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 polyaluminium chloride [PACl]) 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

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, μGAF) 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-μm filter prior to use. The conductivity, pH and dissolved organic carbon (DOC) concentration were ~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 (UV_{254}) 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 μm (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-μm) 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-μm 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. NH$_4$HCO$_3$ 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 SI-1).

Untreated water and some treated samples were selected for analysis of THM formation potential. For these tests, 20 mg/L Cl$_2$ 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 Cl$_2$

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