Membrane fouling in ultrafiltration of natural water after pretreatment to different extents

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ABSTRACT

The combined fouling during ultrafiltration (UF) of surface water pretreated to different extents was investigated to disclose the roles of polysaccharides, proteins, and inorganic particles in UF membrane fouling. Both reversible and irreversible fouling decreased with enhanced pretreatment (biologically active carbon (BAC) treatment and sand filtration). The sand filter effluent fouled the membrane very slowly. The UF membrane removed turbidity to less than 0.1 nephelometric turbidity unit (NTU), reduced polysaccharides by 25.4%–29.9%, but rejected few proteins. Both polysaccharides and inorganic particles were detected on the fouled membranes, but inorganic particles could be effectively removed by backwashing. The increase of turbidity in the sand filter effluent to 3.05 NTU did not significantly increase the fouling rate, but an increase in the turbidity in the BAC effluent to 6.11 NTU increased the fouling rate by more than 100%. The results demonstrated that the polysaccharide, not the protein, constituents of biopolymers were responsible for membrane fouling. Membrane fouling was closely associated with a small fraction of polysaccharides in the feed water. Inorganic particles exacerbated membrane fouling only when the concentration of fouling-inducing polysaccharides in the feed water was relatively high. The combined fouling was largely reversible, and polysaccharides were the predominant substances responsible for irreversible fouling.

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Introduction

Ultrafiltration (UF) has been increasingly applied for drinking water production due to its consistently high performance in terms of particle and microorganism removal (Boudaud et al., 2012; Hagen, 1998; Xiao et al., 2012). Optimally, UF can be operated as a stand-alone process with no requirement for pretreatment operations. However, one major challenge facing UF is membrane fouling, which impairs its cost efficiency, in that membrane fouling can decrease filtration flux and increase operational cost and, most severely, result in system failure. An understanding of membrane fouling is therefore crucial for better design and operation of UF processes.

Membrane fouling is caused by the accumulation of any substance (i.e., a foulant) on the membrane surface or in the membrane material; a foulant restricts water flowing across the membrane. The foulants in natural waters include inorganic particles, natural organic matter (NOM), microorganisms, mineral ions (e.g., calcium), and mixtures of these substances due to mutual interactions (Buffie et al., 1998). Nevertheless, NOM was demonstrated to be primarily responsible for UF membrane fouling (Cho et al., 2000; Escobar et al.,

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particles in two size ranges (0.5 μm and 45 μm) in the presence of silica particles (Munla et al., 2008; Kennedy et al., 2008). Measurements using a liquid chromatograph-organic carbon detector (LC-OCD) demonstrated that biopolymers were easily retained by UF membranes (Halle et al., 2009; Huang et al., 2011; Kennedy et al., 2005; Subhi et al., 2012). The major components of biopolymers are polysaccharides and proteins, but the polysaccharide component tends to contribute more to membrane fouling. Analyses using Fourier transform infrared (FT-IR) spectroscopy showed that polysaccharides were abundant on the fouled membrane surface (Cho et al., 1998; Kimura et al., 2004). Many polysaccharides in water, sometimes aided by calcium ions, can form a gel-like structure, which usually has very low filterability. Calcium ions are usually abundant in most natural waters and exceed the quantity needed for gel formation. Nevertheless, membrane fouling by polysaccharides can also be aggravated in the presence of proteins and humic substances (Gray et al., 2011). Fluorescence excitation-emission matrix (EEM) measurements showed that the protein peaks had some correlation with the membrane fouling rate (Kimura et al., 2014). Peldszus et al. (2011) found that protein-like substances contributed to both reversible and irreversible fouling.

Recently, much attention has been paid to the combined fouling caused by NOM coexisting with inorganic particles. The inorganic particles that are naturally present in or intentionally added to water include silts, clays, and precipitated crystals, as well as iron and aluminum oxyhydroxides (Yiantsios and Karabelas, 1998). Although inorganic particles alone usually do not lead to severe membrane fouling (Tian et al., 2013) and whatever fouling does occur is mostly reversible and easily removed by physical cleaning (Li et al., 2010; Peiris et al., 2010), previous studies showed that inorganic particles could aggravate membrane fouling caused by NOM. For example, membrane fouling by NOM “model” compounds (such as bovine serum albumin, humic acid and sodium alginate) increased in the presence of silica particles (Munla et al., 2012). Tian et al. (2013) also found that the membrane fouling rate was proportional to the concentration of silica particles in two size ranges (0.5–10 μm and 45 μm) in the range of 10–50 mg/L. However, a few studies showed that the coexistence of inorganic particles with NOM alleviated membrane fouling. Notwithstanding the above efforts, little is known about the combined fouling of membranes by NOM and inorganic particles found in natural water.

Pretreatment of water prior to filtration, usually using conventional drinking water treatment processes, has been proposed as a means to control membrane fouling. Coagulation was found to be effective in reducing membrane fouling (Chen et al., 2007; Citulski et al., 2008; Song et al., 2008) in that NOM could be substantially adsorbed to flocs of hydrolyzed coagulants that are highly filterable. Coagulation in combination with sedimentation was more effective than coagulation alone in reducing membrane fouling (Liang et al., 2008), because the pretreatment could effectively remove both NOM and inorganic particles from the water (Liu et al., 2011). Sand filtration was added following coagulation to control membrane fouling, but the additional benefit was found to be minimal (Xia et al., 2004). Ozonation reduced membrane fouling because of its effectiveness in degrading biopolymers to small molecules that would be less likely to foul the membrane (Geismar et al., 2012; Guo et al., 2013, 2014). Biologically active carbon (BAC) filtration was shown to effectively decrease membrane fouling due to the retention of biopolymers in the filter (Guo et al., 2013; Halle et al., 2009; Huang et al., 2011).

In the study reported here, we investigated the combined fouling of UF membranes by NOM and inorganic particles found in natural water. The effects of various pretreatment techniques were examined, and the relative importance of polysaccharides and proteins in UF membrane fouling was evaluated. The water samples used as feed to the UF membrane were collected from a full-scale drinking water treatment plant (DWTP) at various stages in the treatment process. The full treatment process consisted of coagulation, followed by sedimentation, ozonation, up-flow BAC (UBAC) degradation, sand filtration, and chlorination (disinfection). The UBAC functioned more as a biological reactor than as a conventional down-flow BAC filter (Han et al., 2013). It was expected that both biopolymers and inorganic particles would be gradually removed throughout the treatment process. Special attention was paid to the differences in fouling potential of different polysaccharides in the feed water. A previous study showed that the polysaccharides could be roughly grouped into gelling and non-gelling components (Wang and Waite, 2009).

1. Materials and methods

1.1. Feed water

The feed water for the UF membrane experiments was from grab samples collected from three stages of treatment in the DWTP: after sedimentation (denoted as “FW-S” hereafter); after UBAC treatment (denoted as “FW-B”); and after sand filtration (denoted as “FW-F”). The dissolved oxygen (DO), conductivity, and pH of samples were measured on site. Thereafter, all samples were transported to the laboratory within 24 hr, where other water quality parameters including dissolved organic carbon (DOC), spectral absorption (UV254), polysaccharide concentration, and turbidity were measured immediately upon arrival. The feed water samples were then stored in a refrigerator at 4°C and warmed to room temperature prior to use in the ultrafiltration experiments.

1.2. Ultrafiltration procedure

A laboratory-scale membrane filtration apparatus was used for all filtration experiments. The apparatus consisted of a home-made tubular filtration cell with an effective volume of 500 mL, two peristaltic pumps (BP100-1L, Longer, Hebei, China) to add feed water and provide permeate suction, a pressure transducer (CX-203, Futexin, Beijing, China) to measure trans-membrane pressure (ΔP), and other accessories (Fig. 1). A hollow fiber UF membrane module (Litree, Hainan, China) with an effective filtration area of 0.04 m² was installed in the tubular filtration cell. The membrane material was polyvinyl chloride and the nominal membrane pore size was 0.01 μm.
All filtrations were conducted in a constant-flux, dead-end mode. Before filtrations, the membranes were cleaned by filtering DI water. The filtration flux was set at 30 L/m²/hr (LMH). Each feed water sample was filtered for six consecutive cycles. Each cycle consisted of a filtration period of 1 hr and a backwash period of 2 min with DI water. The backwash process was conducted out of the filtration cell, for which the flux was set at 60 LMH, and the backwash waste was discharged. During the filtration, the trans-membrane pressure was monitored and automatically recorded (XSR, olet, USA). The DO concentration, conductivity, and pH of water samples were determined using a portable meter with multiple probes. The absorbance at 254 nm (UV254) was determined using an ultraviolet-visible spectrophotometer (TU1901, Puxi, Beijing, China).

### 2. Results and discussion

#### 2.1. Effect of pretreatment on membrane fouling

The feed water for ultrafiltration experiments was collected from a full-scale DWTP. Because the samples were collected at such low UV absorbance, no significant absorbance fouling was observed. The total organic carbon (TOC) and the total dissolved organic carbon (DOC) content were determined using a total organic carbon analyzer (Aurora 1030 W TOC, OI, USA). The TOC content of the feed water was 4.6 mg/L, while the DOC content was 1.1 mg/L. The specific UV absorbance at 254 nm (SUVA254) was determined using an ultraviolet-visible spectrophotometer (TU1901, Puxi, Beijing, China). It was calculated as SUVA254 = SUVA254/TOC.

#### 2.2. Model of membrane fouling

The total filtration resistance ($R_t$) is the sum of the intrinsic membrane resistance ($R_m$) and the fouling layer resistance ($R_f$), as given by the Darcy equation (Eq. (1)):

$$R_t = R_m + R_f = \frac{\Delta P}{\mu J}$$

where, $R_t$ (1/m) is the total filtration resistance (equal to the sum of the intrinsic membrane resistance ($R_m$) and the fouling layer resistance ($R_f$)), $\mu$ (Pa·sec) the water viscosity and $J$ (m³/sec) the filtration flux. The total resistance increased with time after filtration started, when it was equal to the intrinsic membrane resistance. Every backwash restored the membrane filterability to some extent. The removed and remaining fouling after backwashes were termed as “reversible” and “irreversible” fouling, respectively. The corresponding filtration resistances were denoted as $R_b$ and $R_f$, respectively, and in combination determined the fouling layer resistance ($R_f$) (Eq. (2)):

$$R_f = R_b + R_{fr}$$

#### 2.3. Membrane and fouling layer characterization

Samples of membranes in their virgin, fouled, backwashed, and cleaned states were examined using a scanning electron microscope (SEM) (Quanta 200, FEI, The Netherlands) after appropriate pretreatment. The virgin membrane samples were rinsed with ultrapure water and subsequently oven-dried at 35°C for 12 hr. The fouled, backwashed, and cleaned membrane samples were first gently rinsed with ultrapure water to remove any loosely attached substances and then oven-dried at 35°C for 12 hr. All samples were coated with a uniform layer of platinum in a sputter-coating chamber (EM ACE600, Leica, Germany) prior to SEM observation. The chemical elements in the fouling layers on some membrane samples were also analyzed using an elemental analysis system (Genesis, EDAX, USA) integrated with the SEM.

The virgin, fouled, backwashed, and cleaned membrane samples were also analyzed for chemical composition using an FT-IR spectrometer (Nicolet 6700, Thermo Fisher, USA) equipped with a single reflection attenuated total reflectance (ATR) accessory (ZnSe crystal) at a nominal incident angle of 45°. The FT-IR spectra were collected as the average of 32 scans in the wavenumber range from 4000 to 650 cm⁻¹ at a 4 cm⁻¹ interval.

#### 2.4. Analytical methods

Polysaccharide concentrations in water were determined using the phenol-sulfuric acid method with glucose as the standard. Significant differences in polysaccharide rejection for different feed waters by UF were analyzed by SPSS (SPSS, USA) software. The absorbance at 490 nm was measured, and the polysaccharide concentration was expressed as glucose equivalent. Protein concentrations in water were determined using three-dimensional fluorescence excitation-emission matrix (3D-EEM) spectra (F-7000, Hitachi, Japan). The excitation wavelength (Ex) range was between 220 and 450 nm, and the emission wavelength (Em) was between 240 and 600 nm. The sampling interval was 5 nm, the response time was 0.01 sec and the scanning speed was 2400 nm/min. The spectral data were analyzed using Origin (OriginLab, USA) software. Spectral subtraction was performed to remove blank spectra that were mainly caused by Raman scattering (Xiao et al., 2012).

The DO concentration, conductivity, and pH of water samples were determined using a portable meter with multiple probes (HQ30D, HACH, USA). The DOC content was determined using a total organic carbon analyzer (Aurora 1030 W TOC, OI, USA) after sample filtration through a 0.45 μm membrane. Ultraviolet absorbance at 254 nm (UV254) was determined using an ultraviolet-visible spectrophotometer (TU1901, Puxi, Beijing, China). Turbidity was determined using a turbidimeter (2100Q, HACH, USA).
three stages in the treatment process, each sample type represented natural water that had been “pretreated” (relative to UF) to a different extent. The extent of pretreatment was the cumulative effect of all unit treatment processes in the DWTP prior to and including the sample collection point. The water qualities of samples, including turbidity and DOC content, are listed in Table 1.

As shown in Table 1, the turbidity, DOC, UV254, and polysaccharides and proteins (indications of biopolymers) all decreased as the extent of water treatment increased. Generally, inorganic particles were more easily removed than organic compounds, and biopolymers were removed more than other NOM. It was believed that the organic substances were removed primarily by physical interception in the sand filter and by biological degradation and physical interception in the UBAC, aided by ozonation.

Ultrafiltration of the three feed waters showed that FW-S (i.e., water with the least pretreatment) fouled the membrane the most, and FW-F (i.e., the most highly pretreated water) fouled the membrane the least (Fig. 2). The UF membrane module was periodically backwashed during each filtration. The intrinsic membrane resistance was 3.0 – 3.3 × 10¹² 1/m. After operation for six consecutive filtration cycles, the irreversible fouling resistance (R_i) increased to 2.6 × 10¹², 2.1 × 10¹² and 0.5 × 10¹² 1/m when FW-S, FW-B and FW-F were filtered, respectively. In the sixth filtration cycle, the reversible fouling resistance (R_r) that developed was 2.2 × 10¹², 1.9 × 10¹² and 0.5 × 10¹² 1/m, respectively. The beneficial effect of water pretreatment on membrane fouling control has been extensively reported in the literature (Citulski et al., 2008; Halle et al., 2009; Peldszus et al., 2011; Zhao et al., 2010). However, a previous study (Xia et al., 2004) showed that sand filtration had no additional effect on membrane fouling control (although the relevant water qualities were not provided in the study), which was in a sharp contrast to the significant positive effect observed in this study (Fig. 2). Water pretreatment reduced both irreversible and reversible fouling. After operation for six filtration circles, irreversible fouling became the dominant form of fouling for all three of the feed waters.

The order of membrane fouling propensity was in accordance with that of the feed water qualities in terms of turbidity, DOC content, UV254, polysaccharide and protein concentrations (Table 1), with higher foulant concentrations generally causing faster membrane fouling (Zhang et al., 2012). Both inorganic particles and organic substances were potential foulants.

Chemical cleaning of fouled membranes at the end of six filtration cycles was conducted to determine its effect on irreversible fouling. It was found that cleaning for 30 min with 200 mg/L sodium hypochlorite solution could largely recover the membrane filterability (Fig. 2), recovering 26.1%, 32.2%, and 34.4% of fouling layer resistance caused by FW-S, FW-B, and FW-F, respectively, after backwash at the end of the last filtration cycle. The effectiveness of sodium hypochlorite in removing the hydraulically irreversible fouling was also reported in a number of previous studies (Zhang et al., 2012; Kimura et al., 2004; Yamamura et al., 2007). Sodium hypochlorite was believed to effectively remove the hydrophilic organic matter (Strugholtz et al., 2005). These results indicate that in the present study, membrane fouling was mainly caused by organic matter. Citric acid at a concentration of 2%, which was used mainly to remove inorganic scales (Munla et al., 2012), could remove 8.51%, 7.36%, and 6.90% more of the fouling layer resistance that remained after cleaning with sodium hypochlorite, respectively. After cleaning by citric acid, the total fouling resistance was removed by 80.1% to 90.8%, which represented most of the total fouling resistances.

### 2.2. Foulant retention on the membrane

Although a higher foulant concentration in the feed water to a filtration membrane usually corresponds to a higher fouling rate, membrane fouling occurs due to both the deposition and accumulation of foulants on the membrane. As such, the difference in water qualities between the feed water to, and permeate from, a membrane was used to illustrate fouling.

The retention of biopolymers by the membrane was first considered, in that a number of previous studies showed that biopolymers were important in membrane fouling (Subhi et al., 2012; Halle et al., 2009; Huang et al., 2011; Kennedy et al., 2005). In the present study a significantly large portion of polysaccharides were retained on the UF membrane (Fig. 3). The rejected polysaccharide content was 0.32 ± 0.02, 0.26 ± 0.03 and 0.17 ± 0.02 mg/L when FW-S, FW-B and FW-F samples were filtered, respectively. The rejected polysaccharides constituted 29.9% ± 0.34%, 29.3% ± 1.69% and 25.0% ± 1.60% of the polysaccharides contained in the FW-S, FW-B and FW-F feed water, respectively, and were lower than those reported previously.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>FW-S (after sedimentation)</th>
<th>FW-B (after UBAC)</th>
<th>FW-F (after sand filtration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>4.25 ± 0.87</td>
<td>2.87 ± 0.42</td>
<td>0.29 ± 0.02</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>2.75 ± 0.02</td>
<td>2.36 ± 0.01</td>
<td>2.08 ± 0.01</td>
</tr>
<tr>
<td>UV254 (1/cm)</td>
<td>0.036 ± 0.001</td>
<td>0.022 ± 0.001</td>
<td>0.020 ± 0.001</td>
</tr>
<tr>
<td>pH</td>
<td>8.34 ± 0.18</td>
<td>8.15 ± 0.01</td>
<td>8.05 ± 0.01</td>
</tr>
<tr>
<td>Polysaccharide (mg/L)</td>
<td>1.07 ± 0.07</td>
<td>0.87 ± 0.05</td>
<td>0.67 ± 0.03</td>
</tr>
<tr>
<td>Peak intensity of protein (AU)</td>
<td>613.5 ± 25.4</td>
<td>416.3 ± 17.8</td>
<td>366.9 ± 11.3</td>
</tr>
</tbody>
</table>

UBAC = up-flow biologically active carbon.

Concentration of polysaccharides is expressed as glucose equivalent; protein content is expressed as the arbitrary unit (AU) found using fluorescence spectroscopy.
(Halle et al., 2009; Huang et al., 2011); this discrepancy could be due to differences in the feed water qualities in the various studies. The significant differences of polysaccharide rejection for FW-S, FW-B and FW-F by UF are shown in Table 2. There were no significant differences between FW-S and FW-B, a remarkable significant difference between FW-B and FW-F, and some significant difference between FW-S and FW-F. However, all studies, including this one, indicated that only a fraction of the polysaccharides in feed water are retained by the membrane. In other words, not all polysaccharides in the feed water cause membrane fouling. The organic matter was settled by coagulation-sedimentation in the sedimentation tank, eliminated by the metabolism of microorganisms in the BAC (Kim et al., 1997), and intercepted in sand filtration. Therefore, the polysaccharides in FW-S, FW-B and FW-F that caused severe membrane fouling were different. Nevertheless, our results showed that as more polysaccharides were retained on the membrane, the extent of membrane fouling was more severe, although a quantitative relationship between the fouling rate and the retained polysaccharide content was not established.

The retention of proteins by the UF membrane was also investigated. The protein contents in the feed water and permeate were calculated from their respective 3D EEM spectra (Fig. 4). According to the literature (Chen et al., 2003), the EEM spectra for protein can be divided into five regions representing aromatic protein I (tyrosine); aromatic protein II; fulvic acid-like substances; substances similar to soluble microbial by-products; and humic acid-like organic substances, respectively. The excitation and emission wavelength ranges in the EEM spectra for proteins are 200–250 nm and 330–380 nm, respectively. The highest spectral peaks of the FW-S, FW-B and FW-F feed waters were 615.3, 416.3 and 366.9 (Em: 340 nm, Ex: 235 nm), respectively. After ultrafiltration, the highest peaks were 635.0 (Em: 335 nm, Ex: 230 nm), 432.5 (Em: 340 nm, Ex: 235 nm), and 379.6 (Em: 335 nm, Ex: 235 nm) for the FW-S, FW-B and FW-F feed waters, respectively. A comparison of the fluorescence intensities (for proteins) in the feed water and permeate showed that there was little difference between the two for any of the feed waters, clearly indicating that very few proteins were retained by the UF membrane. Thus, compared with polysaccharides, proteins contribute much less to membrane fouling. Dissolved organic carbon is a gross indicator of the NOM concentration in water. Results showed that the DOC content removed by the UF membrane ranged from 0.194 to 0.271 mg/L, corresponding to a rejection percentage from 9.4% to 9.9%.

In contrast to organic substances, inorganic particles (denoted by turbidity) in feed water were almost completely retained by the UF membrane (Fig. 3). Regardless of the feed water turbidity (which was 4.25, 2.87 and 0.29 NTU for the FW-S, FW-B and FW-F feed waters, respectively), the permeate turbidity was always less than 0.1 NTU. This high retention was due to the small nominal pore size (0.01 μm) of the UF membrane used. Although inorganic particles alone do not significantly contribute to the overall membrane fouling (Jermann et al., 2008; Law et al., 2010; Munla et al., 2012; Tian et al., 2013), a previous study (Nakatsuka et al., 1996) showed that membrane fouling increased as feed water turbidity increased, and that a linear relationship existed between the flux decrease and the logarithm of turbidity. A higher fouling rate was also observed for the feed water of higher turbidity in the present study. However, this observation might be a coincidence because the polysaccharide concentration was also higher when the turbidity was higher.
The relative importance of polysaccharides and inorganic particles in membrane fouling will be described in Section 2.4.

2.3. Fouling layer characterization

The predominance of polysaccharides as organic substances in the fouling layer was further confirmed by ATR-FTIR spectrum scans of the fouled membranes. The FT-IR spectrum can be used to identify the characteristic functional groups of the various foulants on the membrane. Characteristic bands of polysaccharides, which include those at 3000–3600, 2927, 1240 and 1090 cm$^{-1}$, could be found in the spectra of membranes fouled by FW-S, FW-B and FW-F (Fig. 5). Polysaccharides contain a significant number of hydroxyl groups, which would exhibit a broad, rounded absorption peak above 3000 cm$^{-1}$ (Howe et al., 2002). The peak at 2925 cm$^{-1}$ corresponds to O–H stretching and the peak at 1074 cm$^{-1}$ is C–O stretching of polysaccharides (Lee et al., 2006). However, the peak at around 1650 cm$^{-1}$ corresponds to carboxylate, carbonyl, or amide I (Howe et al., 2002), which might indicate the existence of proteins, too (Jarusutthirak and Amy, 2006).

However, as mentioned in Section 2.2, protein cannot be

<table>
<thead>
<tr>
<th>The pairs of feed water</th>
<th>p-Value</th>
<th>Significant difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FW-S and FW-B</td>
<td>0.546</td>
<td>No</td>
</tr>
<tr>
<td>FW-B and FW-F</td>
<td>0.001</td>
<td>Remarkable</td>
</tr>
<tr>
<td>FW-S and FW-F</td>
<td>0.023</td>
<td>Exist</td>
</tr>
</tbody>
</table>

Table 2 – The significant differences of polysaccharide rejection of FW-S, FW-B and FW-F by UF.

Fig. 4 – Three-dimensional excitation–emission matrix (3D EEM) spectra of FW-S (water after sedimentation), FW-B (water after up-flow biologically active carbon treatment), and FW-F (water after sand filtration) before and after ultrafiltration (UF).
The intensity of the transmittance in the spectral band at 3000–3600 cm$^{-1}$ was weakest for the fouled membranes filtering FW-S and strongest for those fouled by FW-F samples. This spectral response was in accordance with the order of fouling rates shown in Fig. 2 and the retained contents of polysaccharides shown in Fig. 3. Furthermore, transmittance in the bands at around 3000–3600, 2927, 1650, 1240, and 1090 cm$^{-1}$ increased by backwashing with ultrapure water compared to the transmittance for fouled membranes, but not totally restored to the value for virgin membranes. This response demonstrated that polysaccharides were at least partially responsible for the hydraulically reversible fouling. After cleaning with sodium hypochlorite solution, these bands were further increased, which demonstrated that this solution was more effective in removing more polysaccharides than water alone, and indicated that polysaccharides were also responsible for hydraulically irreversible fouling. Similar phenomena were observed for the membranes fouled by FW-B and FW-F waters. These results indicated that polysaccharides were the main organic foulant and contributed to both hydraulically reversible and irreversible fouling. A few previous studies (Gray et al., 2011; Katsoufidou et al., 2010; Peiris et al., 2010) demonstrated that the fouling caused by polysaccharides was partially reversible and irreversible, while some other studies (Xiao et al., 2012; Yamamura et al., 2007) regarded polysaccharides as the major source of irreversible fouling. It is worth noting that in the present study a noticeable spectral response appeared at around 1550 cm$^{-1}$ on the membranes fouled by FW-S and FW-B waters (Fig. 5), but not on the membrane fouled by FW-F, nor on the virgin membrane or any cleaned membranes.

The fouled, backwashed, and cleaned membranes were also analyzed using SEM equipped with EDX. The images and spectra of membranes fouled by FW-S, FW-B, and FW-F waters are shown in Fig. 6a–c. Images and spectra of the fouled (by FW-S) membranes after being cleaned with ultrapure water and sodium hypochlorite solution are shown in Fig. 6d and e, respectively.

Inorganic particles were found on membranes fouled by FW-S and FW-B waters, and the main chemical elements of these particles were silicon, aluminum, magnesium, sodium, and calcium (Fig. 6a and b). Silicon was the major component of clay, which is commonly found in surface water. Silicon could also be sourced from the few diatoms that were retained on the membrane. Aluminum was a component in the coagulant added in the DWTP coagulation process. However, few inorganic particles were found on the membrane fouled by FW-F (Fig. 6c) because sand filtration removed most inorganic particles from the water. Moreover, few inorganic particles were observed on the membranes after they were cleaned with ultrapure water (Fig. 6d), indicating that water backwashing was very effective in removing inorganic particles from the membrane fouling layer. No inorganic particles were found on the membranes cleaned with sodium hypochlorite solution (Fig. 6e). It appears that, in contrast to polysaccharides, inorganic particles in the fouling layer only contributed to reversible fouling. Peiris et al. (2010) also found that colloidal and particulate substances were the major contributors to reversible fouling.

### 2.4. Effect of increasing turbidity

The foregoing results revealed that both polysaccharides and inorganic particles were responsible for reversible fouling, while irreversible fouling was primarily caused by polysaccharides. Previous studies showed that NOM (e.g., biopolymers) and inorganic particles could behave synergistically in causing membrane fouling (Munla et al., 2012; Tian et al., 2013). However, the present study showed that not all polysaccharides in the feed water were rejected or retained by the membrane. A previous study also found that polysaccharides could be grouped into gelling (or fouling-inducing) and non-gelling fractions (Wang and Waite, 2009). To further clarify the respective roles of polysaccharides and inorganic particles in membrane fouling, kaolinite particles were added to FW-F and FW-B feed waters to increase their turbidity. After amendment with kaolinite, FW-F had the lowest fouling propensity and contained the least fouling-inducing polysaccharide content. FW-B contained more polysaccharides that could cause membrane fouling than FW-F. The filtration resistance development after adding kaolinite is shown in Fig. 7.

When the turbidity (after kaolinite addition) in the FW-F increased to 1.06–3.05 NTU from its original value of 0.29 NTU, membrane fouling only slightly increased (Fig. 7). In the third filtration cycle, the total fouling resistance increased only to $1.0 \times 10^{12}$, $1.0 \times 10^{12}$ and $1.1 \times 10^{12}$ m$^{-1}$ for the feed water with turbidity at 1.06, 2.09 and 3.05 NTU, respectively. These fouling resistances were close to those measured for non-amended FW-F water. In comparison, when the turbidity in FW-B increased from its original value of 2.87 NTU to 4.07–6.11 NTU through kaolinite addition...
addition, the membrane fouling rate increased substantially (Fig. 8). In the third filtration cycle, the total fouling resistance caused by kaolinite-amended FW-B water increased to $3.3 \times 10^{12}$, $3.7 \times 10^{12}$, and $3.9 \times 10^{12}$ 1/m for the feed water with turbidity at 4.07, 5.06, and 6.11 NTU, respectively. These fouling resistances were 29.9%–55.7% greater than those measured for non-amended FW-B water. However, this increased fouling resistance was largely reversible. After operation for three filtration cycles, the reversible fouling resistances were $1.3 \times 10^{12}$, $1.6 \times 10^{12}$, and $1.7 \times 10^{12}$ 1/m, which were 63.2%–112.3% greater than those measured for non-amended FW-B water, further demonstrating the insignificant role of inorganic particles in irreversible fouling.

Thus, when feed water to a membrane contains a relatively high concentration of membrane fouling-inducing polysaccharides (as did FW-B), inorganic particles can exacerbate reversible membrane fouling, probably through the synergistic fouling effect observed in a number of previous studies (Munla et al., 2012; Tian et al., 2013). In the present study, the polysaccharides acted as the “gluing” substances that bound the inorganic particles to form a poorly filterable cake layer on the membrane. There was probably a critical ratio of inorganic particle content to polysaccharide content, above which there would have been either a negligible effect on, or even a reduction of, the fouling rate; this speculation needs future verification. The foregoing results also indicated that even when the inorganic particles were bound with polysaccharides, the particles could be easily removed from the fouling layer by backwashing, leaving predominantly

![Fig. 6](image_url) - Elemental analyses and scanning electron microscopy images of membranes in different conditions. (a) Fouled by FW-S (water after sedimentation); (b) fouled by FW-B (water after up-flow biologically active carbon treatment); (c) fouled by FW-F (water after sand filtration); (d) fouled by FW-S and backwashed with ultrapure water; and (e) fouled by FW-S and backwashed with sodium hypochlorite solution.

![Fig. 7](image_url) - Membrane fouling development (as measured by total resistance, $R_t$) during three cycles of ultrafiltration of FW-F (water after sand filtration) at different levels of artificially induced turbidity (as measured by NTU).

![Fig. 8](image_url) - Membrane fouling development (as measured by total resistance, $R_t$) during three cycles of ultrafiltration of FW-B (water after up-flow biologically active carbon treatment) at different levels of artificially induced turbidity (as measured by NTU).
polysaccharides as residuals on the membrane. In comparison, when feed water contained few fouling-inducing polysaccharides (as did FW-F), the addition of inorganic particles had a negligible effect on membrane fouling due to the lack of the “gluing” effect of polysaccharides. In other words, the cake layer consisting of inorganic particles and only a few polysaccharides was relatively filterable, and the fouling caused by the cake was hydraulically reversible.

3. Conclusions
This study of UF on water collected from different treatment stages in a full-scale DWTP permits several conclusions. Biopolymers (polysaccharides and proteins) and inorganic particles in water contribute to the combined fouling of UF membranes used in drinking water treatment. The extent to which these substances foul UF membranes is affected by the extent of pre-treatment afforded to the membrane feed water; thus, the point at which UF is used in the drinking water treatment process is an important operational consideration. Membrane feed water collected after sedimentation, after BAC treatment, and after sand filtration fouls UF membranes at different rates and in different ways. Relative to more highly treated feed water, water that has been subjected only to coagulation and sedimentation has the highest biopolymer concentration and turbidity, and causes the greatest membrane fouling in terms of either hydraulically reversible or irreversible fouling. In contrast, highly treated UF feed water (such as that subjected to a combination of coagulation, sedimentation, ozonation, BAC treatment, and sand filtration) has little fouling effect on membranes, and the effect is very slow to develop. Polysaccharides, not proteins, are primarily responsible for membrane fouling. Polysaccharides are moderately (25.4%-29.9% in this study) rejected by UF membranes, but proteins are negligibly rejected; in addition, the foulant on membranes contains much more polysaccharides than proteins. UF membranes can effectively remove turbidity (to less than 0.1 NTU in this study), and inorganic particles can be observed on membranes that filter water pretreated by only coagulation and sedimentation as well as by coagulation and sedimentation combined with ozonation and BAC. Both polysaccharides and inorganic particles are responsible for reversible fouling, but irreversible fouling is primarily caused by polysaccharides, which remain on the membrane after backwashing. Backwashing membranes with water can effectively remove inorganic particles from the fouling layer. A synergistic effect of polysaccharides and inorganic particles on reversible fouling seems to occur only when the concentration of fouling-inducing polysaccharides in the feed water is sufficiently high. When the concentration of polysaccharides is high, increased turbidity in feed water has a significant effect on the membrane fouling rate; in this study, turbidity in the range 4.07–6.11 NTU increased membrane fouling by over 100% for some samples. In contrast, inorganic particles contribute little to reversible fouling when the polysaccharide content of feed water is low; in this study, an artificially produced increase (to 3.05 NTU) in the turbidity of highly pretreated membrane feed water did not significantly increase the fouling rate.

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References


