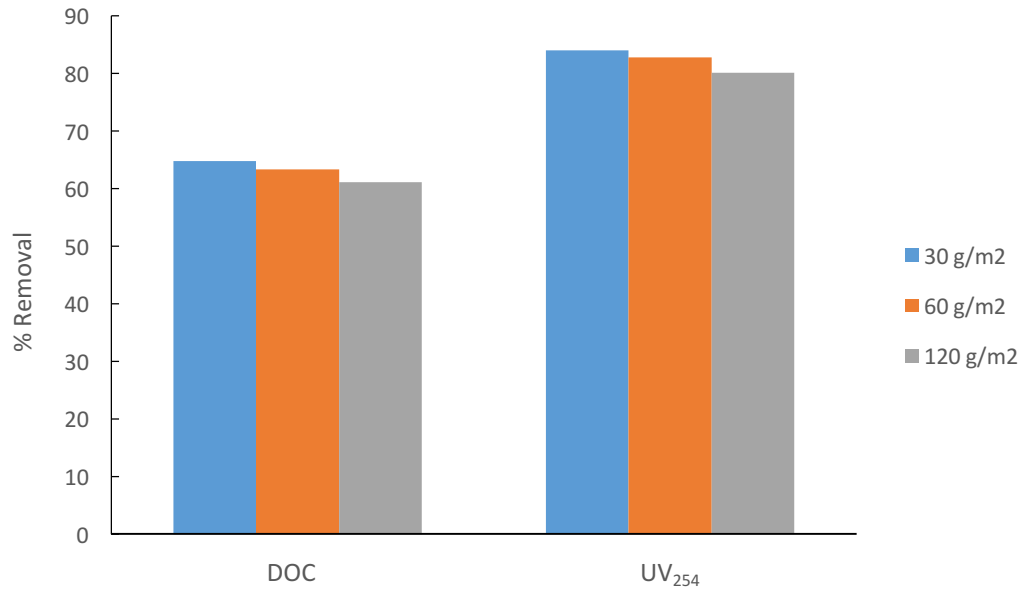


Figure 4-32 Composite filtrate quality of HAOPs- μ GAF with different adsorbent surface loading.

Size exclusion chromatography of the composite filtrates from the μ GAF units indicated a gradual increase in the removal of humic substances with decreasing HAOPs surface loading (Figure 4.33), consistent with the enhancement of humic substances removal with an increase in the ratio of HAOPs layer surface to total volume of water treated, discussed in section 4.4.1.

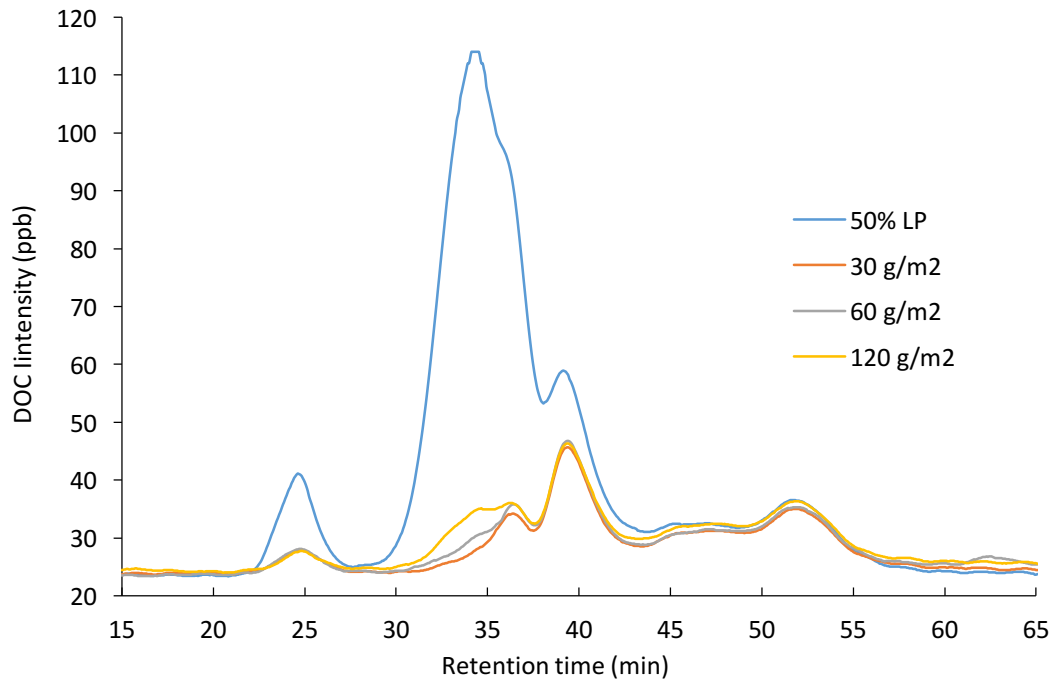


Figure 4-33 SEC chromatograms of composite filtrate of 50% LP water treated with different HAOPs surface loadings.

The TMP profiles across downstream membranes that were fed the composite filtrates from the preceding runs are shown in Figure 4.34. The rate of pressure increase was similar for all the membranes. However, the TMP increase for the membrane fed the filtrate from μ GAF with a surface loading of 30 g/m^2 was slightly lower than the TMP increase for the other two membranes. The TMP of the membrane fed the μ GAF filtrate with a surface loading of 30 g/m^2 at a V_{sp} of 750 LMH was 1.1 psi, whereas this value for membranes fed with the μ GAF filtrates with surface loadings of 60 and 120 g/m^2 were 1.7 and 1.6 psi, respectively. This slightly better performance is consistent with the higher NOM removal by the μ GAF system with 30 g/m^2 of HAOPs loading.

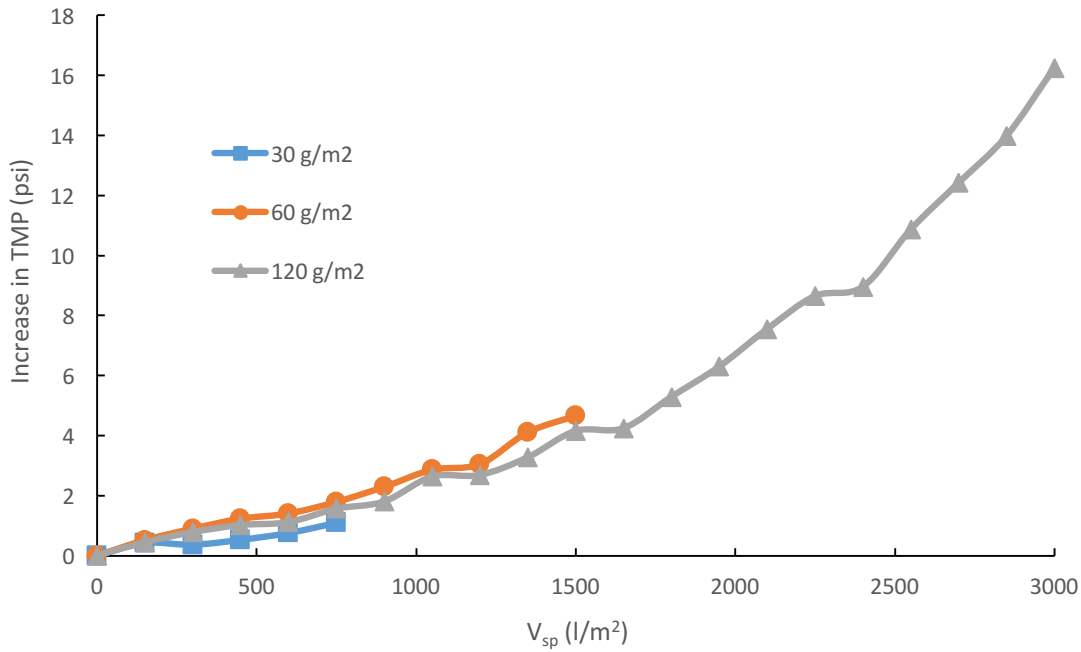


Figure 4-34 Increase in TMP for downstream membrane units fed with composite filtrate from upstream μ GAF units.

4.5.2.2 Effect of SA SUPER surface loading on μ GAF process performance

Experiments similar to those described in the preceding section were conducted with SA SUPER instead of HAOPs as the adsorbent. Analogous to when HAOPs was used, the rate of pressure increase across the three μ GAF units with different surface loadings was very similar (Figure 4.35).

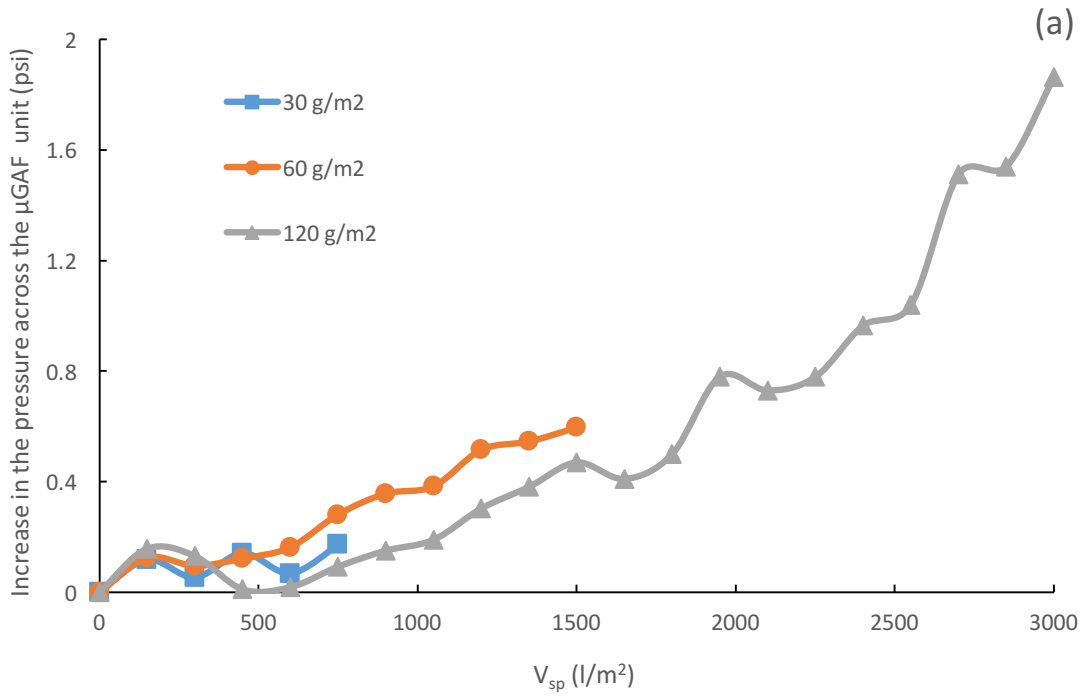


Figure 4-35 Pressure increase profiles of SA SUPER- μ GAF units with different adsorbent surface loading and proportionally different total volume of water treated at a fixed adsorbent effective dose of 40 mg/l.

NOM removal by the μ GAF filtrate increased slightly but steadily with increasing SA SUPER surface loading (Figure 4.36).

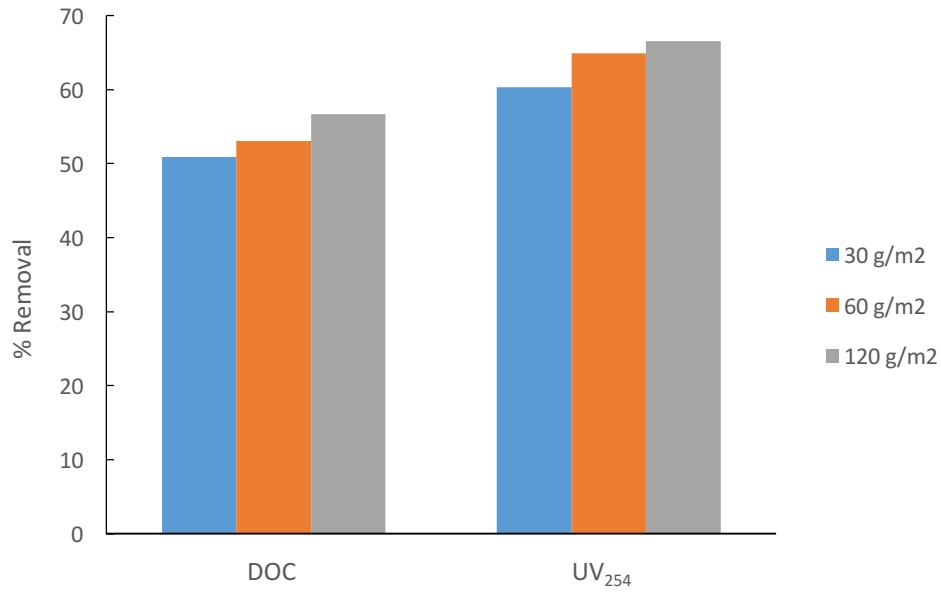


Figure 4-36 Composite filtrate quality of SA SUPER- μ GAF with different adsorbent surface loadings.

SEC analysis of the μ GAF filtrates indicated that increasing the SA SUPER surface loading increased the removal of the biopolymer fraction and, to a lesser extent, the humic substances (Figure 4.37).

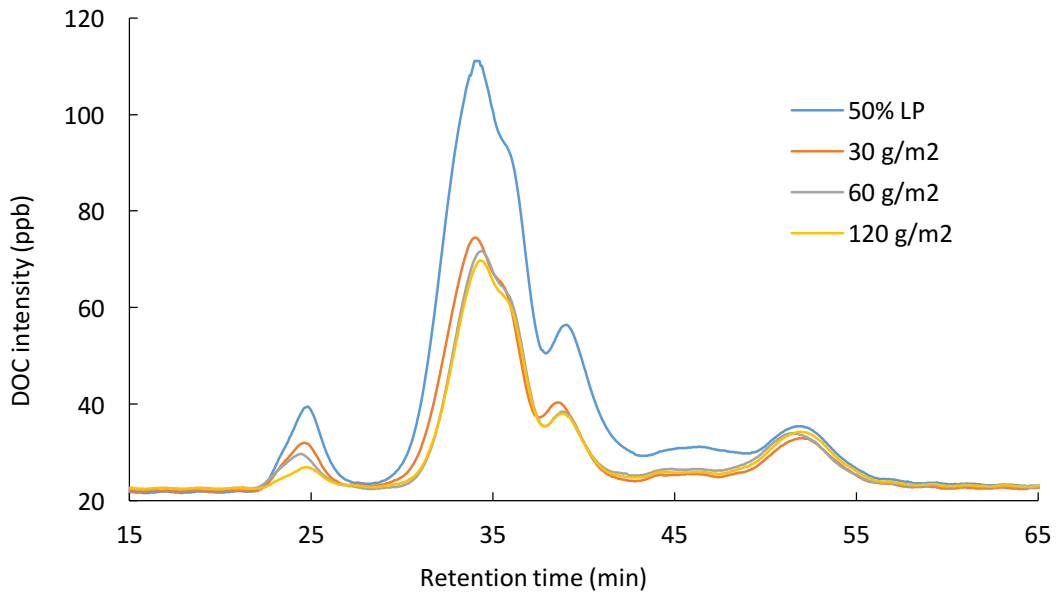


Figure 4-37 SEC chromatograms of composite filtrate of 50% LP water treated with different SA SUPER surface loadings.

When the composite filtrates from the μ GAF units were fed to the downstream membrane, significant differences in membrane fouling were observed (Figure 4.38). At a V_{sp} of 750 LMH, the TMP increase across the membranes downstream of μ GAF units with 30, 60, and 120 g/m^2 of SA SUPER were 5, 2.6, and 1.2 psi, respectively, indicating that more foulant was collected by the SA SUPER layer when the adsorbent surface loading was increased.

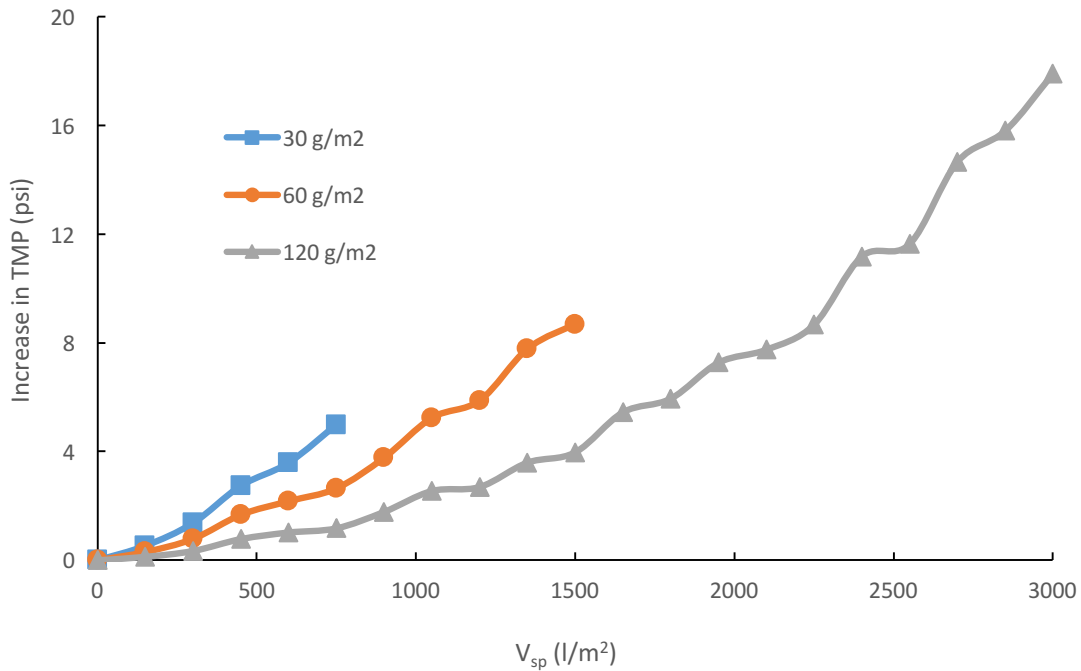


Figure 4-38 Profiles of increase in TMP for downstream membrane units fed with composite filtrate from corresponding upstream μ GAF units.

4.5.3 Effect of flux on μ GAF process performance

Liu (2015) reported that increasing the flux to μ GAF-HAOPs systems from 100 to 400 LMH improved NOM removal efficiency and fouling control of a downstream membrane. Experiments to confirm these results and also to investigate the effect of flux on μ GAF-SA SUPER process performance were conducted using 50% LP water as feed and an adsorbent surface loading of 40 g/m². Fluxes of 400, 250, and 100 LMH were applied to the upstream μ GAF unit. The total volume of treated water was kept the same in all tests by adjusting the duration of each experiment. The composite filtrate from the upstream μ GAF unit was fed to the downstream membrane at a flux of 100 LMH.

4.5.3.1 Effect of flux on HAOPs- μ GAF process performance

Increasing the flux to the μ GAF-HAOPs unit significantly increased the buildup of pressure across the μ GAF unit (Figure 4.39). Liu (2015) suggested that the NOM molecules mainly adsorb on the surface of HAOPs particles throughout the layer and the HAOPs-NOM layer is incompressible. Hence, the higher rate of headloss buildup at higher fluxes could be attributed to the increase in friction of water passing through the HAOPs-NOM layer.

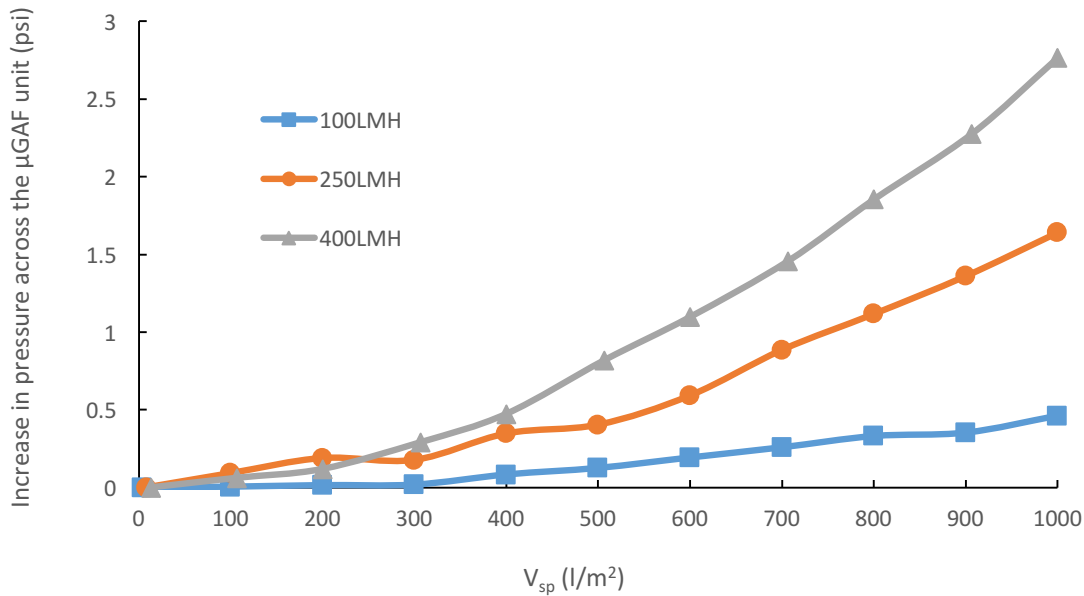


Figure 4-39 Pressure increase profiles of HAOPs- μ GAF units at different fluxes.

Increasing the applied flux to the μ GAF unit had a negligible effect on NOM removal efficiency (Figure 4.40).

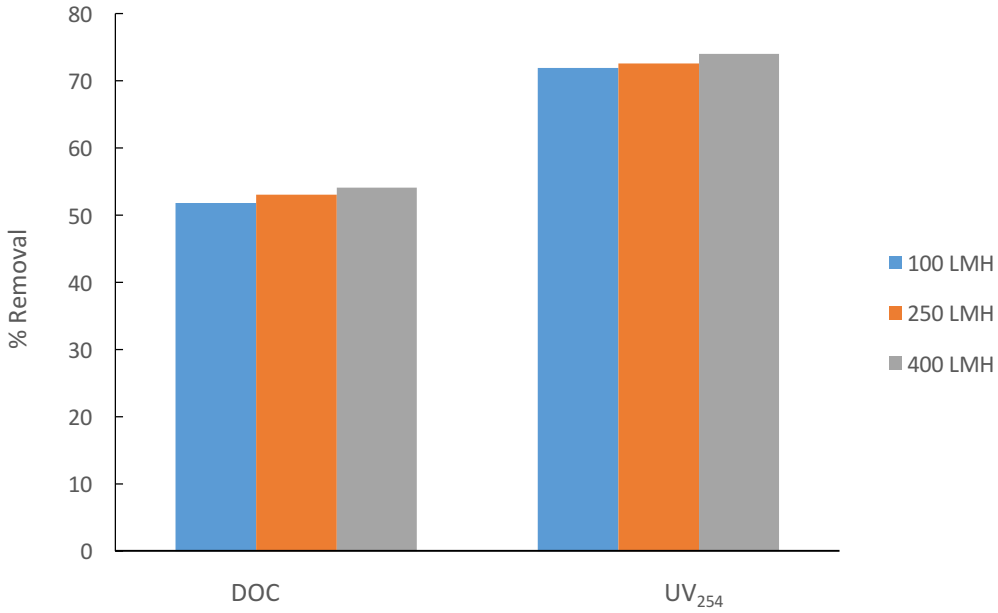


Figure 4-40 HAOPs- μ GAF composite filtrate quality in systems with different fluxes.

When the composite filtrates from the μ GAF unit were fed to membranes, the pressure increase increased with increasing flux in the pretreatment step, but only slightly (Figure 4.41). Thus, although the trend in the TMP profiles was similar to what Liu (2015) found, the magnitude of the effect of pretreatment flux on membrane fouling was much lower.

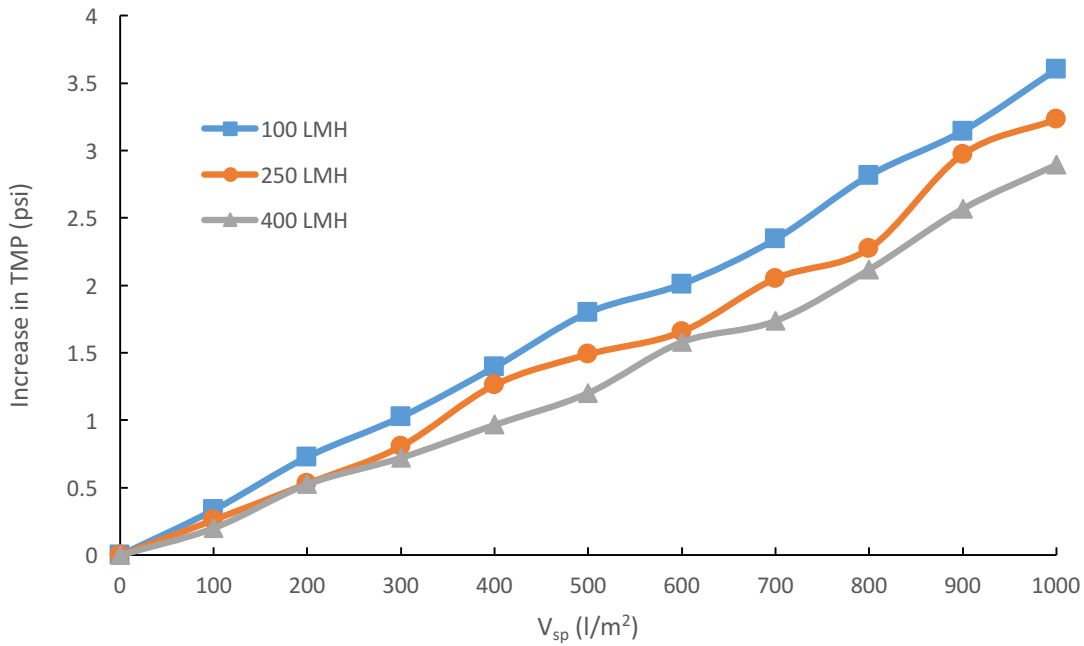


Figure 4-41 Increase in TMP of downstream membranes fed with composite filtrate from corresponding upstream μ GAF units.

4.5.3.2 Effect of flux on SA SUPER- μ GAF process performance

Unlike when HAOPs were used, increasing the flux to the μ GAF unit loaded with SA SUPER did not result in a significant change in the pressure increase (Figure 4.42). This could be due to the higher porosity of the SA SUPER layer due to the larger particle size of SA SUPER compared to HAOPs, mentioned in Table 3.1.

Similar to when HAOPs was used, increasing the applied flux to the μ GAF unit had a negligible effect on NOM removal efficiency with SA SUPER (Figure 4.43) and also on fouling of a downstream membrane (Figure 4.44).

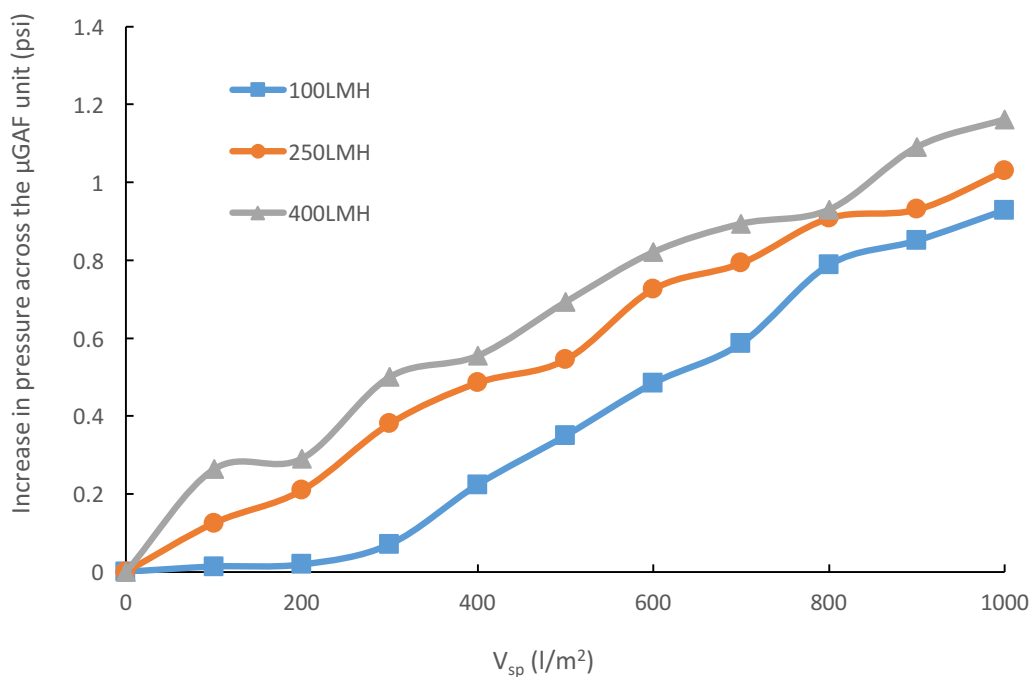


Figure 4-42 Pressure increase profiles of SA SUPER-μGAF units at different fluxes.

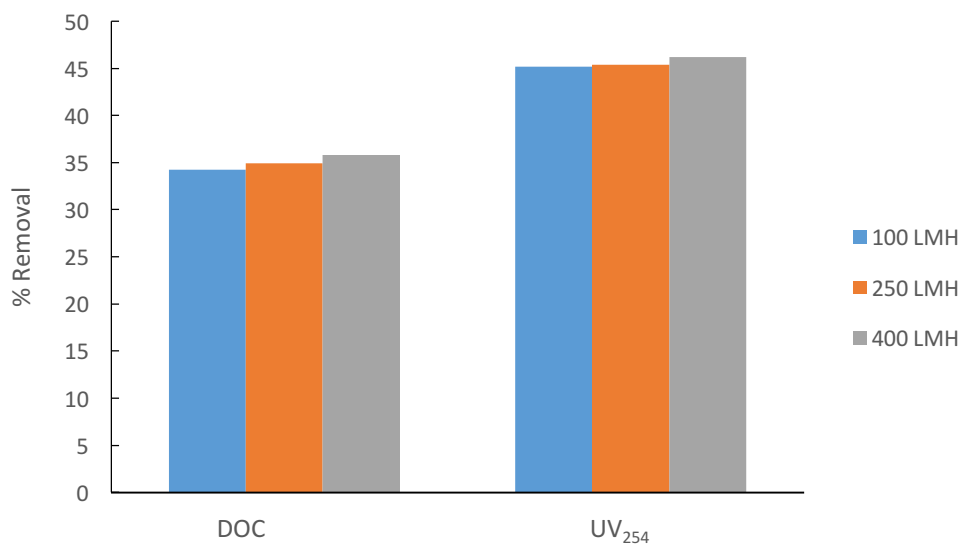


Figure 4-43 SA SUPER-μGAF composite filtrate quality fed with different fluxes.

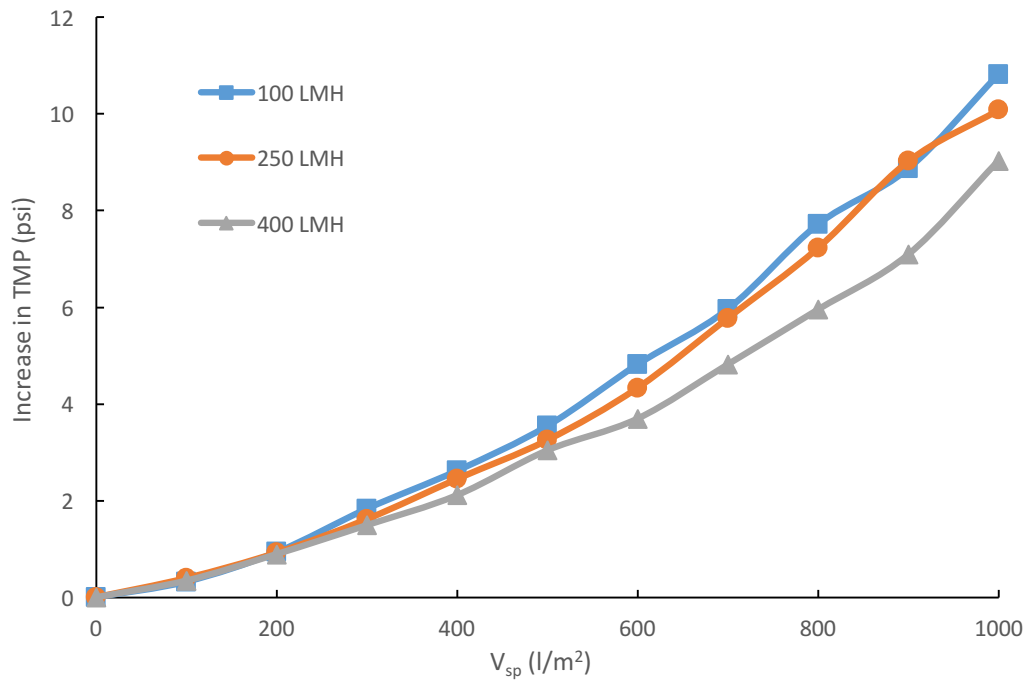


Figure 4-44 Profiles of increase in TMP for downstream membrane units fed with composite filtrate from upstream μ GAF units.

Chapter 5. Summary and conclusions

The goal of this research was to provide a better understanding of the microgranular adsorptive filtration (μ GAF) process and ultimately develop a better NOM pretreatment and membrane fouling control process. The research investigated if PAC can offer the benefits that HAOPs offer in the μ GAF process. It also provided a systematic study of the advantages of the μ GAF process over conventional batch adsorption and investigated combinations of PAC and HAOPs as possible enhancements of NOM pretreatment.

This chapter summarizes the results of the research and proposes efficient process design parameters for μ GAF.

5.1 Summary and conclusions

Different powdered activated carbons behave differently for NOM removal and control of membrane fouling. At low doses, commercially available PAC SA SUPER has a similar NOM removal efficiency to HAOPs. They both outperformed two other tested commercial PACs, WPH and SA UF. SA SUPER and HAOPs had significantly higher adsorption rates than SA UF and WHP even though the latter two adsorbents had lower particle sizes. Pretreatment with SA SUPER or HAOPs in both batch adsorption and μ GAF significantly mitigated fouling of a downstream membrane and were more effective than the other two PACs.

Using a mixture of HAOPs and SA SUPER enhances the NOM removal efficiency. The overall NOM removal efficiency and downstream membrane fouling mitigation are independent of whether HAOPs and SA SUPER are utilized simultaneously or sequentially.

Both adsorbents adsorb some of every NOM fraction, except for low molecular weight neutral NOM molecules that HAOPs are unable to adsorb. SA SUPER is more effective in adsorbing the LMW acids and the biopolymer fraction, whereas HAOPs have higher affinity toward humic substances and building blocks. With a mixture of HAOPs and SA SUPER, NOM with a broad range of molecular sizes can be removed, resulting in an overall NOM removal higher than what is achieved by HAOPs or PAC alone.

Enhancement in removal efficiency is more pronounced at low adsorbent doses where the fractions of the NOM that each adsorbent collects do not significantly overlap. Compared to using HAOPs or SA SUPER alone, a mixture of HAOPs and SA SUPER at a given total dose of adsorbent reduces the DBP formation potential of the water considerably, especially for THMs. It is, hence, possible to reach a given DBP formation potential in the treated water using a lower total amount of adsorbent by using a mixture of HAOPs and SA SUPER.

With an equal amount of adsorbent used in a sequential process of pretreatment-membrane filtration, μ GAF pretreatment leads to dramatically less total headloss than batch pretreatment does, due to enhancement of removal of the HMW NOM, including the biopolymer and humics fractions. This enhancement is more pronounced for HAOPs than SA SUPER.

SA SUPER is more effective than HAOPs in adsorbing fluorescent NOM, whether used in batch adsorption or μ GAF. However, when applied in μ GAF, HAOPs is more effective in capturing membrane foulants. Hence, there is not a reasonable correlation between the removal of fluorescent NOM and capturing dominant foulants of the downstream membrane.

In μ GAF with HAOPs, increasing the adsorbent layer surface area increases the removal of large humic substances. HAOPs have high affinity toward the large UV_{254} absorbing humic substances, and even when the layer's adsorption capacity is used up, some of the adsorbed

building blocks and low-MW acids are released from the HAOPs and instead humic substances are adsorbed. Increasing the HAOPs layer surface area also improves fouling control of the downstream membrane.

For a given adsorbent effective dose, increasing the adsorbent surface loading decreases the NOM removal (mainly humics) in μ GAF with HAOPs, as a result of the decrease in the ratio of the HAOPs layer surface area to the total volume of water treated. Increasing the flux to the unit significantly increases the pressure drop across the μ GAF unit, but it does not significantly affect the removal of NOM or fouling control of the downstream membrane.

Therefore, for a given effective adsorbent dose, it is more efficient to operate μ GAF with a low HAOPs surface loading, resulting in a high ratio of HAOPs layer surface to total volume of water treated. Since increasing the flux to the system does not significantly affect the quality of the treated water or the fouling of the downstream membrane, the rate of headloss buildup on the pretreatment unit would be the limiting factor for increasing the flux.

For μ GAF with SA SUPER, removal of NOM (mainly the biopolymer fraction) and fouling control of the downstream membrane are directly correlated to the adsorbent surface loading. On the other hand, increasing the flux to the unit does not affect either NOM removal or headloss buildup on the μ GAF unit. Hence, to run a SA SUPER- μ GAF pretreatment system, it is better to increase the surface loading and increase the flux (increase the process throughput) as high as possible.

References

Allpike, B. P., Heitz, A., Joll, C. A., Kagi, R. I., Braunand, G. A., Frimmel, F. H., Brinkmann, T., Her, N., Amy, G., 2005. Size exclusion chromatography to characterize DOC removal in drinking water treatment, *Environ. Sci. Technol.* 39, 2334-2342

Allpike, B.P., Heitz, A., Joll, C.A., Kagi, R.I., 2007. A new organic carbon detector for size exclusion chromatography. *J. Chromatogr. A* 1157, 472–476

Amy, G., 2008. Fundamental understanding of organic matter fouling of membranes, *Desalination* 231, 44–51

Amy, G. and Cho, J., 1999. Interactions between natural organic matter (NOM) and membranes: rejection and fouling. *Water Sci. Technol.* 40 (9), 131–139

Ando, N., Matsui, Y., Kurotobi, R., Nakano, Y., Matsushita, T., Ohno, K. 2010. Comparison of natural organic matter adsorption capacities of super-powdered activated carbon and powdered activated Carbon, *Water Res.* 44, 4127-4136

Andrzejewski, P., Kasprzyk-Hordern, B., Nawrocki, J., 2005. The hazard of N-nitrosodimethylamine (NDMA) formation during water disinfection with strong oxidants. *Desalination* 176 (1-3), 37–45

Baghoth, S.A., Sharma, S.K., Amy, G.L., 2011. Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation-emission matrices and PARAFAC, *Water Res.* 45, 797-809

Belfort, G., Davis, R. H., Zydney, A. L., 1994. The behavior of suspensions and macromolecular solutions in crossflow microfiltration, *J. Membr. Sci.*, 96 (1) 1–58

Bond, T., Goslan, E.H., Parsons, S.A., Jefferson, B., 2010. Disinfection by-product formation of natural organic matter surrogates and treatment by coagulation, MIEX[®] and nanofiltration, *Water Res.* 44 1645-1653

Cai, Z., Kim, J., Benjamin, M. M., 2008. NOM Removal by Adsorption and Membrane Filtration Using Heated Aluminum Oxide Particles, *Environ. Sci. Technol.* 42, 619–623

Cai, Z., 2011. Investigation of microgranular adsorptive filtration system, University of Washington, USA

Carrière, A., Vachon, M., Bélisle, J.-L., Barbeau, B., 2009. Supplementing coagulation with powdered activated carbon as a control strategy for trihalomethanes: application to an existing utility. *J. Water Supply Res. Technol.* 58, 363–371

Chen, W., Westerhoff, P., Leenheer, J. A., Booksh, K., 2003. Fluorescence Excitation-Emission Matrix Regional Integration to Quantify Spectra for Dissolved Organic Matter, *Environ. Sci. Technol.* 37, 5701-5710

Chen, Z., Valentine, R.L., 2007. Formation of Nnitrosodimethylamine (NDMA) from humic substances in natural water. *Environ. Sci. Technol.* 41 (17), 6059-6065

Choo, K.-H., Park, I.-H., Choi, S.-J., 2004. Removal of natural organic matter using iron oxide-coated membrane systems. *Wa. Sci. Technol: water supply*, 4, (5-6), 7

Croué, J.-P.; Debroux, J.-F.; Amy, G. L.; Aiken, G. R.; Leenheer, J. A. Natural Organic Matter: Structural Characteristics and Reactive Properties. In *Formation and Control of Disinfection By-Products in Drinking Water*; Singer, P., Ed., AWWA: Denver, CO, 1999, 65–93.

Croué, J.-P., Korshin, G.V., Benjamin, M.M., 2000. Characterization of Natural Organic Matter in Drinking Water. AWWARF, Denver, CO

Edzwald, J.K., Tobiason, J.E., 1999. Enhanced coagulation: USA requirements and a broader view. *Water Sci. Technol.* 40 (9), 63–70

Fan, L., Harris, J.L., Roddick, F.A., Booker, N.A., 2001. Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes. *Water Res.* 35, 4455–4463

Gan, X., Karanfil, T., Bekaroglu, S. S. K., Shan, J., 2013. The control of N-DBP and C-DBP precursors with MIEX[®], *Water Res.*, 47, 1344-1352

Gao, W., Liang, H., Ma, J., Han, M., Chen, Z., Han, Z-S., Li, G-B., 2011. Membrane fouling control in ultrafiltration technology for drinking water production: A review, *Desalination* 272, 1–8

Guo, W., Ngo, H., Li, J., 2012, A mini-review on membrane fouling, *Bioresource Technol.* 122, 27–34

Halle, C., Huck, P.M., Peldszus, S., Haberkamp, J., Jekel, M., 2009. Assessing the performance of biological filtration as pretreatment to low pressure membranes for drinking water, *Environ. Sci. Technol.* 43 (10), 3878-3884

Haberkamp, J., Ruhl, A. S., Ernst, M., Jekel, M., 2007. Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behavior in ultrafiltration, *Water Res.* 41, 3794-3802

Her, N., Amy, G., Foss, D., Cho, J., 2002. Variations of molecular weight estimation by HP-size exclusion chromatography with UVA versus online DOC detection, *Environ. Sci. Technol.* 36, 3393-3399

Ho, L., Hainthaler, M., Newcombe, G., 2013. Using UV spectroscopy and molecular weight determinations to investigate the effect of various water treatment processes on NOM removal:

Australian case study, *J. Environ. Eng.* 139, 117-126

Howell, J. A., 1995. Sub-critical flux operation of microfiltration, *J. Membr. Sci.*, 107 (1) 165–171

Hua, G., Reckhow, D. A., 2007. Characterization of disinfection by-product precursors based on hydrophobicity and molecular size, *Environ. Sci. Technol.* 41, 3309-3315

Jermann, D., Pronk, W., Meylan, S., Boller, M., 2007. Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production, *Water Res.* 41, 1713-1722

Jones, K., O'Melia, C., 2000. Protein and humic acid adsorption onto hydrophilic membrane surface: effects of pH and ionic strength, *J. Membr. Sci.* 165, 31–46

Jones, K., O'Melia, C., 2001. Ultrafiltration of protein and humic substances: effect of solution chemistry on fouling and flux decline, *J. Membr. Sci.* 193, 163–173

Kim, J., Cai, Z., Benjamin, M. M., 2008. Effects of adsorbents on membrane fouling by natural organic matter, *J. Membr. Sci.* 310, 356-364

Kim, J., Cai, Z., Benjamin, M. M., 2010. NOM fouling mechanisms in a hybrid adsorption/membrane system, *J. Membr. Sci.* 349, 35-43

Kimura, K., Tanaka, K., Watanabe, Y., 2014. Microfiltration of different surface waters with/without coagulation: Clear correlations between membrane fouling and hydrophilic biopolymers, *Water Res.* 49, 434-443

Kitis, M., Karanfil, T., Wigton, A., Kilduff, J., E., 2002. Probing reactivity of dissolved organic matter for disinfection by-product formation using XAD-8 resin adsorption and ultrafiltration fractionation, *Water Res.* 36, 3834–3848

Korshin, G. V., Benjamin, M. M., Chang, H. -S., 2004. Modeling DBP formation kinetics: Mechanistics and spectroscopic approaches, Report no. 91000, Am. Water Works Assoc. Research Foundation, USA

Korshin, G., Chow, C.W.K., Fabris, R., Drikas, M., 2009. Absorbance spectroscopy based examination of effects of coagulation on the reactivity of fractions of natural organic matter with varying apparent molecular weights, *Water Res.* 43, 1541–1548

Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Scilimenti, M.J., Onstad, G.D., Thruston Jr., A.D., 2006. Occurrence of a new generation of disinfection byproducts. *Environ. Sci. Technol.* 40 (23), 7175–7185

Kristiana, I., Joll, C., Heitz, A., 2011. Powdered activated carbon coupled with enhanced coagulation for natural organic matter removal and disinfection by-product control: Application in a Western Australian water treatment plant, *Chemosphere* 83, 661–667

Kristiana, I., Tan, J., Joll, C. A., Heitz, A., Gunten, U., Charrois, J. W. A., 2013. Formation of N-nitrosamines from chlorination and chloramination of molecular weight fractions of natural organic matter, *Water Res.* 47, 535-546

Kweon, J. H., Hur, H. W., Seo, G-T., Jang, T-R., Park, J-H., Choi, K. Y., Kim, H. S., 2009. Evaluation of coagulation and PAC adsorption pretreatments on membrane filtration for a surface water in Korea: A pilot study, *Desalination*, 249, 212-216

Lee, E.K., Chen, V., Fane, A.G., 2008. Natural organic matter (NOM) fouling in low-pressure membrane filtration – effect of membranes and operation modes, *Desalination* 218, 257–270

Lee, K.-W.; Choo, K.-H.; Choi, S.-J.; Yamamoto, K., 2002. Development of an integrated iron oxide adsorption/membrane separation system for water treatment, *Wa. Sci. Technol. Wa. Supp.* 2, (5-6), 8

Choo, K.-H.; Park, I.-H.; Choi, S.-J., 2004. Removal of natural organic matter using iron oxide-coated membrane systems, *Wa. Sci. Technol. Wa. Supp.* 4, (5-6), 7

Leenheer, J.A., 1981. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environ. Sci. Technol.* 15 (5), 578–587

Leenheer, J. A., Croué, J. –P., 2003. Characterizing Aquatic Dissolved Organic Matter. Understanding the unknown structures is key to better treatment of drinking water, *Environ. Sci. Technol.*, 2003, 37 (1), 18A–26A

Leenheer, J.A., 2009. Systematic approaches to comprehensive analyses of natural organic matter. *Ann. Environ. Sci.* 3, 1-130

Li, Q., Elimelech, M., 2004. Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms. *Environ. Sci. Technol.* 38 (17), 4683–4693

Liang, L.; Singer, P. C., 2003. Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. *Environ. Sci. Technol.* 37 (13), 2920-2928

Lin, C.F., Lin, T.Y., Hao, O.J., 2000, Effects of humic substance characteristics on UF performance. *Water Res.* 34 (4), 1097–1106

Liu, J., 2015. Evaluation of Effect of Operational Parameters on Microgranular Adsorptive Filtration (μ GAF). University of Washington, USA

Matilainen, A., Vepsäläinen, M., Sillanpää, M., 2010. Natural organic matter removal by coagulation during drinking water treatment: A review, *Adv. Colloid. Interf. Sci.*, 159, 189-197

Matilainen, A., Gjessing, E. T., Lahtinen, T., Hed, L., Bhatnagar A., Sillanpää, M., 2011. An overview of the methods used in the characterisation of natural organic matter (NOM) in relation

to drinking water treatment, *Chemosphere*. 83, 1431–1442

Matsui, Y., Hasegawa, H., Ohno, K., Matsushita, T., Mima, S., Kawase, Y., Aizawa, T., 2009. Effects of super-powdered activated carbon pretreatment on coagulation and trans-membrane pressure buildup during microfiltration, *Water Res.*, 43, 5160-5170

Miyoshi, T., Yuasa, K., Ishigami, T., Rajabzadeh, S., Kamio, E., Ohmukai, Y., Saeki, D., Ni, J., Matsuyama, H., 2015. Effect of membrane polymeric materials on relationship between surface pore size and membrane fouling in membrane bioreactors, *Appl. Surf. Sci.* 330, 351–357

Najm, I., Tate, C., Selby, D., 1998. Optimizing enhanced coagulation with PAC: A case study, *J. Am Water Works Assoc.* 90 (10) 88-95

Najm, I. N., Snoeyink, V. L., Suidan, M. T., Lee, C. H., Richard, R., 1990. Effect of Particle Size and Background Natural Organics on the Adsorption Efficiency of PAC, *J. Am. Water Works Assoc.* 82 (1) 65-72

Peiris, R.H., Hallé, C., Budman, H., Moresoli, C., Peldszus, S., Huck, P.M., Legge, R.L., 2010. Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation–emission matrices. *Water Res.* 44, 185–194

Peldszus, S., Halle', C., Peiris, R. H., Hamouda, M., Jin, X., Legge, R. L., Budman, H., Moresoli, C., Huck, P. M., 2011. Reversible and irreversible low-pressure membrane foulants in drinking water treatment: Identification by principal component analysis of fluorescence EEM and mitigation by biofiltration pretreatment. *Water Res.* 45, 5161-5170

Pelekani, C., Newcombe, G., Snoeyink, V., Hepplewhite, C., Aeemi, S., Beckett, R., 1999. Characterization of natural organic matter using high performance size exclusion chromatography, *Environ. Sci. Technol.* 33, 2807-2813

Perdue, E. M., 2009. “Natural organic matter” *Encyclopedia of inland water*, G. E. Likens, ed., Elsevier, Amsterdam, Netherlands, 806–819

Piccolo, A., 2001. The supermolecular structure of humic substances, *Soil Sci.* 166 (11), 810-832

Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., DeMarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. *Mutat. Res.* 636, 178-242

Şakol, D., and Konieczny, K., 2004. Application of coagulation and conventional filtration in raw water pretreatment before microfiltration membranes, *Desalination*, 162, 61–73

Sarathy, S.R., Mohseni, M., 2007. The impact of UV/H₂O₂ advanced oxidation on molecular size distribution of chromophoric natural organic matter. *Environ. Sci. Technol.* 41, 8315–8320

Shao, S., Liang, H., Qu, F., Yu, H., Li, K., Li, G., 2014. Fluorescent natural organic matter fractions responsible for ultrafiltration membrane fouling: Identification by adsorption pretreatment coupled with parallel factor analysis of excitation–emission matrices, *J. Membr. Sci.*, 464, 33-42

Skjelkvaale, B.L., 2003. The 15-year report: Assessment and monitoring of surface waters in Europe and North America; acidification and recovery, dynamic modeling and heavy metals. ICP-Waters report 73/2003. Norwegian Institute for Water Research

Song, H., Orr, O., Hong, Y., Karanfil, T., 2009. Isolation and fractionation of natural organic matter: evaluation of reverse osmosis performance and impact of fractionation parameters. *Environ. Monit. Assess.* 153, 307–321

Tranvik, L. J., Wachenfeldt, E. V., 2009. “Interactions of dissolved organic matter and humic substances” *Encyclopedia of inland water*, G. E. Likens, ed., Elsevier, Amsterdam, Netherlands, 754-760

Thurman, E.M., Malcolm, R.L., 1981. Preparative isolation of aquatic humic substances. *Environ. Sci. Technol.* 15, 463–466

U.S. Environmental Protection Agency (EPA), INITIAL DISTRIBUTION SYSTEM EVALUATION GUIDANCE MANUAL- Guidance Manual for the Final Stage 2 DISINFECTANTS AND DISINFECTION BYPRODUCTS RULE-Appendix A, January 2006

U.S. Environmental Protection Agency (EPA), Basic Information about Disinfection By-products in Drinking Water. <http://water.epa.gov/drink/contaminants/basicinformation/disinfectionbyproducts.cfm> (accessed Dec 10, 2014)

Uyak, V., Yavuz, S., Toroz, I., Ozaydin, S., Genceli, E. A., 2007. Disinfection by-products precursors removal by enhanced coagulation and PAC adsorption, *Desalination*, 216, 334–344

World Health Organization (WHO), Progress on drinking water and sanitation-Joint Monitoring Programme update 2014

Yamamura, H., Okimoto, K., Kimura, K., Watanabe, Y., 2014. Hydrophilic fraction of natural organic matter causing irreversible fouling of microfiltration and ultrafiltration membranes, *Water Res.* 54 123-136

Yamamura, H., Kimura, K., Watanabe, Y., 2007. Mechanism involved in the evolution of physically irreversible fouling in microfiltration and ultrafiltration membranes used for drinking water treatment. *Environ. Sci. Technol.* 41 (19), 6789-6794

Yu, W., Xu, L., Qu, J., Graham, N., 2014. Investigation of pre-coagulation and powder activate carbon adsorption on ultrafiltration membrane fouling, *J. Membr. Sci.*, 459, 157–168

Yuan, W., and Zydney, A., L., 1999, Humic acid fouling during microfiltration, *J. Membr. Sci.* 157 (1) 1–12

Yuan, W., and Zydney, A., L., 2000, Humic acid fouling during ultrafiltration, Environ. Sci. Technol., 34 (23) 5043–5050

Zhang, M., Li, C., Benjamin, M. M., Chang, Y., 2003, Fouling and natural organic matter removal in adsorbent/membrane systems for drinking water treatment, Environ. Sci. Technol. 37, 1663-1669

Zhou, Q., Cabaniss, S. E., Maurice, P. A., 2000. Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances, Water Res. 34, 3505-3510

Vita

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