



A multi-spectral approach to differentiate the effects of adsorbent pretreatments on the characteristics of NOM and membrane fouling



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ABSTRACT

Pretreatment of feed water is widely applied to mitigate NOM-induced fouling of low-pressure membranes. This research investigated the effectiveness of two pretreatment modes for NOM removal by heated aluminum oxide particles (HAOPs) and the associated reductions in membrane fouling and trihalomethane (THM) formation potential. One mode, referred to here as pre-adsorption, is the conventional process in which adsorbent particles are added to and thoroughly mixed with the feed, after which the particles are separated from the water either upstream of or by the membrane. By contrast, in the pre-deposition mode, a thin layer of adsorbent particles is deposited on a support media (which could be the membrane) prior to passing feed through the layer and the membrane.

Although both pretreatment methods remove similar amounts of DOC at the same adsorbent dose, pre-deposition is superior with respect to mitigating membrane fouling and reducing DBP formation. UV and fluorescence spectroscopy and HPSEC analysis indicate that a pre-deposited adsorbent layer removes more chromophores and low apparent molecular weight (AMW) material than pre-adsorption does. Based on absorbance ratios at selected wavelengths, a pre-deposited HAOPs layer removes more aromatic moieties than aliphatic carboxyls, especially at higher HAOPs doses. In addition, pre-deposition is more effective than pre-adsorption at reducing the THM formation potential. The results provide new insights into the interactions between HAOPs and NOM molecules and shed light on the significantly different effects of different adsorbent contacting modes on the fouling potential of the pretreated water.

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1. Introduction

Low-pressure membrane (LPM) filtration has emerged as a reliable process for producing high-quality drinking water from surface water sources at relatively low cost (Huang et al., 2009; Shannon et al., 2008; Wiesner and Chellam, 1999). However, membrane fouling, much of it attributable to natural organic matter (NOM), presents a significant impediment to the application and improved performance of these processes (Cho et al., 2000; Fan et al., 2001; Lee et al., 2004). Pretreatment of feedwater prior to LPM filtration can improve the water quality and reduce both its fouling potential and the potential for subsequent formation of disinfection byproducts (DBPs) (Farahbakhsh et al., 2004; Huang et al., 2009).

Numerous conventional physical and chemical treatment

methods, including filtration, clarification, sedimentation, flotation, coagulation, adsorption, softening, and pre-oxidation, have been applied to alleviate NOM-induced fouling. Coagulation of feedwater with polyelectrolytes (e.g., Al^{3+} and Fe^{3+} or polyaluminum chloride [PAC]) can remove a substantial fraction of the NOM from the feed (Howe et al., 2006; Lee et al., 2000; Lin et al., 1999; Yan et al., 2008), but deposition of metal-NOM complexes on the membrane can be problematic, and the hydrous, compressible chemical sludge produced during treatment can lead to secondary problems (Maartens et al., 1999; Yan et al., 2008). To minimize these problems, rigid adsorbents with low solubility, such as powdered activated carbon (PAC) (Stoquart et al., 2012), silica particles and polysulfone colloids (Koh et al., 2006), have sometimes been applied in place of conventional coagulants.

Although powdered adsorbents invariably remove some NOM, their effectiveness at controlling fouling seems to depend at least partially on the manner in which they are contacted with the feed solution (Li and Chen, 2004; Kang and Choo, 2010; Kim et al., 2008; Zhang et al., 2003). These adsorbents can be dosed into the feed to

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generate a dilute suspension (a process we refer to as pre-adsorption) or, if they are not highly compressible, they can be packed into a layer (e.g., in a fixed-bed contactor) through which the feed passes. In a few laboratory-scale tests, pre-deposition of a thin layer of adsorbent directly on a membrane (micro-granular adsorptive filtration, μ GAF) reduced fouling of the membrane much more effectively than pre-adsorption did (Choo et al., 2004; Kim et al., 2008; Zhang et al., 2003). Our group has reported such a result using a pre-deposited layer of micron-sized heated aluminum oxide particles (HAOPs), even though the dissolved organic carbon (DOC) removed by the pre-treatment steps, and therefore the amount reaching the membrane in the two systems, was almost identical (Kim et al., 2008; Cai et al., 2008). We have also reported excellent reduction in fouling potential if the feed is passed through a pre-deposited layer of HAOPs upstream of and separate from the membrane (Kim et al., 2008; Cai et al., 2008; Cai and Benjamin, 2011; Cai et al., 2013).

The different fouling potentials of water that has been pre-treated by pre-deposition vs. pre-adsorption suggest that some foulants that are not adsorbed in well-mixed suspensions can be removed when the feed passes through a pre-deposited adsorbent layer. The identities of these foulants and the mechanisms leading to their removal are not clear. In addition to their effects on fouling potential, the two pre-treatment modes could affect other water quality parameters, including the potential for formation of disinfection byproducts (Farahbakhsh et al., 2004; Huang et al., 2009).

This work explored the interactions of NOM with HAOPs in both contacting modes and the consequent effects on fouling of an ultrafiltration membrane. Various chemical properties (e.g., aromaticity, fluorescence, molecular weight distribution, DBP formation potentials) of the treated waters were examined to better understand how the different pretreatments alter the characteristics and reactivity of NOM.

2. Materials and methods

2.1. Source water, HAOPs and membrane

Feed water was collected from Lake Pleasant in Bothell, WA (47°46'44.59" N, 122°13'3.51" W) and was filtered through a 5- μ m filter prior to use. The conductivity, pH and dissolved organic carbon (DOC) concentration were \sim 1.12 mS/cm, 7.2–7.6 and 19.8 ± 3.5 mg-C/L, respectively, and the turbidity of the pre-filtered water was 3.2 NTU. Concentrations of some key inorganic ions in the diluted lake water are presented in Table 1. The raw water was diluted 1:2 with deionized (DI) water before use in experiments. The UV absorbance of feed water at 254 nm (UV₂₅₄) was 0.204 ± 0.045 cm⁻¹. The feed water was adjusted to pH 7.0 ± 0.2 in all the tests. HAOPs were synthesized by heating precipitated Al(OH)₃, following the procedure of Cai et al. (2008). Membranes used in the tests were 47-mm-diameter polyethersulfone (PES) disks with a nominal pore size of 0.05 μ m (Microdyn-Nadir MP005) and a water contact angle of 48.5° (Kaya et al., 2016).

2.2. Pretreatment of feed water and membrane filtration

The effectiveness of HAOPs at removing NOM in well-mixed batch systems was investigated at adsorbent doses from 0 to 100 mg Al/L. For these tests, HAOPs were added into 100 mL of feed

water, and the solution was mixed on a rotary shaker operating at 200 rpm for 3 h, after which the solids were removed by a syringe filter (0.45- μ m) for subsequent chemical analysis of the water.

To study the effect of pre-adsorption on membrane fouling, feed water was dosed with 5 mg Al/L HAOPs and mixed for 2 h. The HAOPs and associated NOM were then separated from the solution using a nylon mesh with 5- μ m openings (Product 03-5/1, SEFAR Inc., USA), and the solution was fed to the membrane.

In experiments investigating HAOPs pre-deposition, a stock suspension containing 10 mg HAOPs (as Al) was applied to a 47-mm-diameter flat sheet of nylon mesh held in a standard filter cartridge. Feed was pumped through the HAOPs layer at a constant flux of 100 L/m²-h (LMH). The pretreated water was captured in a reservoir from which small-volume samples were collected intermittently for chemical analysis. The data from these analyses were compared to data from the pre-adsorption experiments based on the "effective HAOPs dose" in the pre-deposition experiment (the mass of HAOPs in the system [10 mg as Al] divided by the cumulative volume of water treated at the time the sample was collected). After 2 L of water had been treated, the composite, pretreated solution was applied to a UF membrane to assess the fouling potential of the water. The effective HAOPs dose at this point was 5 mg Al/L, identical to the dose used in the pre-adsorption experiments. A control test was conducted in which diluted lake water was fed to a UF membrane without any pretreatment.

In all membrane filtration tests, a new PES membrane was placed in a polycarbonate in-line filter holder and was conditioned by filtration of DI water for 30 min before the test feed was applied using dead-end filtration at a constant flux of 100 LMH. The transmembrane pressure (TMP) was measured online with a pressure transducer and recorded via a data acquisition system (34970A, Agilent Technologies, Santa Clara, CA).

2.3. Chemical analyses

UV absorbance spectra were recorded using a Shimadzu UV-2700 UV/vis spectrophotometer at wavelengths from 200 to 350 nm, and DOC was measured with a Shimadzu TOC-VCSH analyzer. Excitation-emission matrix (EEM) fluorescence spectra were obtained using a luminescence spectrometer (LS-55, Perkin-Elmer Co., USA) over excitation wavelengths (Ex) from 200 to 450 nm and emission wavelengths (Em) from 300 to 600 nm. The spectra of DI water was recorded as the blank and subtracted from the EEM spectra of samples. The EEM data close to the Rayleigh scattering line were set to zero to eliminate the corresponding interference (Li et al., 2011; Rinnan et al., 2005). The EEM data were processed using parallel factor (PARAFAC) analysis to isolate the contributions of different groups of fluorophores to the EEM spectra. The N-way Toolbox in Matlab 6.5 (MathWorks Inc., USA, <http://www.models.kvl.dk>) was employed for this purpose.

HPSEC measurements employed a DIONEX Ultimate 3000 HPLC system equipped with Ultimate 3000 diode array detector to acquire absorbance data from 200 to 280 nm at 1-nm resolution. NH₄HCO₃ at a concentration of 0.01 M was delivered through a TOSOH TSKgel G3000PW_{XL} column at 0.5 mL/min. AMW values were obtained via calibration with polystyrene sulfonate (PSS) molecular weight standards of 16, 8, 5 and 1.6 kDa (Scientific Polymer Products, Inc.) (Figure S1-1).

Untreated water and some treated samples were selected for analysis of THM formation potential. For these tests, 20 mg/L Cl₂ was added to 130 mL of sample in a brown glass headspace-free bottle, and the solution was incubated for 24 h at room temperature (20 °C). The residual chlorine after 24 h was determined by the DPD ferrous titrimetric method (4500-Cl F, APHA, 1998), and the Cl₂

Table 1
Concentrations of major inorganic ions in 1:2 diluted Lake Pleasant water.

	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
Concentrations (mg/L)	6.61	2.74	2.34	0.89	1.69	2.02	0.61

demand was calculated by difference. The residual chlorine was quenched with excess ammonium chloride. THM concentrations were determined by liquid-liquid extraction and gas chromatography with electron capture detection (USEPA Methods 551.1). Each sample was analyzed in duplicate; deviations between the duplicates were ~5%.

3. Results and discussion

3.1. Fouling of ultrafiltration membrane fed with pretreated water

Fig. 1 characterizes the TMP buildup across the UF membrane fed HAOPs-pretreated water using both the pre-adsorption and pre-deposition contacting modes, as well as in a HAOPs-free control system. The abscissa in these figures is the specific volume filtered (V_{sp}), defined as the volume of permeate produced per unit area of membrane. Both pretreatments mitigated membrane fouling, but the reduction in fouling was much greater in the system with pre-deposited HAOPs, even though the effective HAOPs dose was the same (5 mg Al/L) in both systems. For instance, the V_{sp} at which the TMP rose by 50 kPa above the initial value was approximately 600, 700, and 1400 L/m² in the control, pre-adsorption, and pre-deposition systems, respectively.

3.2. DOC and UV removal by pretreatment

The absorption spectra of feed water and treated water are shown in Figure SI-2. A broad peak near $\lambda \sim 250$ nm, reflecting the aromatic moieties in NOM, was present in all the spectra, with steadily diminishing intensity as the HAOPs dose increased. Non-aromatic groups are thought to contribute absorbance at shorter wavelengths (typically, near 210 nm) from $n-\pi^*$ transitions in carboxylic acids/esters and amides (Her et al., 2008; Korshin et al., 1997; Vance and David, 1991). However, as is typical, no distinct peak was observed in this region of the spectra.

DOC concentrations and UV absorbance at two wavelengths for the same samples are shown in Fig. 2, with additional detail provided in Table SI-1. DOC removal was similar for the two contacting modes, increasing steadily with increasing HAOPs dose up to 50–55% removal at a dose of 20 mg/L as Al; no additional removal was achieved at higher doses. UV₂₅₄ was removed more efficiently than DOC at all HAOPs doses using both pretreatment approaches. The same trend is commonly observed for coagulation in

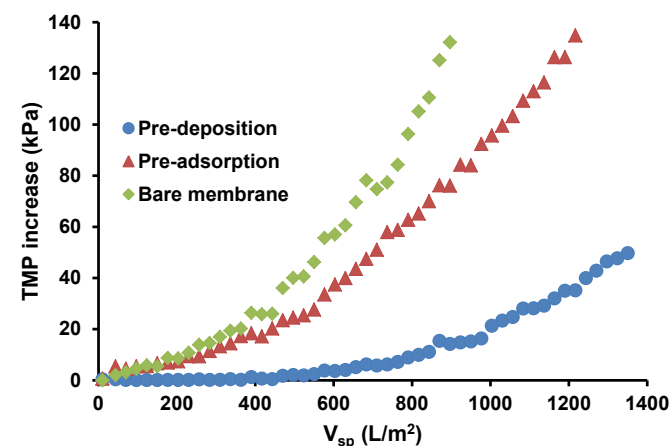


Fig. 1. Membrane fouling using diluted Lake Pleasant water or the same water pre-treated with HAOPs in a pre-adsorption or pre-deposition process. HAOPs dose was 5 mg Al/L throughout for pre-adsorption, and 5 mg Al/L as an equivalent dose at the end of the test for pre-deposition. Flux = 100 LMH.

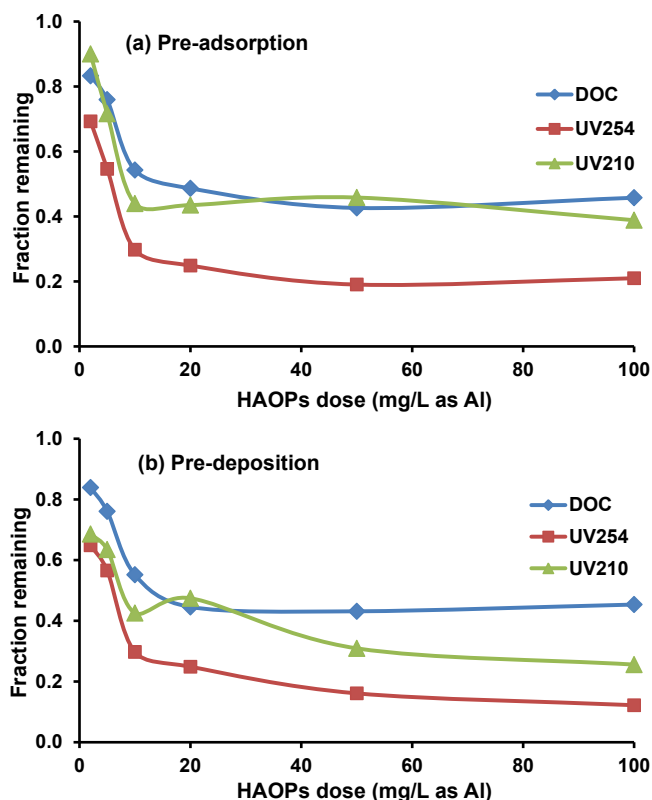


Fig. 2. DOC, UV₂₅₄ and UV₂₁₀ remaining in permeates from (a) pre-adsorption and (b) pre-deposition modes as a function of HAOPs dose.

conventional water treatment systems and is attributed to selectivity of the adsorbent for aromatic NOM.

Removal of UV₂₁₀ closely tracked that of DOC in the pre-adsorption experiments, suggesting that aliphatic carboxyl groups are approximately uniformly distributed on adsorbable NOM molecules. That is, while such groups might play an important role in adsorption, their density in the molecules (number of carboxyl groups per mg DOC) is apparently about the same in adsorbed and non-adsorbed molecules. By contrast, UV₂₁₀ was removed more effectively than DOC (but less effectively than UV₂₅₄) in the pre-deposition experiments, indicating that the molecules removed in those experiments were enriched in UV₂₁₀ relative to DOC.

The SUVA₂₅₄ and SUVA₂₁₀ values for the pretreated waters are shown in Fig. 3. SUVA₂₅₄ declined steadily with increasing HAOPs dose. At doses of 50 and 100 mg/L as Al, pre-deposition induced a sharper decline in SUVA₂₅₄ than pre-adsorption did, indicating that pre-deposition removed aromatic moieties more effectively under those conditions. However, at lower adsorbent doses, the two contacting modes reduced SUVA₂₅₄ approximately equally. SUVA₂₁₀ declined less than SUVA₂₅₄ did and declined more in pre-deposition than in pre-adsorption experiments. In fact, SUVA₂₁₀ barely declined at all in the latter systems, consistent with the prior inference that aliphatic carboxylic groups are present at approximately equal densities on molecules that adsorb and those that do not adsorb in pre-adsorption systems.

3.3. Fluorophore removal by pretreatment

Fig. 4 shows the EEM spectra of untreated and pretreated feed water. For both types of pretreatment, fluorescence intensity decreased significantly as the HAOPs dose increased, especially at lower doses (up to 20 mg Al/L); at higher doses, pre-deposition

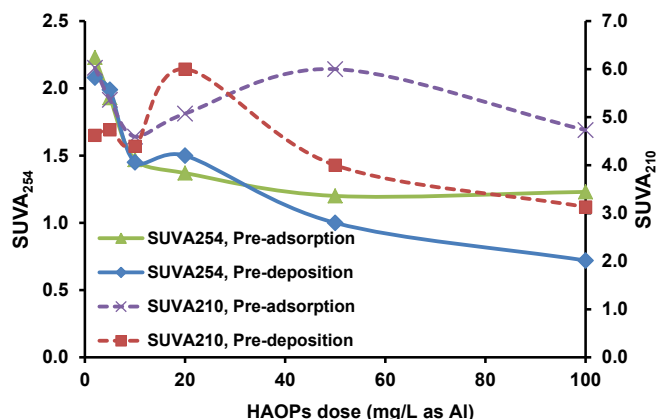


Fig. 3. $SUVA_{210}$ and $SUVA_{254}$ of permeates in both pre-adsorption and pre-deposition mode as a function of HAOPs dose.

reduced the fluorescence intensity more than pre-adsorption did.

Using PARAFAC analysis, the EEM spectrum for feed water was decomposed into three components, as shown in Fig. 5a–c. These components are dominated by peaks at Ex/Em of 380–390/450–470 nm, attributable to the visible fluorescence of humic-like substances; at 330–340/425–430 nm, attributable to fulvic-like substances; and at 220–240/330–350 nm, attributable to aromatic proteins (Henderson et al., 2009; Sheng and Yu, 2006).

The EEM spectra for the treated waters were mathematically decomposed in a similar way. The score vectors for the three individual components were obtained, and the removal efficiencies of the fluorophores were calculated based on those scores. Figs. 5d and 5e illustrate the removal of the three fluorophore groups by pre-adsorption and pre-deposition, respectively. In both cases, the removal of humic-like and fulvic-like substances gradually increased with increasing HAOPs doses. Pre-deposition consistently removed more of this material than pre-adsorption did. By contrast, <10% of the aromatic protein fluorescence was removed by either process at any HAOPs dose.

3.4. Effect of AMW on pretreatment efficiency

Figure SI-3a shows the HPSEC fractionation of feed water at wavelengths of 220, 254 and 272 nm. The curves have a maximum (Peak 1) at 4200 Da, a shoulder (Peak 2) at 740 Da, and a small, wide peak around 30 Da (Peak 3). Pretreatment led to a significant decrease in the two higher-AMW fractions, but less removal of the low-MW fraction (Peak 3), especially based on absorbance at 220 nm (Figure SI-3b–e). This result suggests that many of the carboxyl and other carbonyl-rich groups in the higher-AMW fractions were removed by pretreatment, but those same groups in the low-AMW fraction remained in the solution (Her et al., 2008; Korshin et al., 2009).

Fig. 6 compares HPSEC elution profiles for samples pretreated using the two approaches as a function of the HAOPs dose, based on absorbance at 254 nm, and Fig. 7 shows the removal efficiency for each of the major AMW fractions based on HPSEC peak height. As was the case for the humic and fulvic fractions as identified by EEM, both pretreatment approaches removed the higher-AMW fractions (Peak 1 and 2) efficiently, and pre-deposition was more effective at removing these molecules than pre-adsorption was. These fractions were efficiently removed at HAOPs doses higher than 50 mg Al/L, with both Peaks 1 and 2 gradually breaking through as the HAOPs dose was decreased.

Several recent efforts to interpret the absorbance spectra of

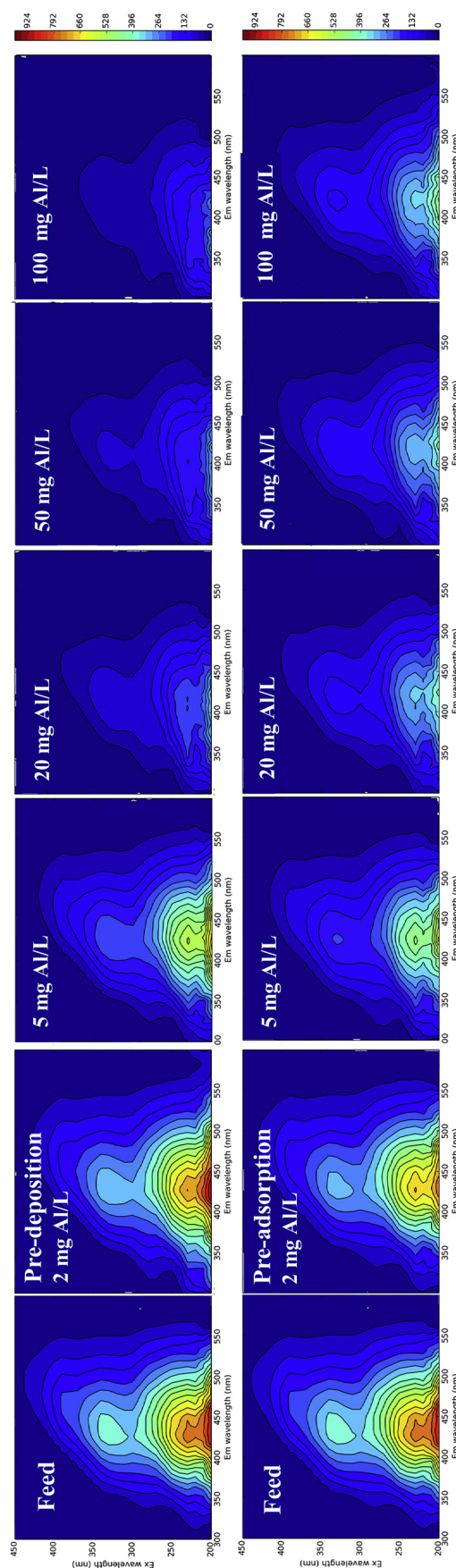


Fig. 4. EEMs of feed water at HAOPs doses from 0 to 100 mg Al/L.

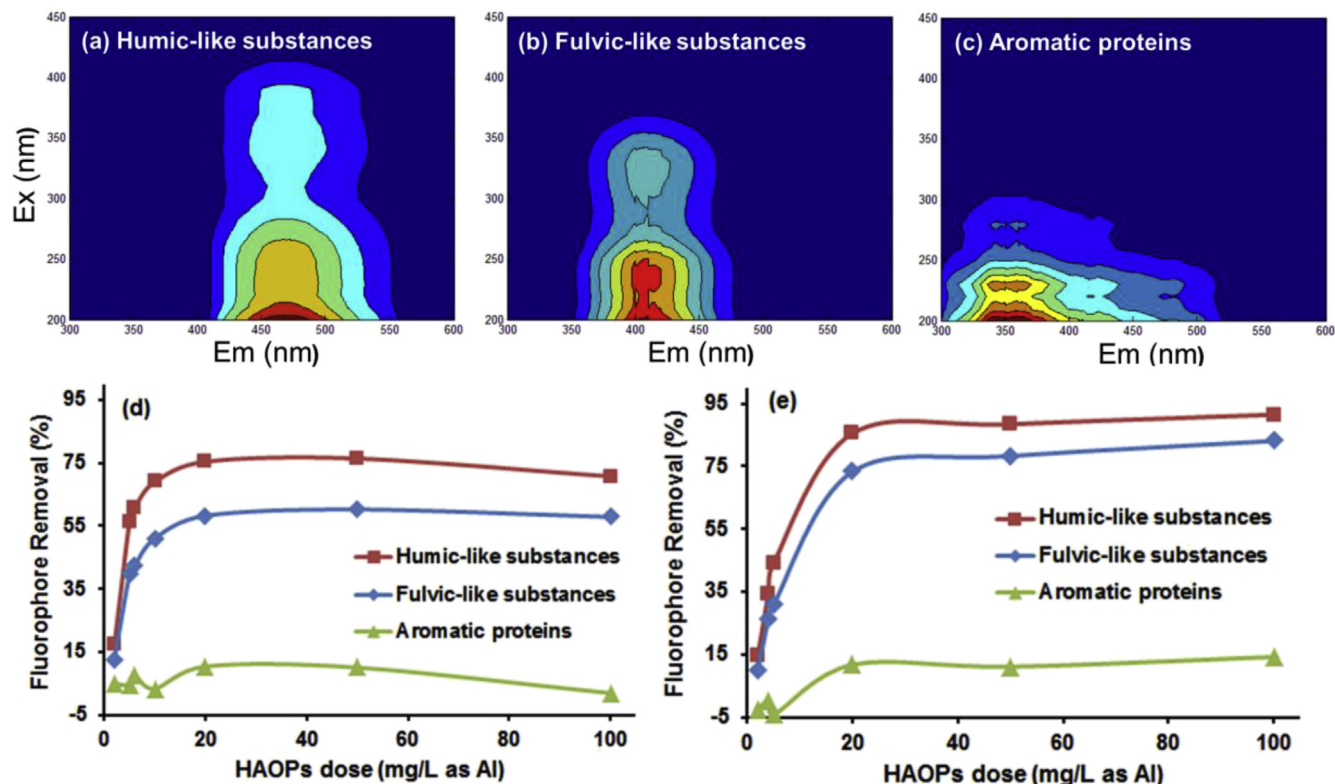


Fig. 5. (a–c) Three components of feed water, as decomposed using PARAFAC. Fluorophore removals in (d) pre-adsorption and (e) pre-deposition mode.

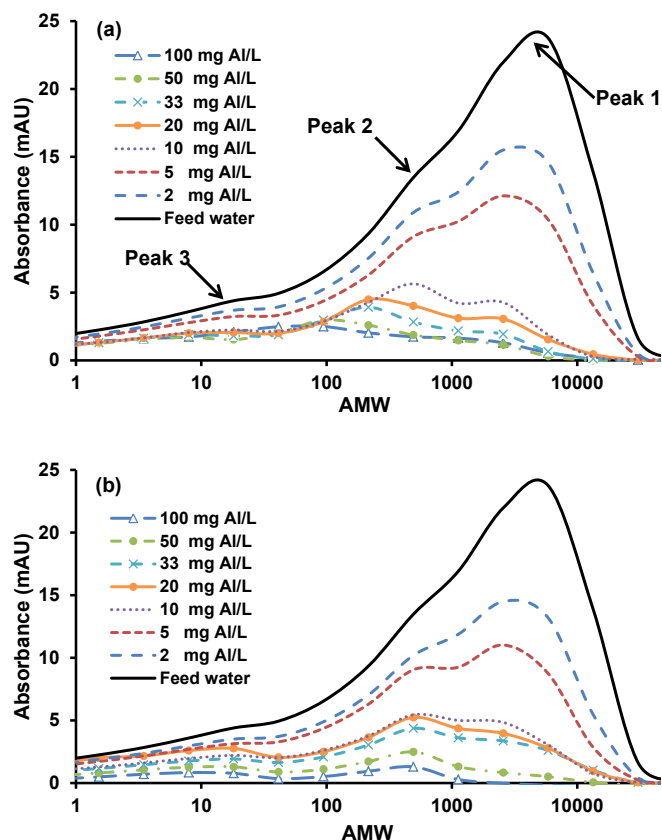


Fig. 6. HPSEC elution profiles for permeates in (a) pre-adsorption and (b) pre-deposition mode at various HAOPs doses. Data are for absorbance at 254 nm.

NOM have focused on the absorbance in the region dominated by activated aromatic groups ($\lambda \sim 254$ nm) relative to that in the region where both carboxylic/hydroxyl and aromatic groups make significant contributions ($\lambda \sim 210$ nm) (Korshin et al., 2009; Li et al., 2006; Stabenau and Zika, 2004). The ratio of the absorbances in these regions can be approximated as follows:

$$\frac{A_{\lambda \sim 254 \text{ nm}}}{A_{\lambda \sim 210 \text{ nm}}} \approx \frac{\bar{A}_{254-259}}{\bar{A}_{210-215}} \quad (1)$$

where \bar{A}_{i-j} is the average absorbance between wavelengths i and j .

The absorbance ratios calculated according to Equation (1) for the untreated and pretreated waters are shown in Fig. 8. For feed water, the ratio was in the range 0.57–0.62 for AMWs from 50 to 5000 Da. When the water was pretreated by pre-adsorption, this ratio decreased steadily across the whole AMW range as the HAOPs dose was increased from 2 to 10 mg Al/L; the data at a HAOPs dose of 20 mg/L were less consistent, but still the ratio was almost always less than in the untreated water (Fig. 8a). The same trend was observed, with larger declines in the absorbance ratio and more consistent effects of the HAOPs dose, when the water was pre-treated by HAOPs pre-deposition (Fig. 8b).

These results reflect the selectivity of HAOPs for aromatic groups over aliphatic carboxyl groups over a wide AMW range. Pre-deposited HAOPs were more selective than dilute, well-mixed HAOPs in this regard, especially at higher HAOPs doses and for low-AMW NOM, consistent with UV₂₅₄ removal and fluorophore removal results in Figs. 2 to 5. Other researchers have also observed that lower-AMW NOM has an absorption peak at 220–230 nm which is absent at 254 nm (Gray et al., 2004, 2008), and Gray et al. (2004) reported that this material has significant fouling potential. Peaks in this region might be due to the presence of proteins or organic acids, possibly present as aggregates with polysaccharides

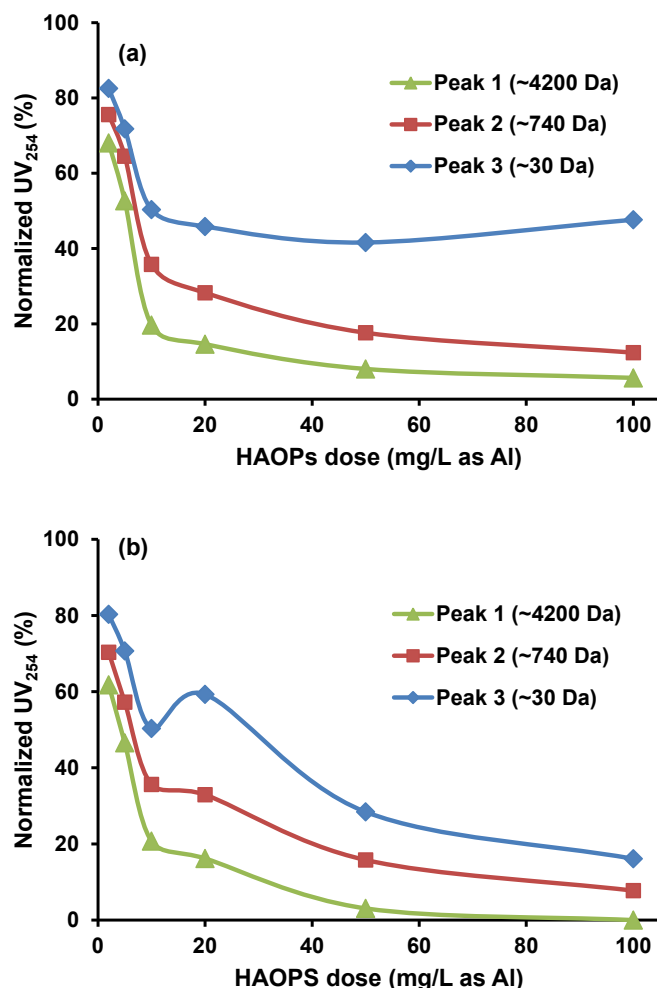


Fig. 7. Normalized breakthrough of different AMW fractions at a function of HAOPs dose in (a) pre-adsorption and (b) pre-deposition experiments.

(Amy, 2004). The enhanced fouling mitigation achieved by HAOPs in pre-deposition as opposed to pre-adsorption mode might be related to better removal of this low-AMW fraction.

3.5. Effect of pre-treatment on THM formation potential

The potential for THM formation from chlorination of feed water and pretreated samples is summarized in Table 2. Both pretreatments reduced the THM formation significantly at a HAOPs dose of 20 mg/L, and even more so at higher doses, with pre-deposition consistently outperforming pre-adsorption in this regard. Chloroform and dichlorobromomethane (DCBM) were the dominant THMs formed in all samples, accounting for more than 78% of the total trihalomethanes formed.

3.6. Mechanisms of NOM fouling in pretreatment/UF system

Adsorption of NOM molecules to Al- (and Fe-) oxides is commonly attributed to “surface complexation” reactions, in which carboxyl and/or hydroxyl groups act as ligands that bind the metal ions at the solid surface. Correspondingly, the correlation between NOM removal by coagulation and/or adsorption and UV_{254} has long been interpreted to reflect the selective affinity of the surface ions for aromatic carboxyl and hydroxyl groups (Edzwald, 1993). A similar interpretation applies to the selective removal of UV_{254} -

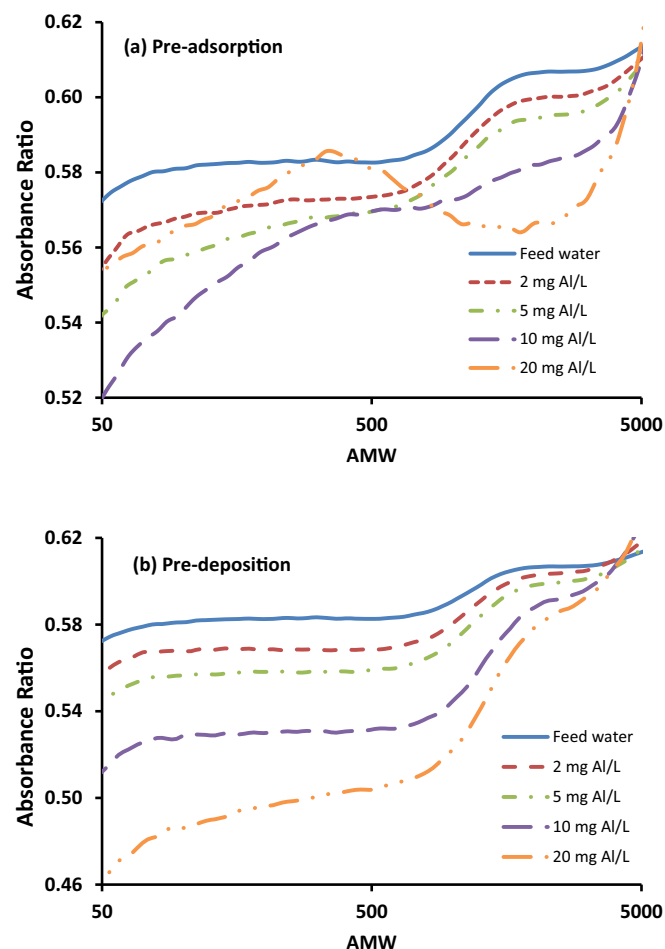


Fig. 8. Absorbance ratios of feed water and treated water as a function of HAOPs dose within an AMW range from 50 to 5000 Da.

absorbing NOM molecules by HAOPs in this work. The close correlation between the fractional removal of UV_{254} and of humic and fulvic substances as indicated by the fluorescence data reinforces the widely held view that much of the UV_{254} absorbance is associated with those groups of NOM molecules, and that they account for the majority of the adsorbable NOM. The HPSEC analyses suggest that larger NOM molecules (several thousand Da) contribute more UV_{254} to the water than intermediate-size (several hundred Da) or smaller (<100 Da) molecules, and that the removal efficiency increases with increasing molecular size. Both of these inferences are consistent with the previous ones regarding overall NOM and UV_{254} removal and the types of molecules that the strongly adsorbed fraction comprises.

As noted earlier, aliphatic carboxyl groups in NOM are thought to absorb strongly at wavelengths near 210 nm. However, in pre-adsorption experiments, UV_{210} was removed no better (and no worse) than DOC, suggesting that these functional groups are distributed approximately uniformly among NOM molecules, and are no more prevalent on those molecules that adsorb than on molecules that do not adsorb. This result does not indicate that the groups are never involved in adsorptive bond formation, but it does indicate that they are not the primary factor controlling the formation of such bonds.

In all of the experiments reported here, passing the water through a pre-deposited layer of HAOPs removed more NOM from the solution than was achieved by contacting the same amount of HAOPs with the solution in a well-mixed, dilute suspension. This

Table 2
THM formation in untreated and pretreated water.

	HAOPs dose (mg Al/L)	Cl ₂ residual (mg/L)	CHCl ₃ (TCM)	CHBrCl ₂ (DCBM)	CHBr ₂ Cl (DBCm)	CHBr ₃ (TBM)	TTHM (Total trihalomethane)
			Compound concentration (µg/L)				
Feed water	0	0.3	211	24	1.3	0.57	237
Pre-deposition	20	4.3	82	14	2.6	0.35	99
	50	5.3	60	13	2.6	0.39	76
	100	8.6	53	11	2.2	0.33	66
Pre-adsorption	20	2.6	106	16	2.5	0.33	125
	50	3.3	84	16	2.5	0.47	102
	100	5.8	72	17	2.5	0.58	92

result applied both to the water as a whole and to every subgroup of molecules analyzed (whether based on AMW or interpretation of the fluorescence spectra), and regardless of whether the measure of NOM concentration was DOC, UV₂₅₄, or UV₂₁₀. This outcome indicates that some mechanism for NOM removal that is active in a pre-deposited layer does not apply (or at least is not as strong) in a dilute slurry. Furthermore, although the incremental NOM removal by the pre-deposited layer was relatively small in terms of DOC or UV absorbance, it was large in terms of the mitigation of fouling of a UF filter and the reduction in THM formation when the pretreated water was chlorinated.

At least two phenomena can be invoked to explain the enhanced removal of NOM by pre-deposition relative to pre-adsorption, as well as the other differences between the two contacting modes. First, the hydraulics of the pre-adsorption process assure that all the adsorbent particles are in contact with a solution from which some of the NOM has already been removed. By contrast, in the pre-deposition process, feed water with its full NOM concentration enters the adsorbent layer. As a result, the driving force for adsorption is higher at that location than it is anywhere in the pre-adsorption system, and the extent of adsorption is expected to be greater. This difference between the two contacting schemes is identical to that between conventional well-mixed and packed-bed adsorption reactors, for which the advantages of the latter systems are well understood.

Second, the combination of the tight packing of the micron-sized HAOPs in the pre-deposited layer and the entry of full-strength feed water into that layer might provide conditions for a transformation of the NOM from individual molecules to a condensed phase (e.g., a gel). Such gels are widely suspected to form on membranes and to cause severe fouling if sufficient NOM has been applied to them. It is possible that the critical concentration for formation of these gels does not develop on individual, suspended adsorbent particles. Although no direct proof exists that such gels formed in the systems we studied, it is noteworthy that a dramatic color gradient does develop across the HAOPs deposit, with a thin, dark brown layer forming at the water/HAOPs interface but not penetrating deeper into the deposit (Cai et al., 2008; Kim et al., 2010). The organic carbon concentration near the top of the deposited layer is very high, so it seems likely to include a condensed phase containing a large concentration of NOM, rather than just individual molecules adsorbed on the HAOPs' surfaces. This layer could be responsible for the dramatic mitigation of membrane fouling achieved by pre-deposition, e.g., if the condensed NOM phase efficiently captures foulant molecules that are not strongly adsorbed by dispersed HAOPs. A similar interaction might account for the selective removal of THM precursors relative to other NOM in the pre-deposition systems.

Finally, note that even though both pretreatments selectively removed the large-AMW, humic and fulvic fractions of the NOM, the fouling behaviors of the pretreated waters were quite different. This outcome suggests that the aforementioned fractions were not

primarily responsible for membrane fouling. By contrast, pre-deposition removed the lower-AMW (~30 Da), non-humic fraction much better than pre-adsorption did (e.g., 84% vs. 53% removal at a dose of 100 mg Al/L), so removal of that fraction did correlate with the mitigation of membrane fouling. The importance of low-AMW NOM for fouling has also reported in previous work. For example, Henderson et al. (2011) found that low-AMW neutral molecules in tertiary wastewater effluents are particularly strong foulants of UF membranes. In addition, the very different effects of the two pretreatments on fouling, despite the fact that they achieved similar DOC and UV₂₅₄ removals, indicate that the key foulants comprise only a small portion of the total NOM. Together, these observations suggest that the fraction of the NOM that is most responsible for membrane fouling comprises low-MW, non-UV absorbing organics that are present at very low concentration in the test water, and in all likelihood other natural waters as well.

4. Conclusions

Pretreating a natural water with HAOPs in both pre-adsorption and pre-deposition contacting modes removed a substantial fraction of the DOC, selectively removing UV₂₅₄-absorbing molecules, humic and fulvic substances, and high-AMW fractions of the NOM. However, in all cases, a pre-deposited HAOPs layer retained more NOM than an equivalent amount of HAOPs contacted with the water in a dilute, well-mixed suspension. The absorbance ratios derived from multi-wavelength HPSEC data confirmed the adsorptive selectivity for aromatic over aliphatic groups over a wide AMW range. The selective removal of aromatic fractions from lower-AMW fractions was most noticeable at higher HAOPs doses. The results support the view that the key foulants comprise only a small portion of the NOM in the source water and that they can be substantially retained by a HAOPs layer, perhaps due to the formation of a condensed NOM phase (e.g. a gel) that efficiently collects molecules responsible for membrane fouling. Pre-deposition also outperforms pre-adsorption with respect to removal of THM precursors.

Disclosure

Mark Benjamin is a principal in a company that is attempting to commercialize HAOPs and the treatment process described in this article.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.03.066>.

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