Transparent exopolymer particles (TEP) removal efficiency by a combination of coagulation and ultrafiltration to minimize SWRO membrane fouling

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Abstract

This study investigated the impact of coagulation on the transformation between colloidal and particulate transparent exopolymer particles (TEP) in seawater; and the effectiveness of a combined pretreatment consisting of coagulation and UF on minimizing TEP fouling of seawater reverse osmosis (SWRO) membranes. Coagulation with ferric chloride at pH 5 substantially transformed colloidal TEP (0.1-0.4) into particulate TEP (>0.4) leading to a better membrane fouling control. Both 50 and 100 kDa molecular weight cut-off (MWCO) UF membranes removed most of particulate and colloidal TEP without the assistance of coagulation, but coagulation is still necessary for better UF fouling control. The improvement of combined SWRO pretreatment with coagulation and 50 kDa UF membranes was not that much significant compared to UF pretreatment with 50 KDa alone. Therefore, the minimal coagulant dosage for seawater containing TEP should be based on the UF fouling control requirements rather than removal efficiency.

Keywords: Coagulation, Fouling, UF pretreatment, TEP, SWRO.

1. Introduction

Seawater reverse osmosis (SWRO) membrane filtration process has been widely applied in seawater desalination globally for a few decades due to its relatively low cost compared to traditional distillation processes (e.g., multi-stage flash (MSF) and multi-effect distillation (MED)) (Ghaffour et al., 2013). However, biofouling of SWRO membranes continues to be the main problem in seawater desalination (Mansouri et al., 2010, Matin et al., 2011).

Transparent exopolymer particles (TEP) have been reported as a major component of biofilms (Bar-Zeev et al., 2009, Berman et al., 2011). TEP are ubiquitous in both sea and fresh waters, and are defined as sticky particles larger than 0.4 μm , mainly composed of acidic polysaccharides that are stainable with alcian blue (Passow 2002b). Algae and bacteria have been generally considered to be the major source of TEP in water ecosystems (Passow 2002a, Wetz and Wheeler 2007), either releasing dissolved TEP precursors during exponential growth (Alldredge et al., 1993, Passow 2002a) or excreting TEP directly via sloughing and lysis of senescent cells (Beauvais et al., 2003). Some studies demonstrated that spontaneous self-assembly of dissolved precursors is a major process of TEP formation (Chin et al. 1998, Passow 2000). In the Red Sea and Arabian Gulf, some desalination plants have been forced to shut down due to serious fouling during an algal bloom period, which may have been attributable to the presence of TEP in seawater (Richlen et al., 2010). A recent pilot study using real Red Sea water as feed has also revealed a severe SWRO membrane fouling where the conventional dual media filtration performance was poor in removing TEP substances (Li et al., 2016). Membrane fouling studies have been extensively conducted using humic substances and algal organic matter (AOM) as model compounds (Panglisch et al. 2008, van de Ven et al. 2008, Villacorte et al. 2015).

However, TEP is different from these model compounds in terms of size and composition. Comparing to humic substances, TEP has a higher molecular weight and more carbohydrates and protein contents (Li et al. 2015). TEP released from bacteria are mainly detected as biopolymers in the liquid chromatography with organic carbon detection (LC-OCD) analysis, whose molecular weight is around 20,000 Da and higher than the 1,000 Da of humic substances (Li et al. 2015). AOM was also proven to be one of the major foulants on SWRO membranes (Villacorte et al. 2013). A significant amount of TEP is present within the AOM, but AOM also includes some other biopolymers and low molecular weight neutrals which are not TEP and not stainable with alcian blue dye (Villacorte et al. 2015). Therefore, the studies on RO membrane fouling control based on AOM removal do not truly reflect the impact of TEP pre-removal on membrane fouling. Due to the composition difference between TEP and other model fouling compounds, a study on the pre-removal of TEP on minimizing SWRO fouling is meaningful. However, membrane fouling caused by TEP and how it can be minimized via TEP pre-removal has not been systematically investigated.

Coagulation followed by ultrafiltration (UF) is currently a common pretreatment practice to prevent SWRO fouling. Most of investigations on using coagulation and UF combination as pretreatment for SWRO membrane fouling prevention have been conducted in terms of dissolved organic carbon (DOC) removal (Kumar et al. 2006, Shon et al. 2008). TEP has been reported to appear on fouled ceramic UF membranes used as SWRO pretreatment (Hamad et al. 2013), and the combination of coagulation and UF has been reported to be efficient for TEP removal in some RO plants' performance evaluation studies (Kennedy et al. 2009, Schurer et al. 2013, Villacorte et al. 2009, Villacorte et al. 2010). However, these studies did not optimize the coagulation and UF for the TEP removal due to the difficulty of changing the operation

parameters in the RO plants. The pretreatment optimization using coagulation and UF was still based on the DOC removal, instead of TEP (Hamad et al. 2013). Because TEP is only part of DOC, using DOC removal to evaluate RO membrane fouling control might underestimate the influence of coagulation and UF on TEP pre-removal. To our knowledge, there is no reported research on the effect of coagulation on aggregating colloidal TEP into particulate TEP. Moreover, the combined effectiveness of coagulation and UF on minimizing TEP fouling on SWRO membranes has not been investigated.

In this study, the effect of coagulation on aggregating colloidal TEP released from marine bacteria and its impact on UF/SWRO membrane fouling were investigated. Variations in the particulate and colloidal TEP concentrations in seawater were determined under different coagulation conditions, and the MFI-UF (MFI: modified fouling index) of different coagulated waters was also determined on two UF membranes having different pore sizes of 50 kDa and 100 kDa to check whether the reduction of colloidal TEP can reduce the fouling potential of the corresponding coagulated water or not.

2. Materials and methods

2.1 Marine bacteria cultivation and BOM harvesting

Bacterial TEP substances were harvested by culturing marine bacteria isolated from the Red Sea. Detail of the isolation and harvesting procedure has been reported elsewhere (Li et al., 2015). Since TEP and TEP precursors can be produced from bacteria, the harvested bacterial organic matter (BOM) included bacterial TEP and its precursors. As reported previously, during marine bacteria growth, different organics were produced, including biopolymers, building blocks and

low molecular weight neutrals. Bacterial TEP and its precursors are mainly biopolymers as detected.

2.2 Feed water quality

The feed water of each experiment is composed of real Red Sea water and isolated BOM. Seawater was collected from the intake pipe located about 2.5 km from King Abdullah University of Science and Technology (KAUST) coastline, Saudi Arabia (Rahmawati et al., 2012). Raw water quality is presented in Table 1. 2.5 mg TOC/L BOM was added to seawater to mimic a high TEP concentration event. This TOC concentration was encountered in Oosterschelde area, South-Western of the Netherlands during high TEP events that coincided with very high fouling potential in UF systems (Schurer et al., 2012). The 2.5 mg TOC/L BOM contained 1.5 mg xanthan gum eq./L particulate and colloidal TEP (analyzed by alcian blue assay).

Table 1: Feed water quality used in this study

	Red Sea water	Red Sea water with TEP
pH	7.9–8.1	7.9–8.1
Turbidity (NTU)	0.75–0.85	1.04–1.15
Conductivity (mS/cm)	59.0–60.1	59.0–60.1
TOC (mg/L)	0.92–1.01	3.41–3.59
Particulate TEP (mg xanthan gum eq./L)	0.25	0.95
Colloidal TEP (mg xanthan gum eq./L)	0.15	0.55

2.3 Coagulation protocol

Coagulation was performed on a standard jar-tester (PB-900). The pH of water samples was first adjusted to 5 with H₂SO₄. Afterwards, since the preliminary UF tests with different coagulated feed water showed that there were no significant differences in terms of UF membrane fouling

when the coagulant dosage was more than 1.0 mg Fe/L, different amounts of coagulants were dosed in the TEP added seawater (0, 0.1, 0.2, 0.5, and 1 mg Fe/L). Besides that, in order to investigate an over dosage of coagulant on the performance of SWRO, 6 mg Fe/L was also tested. After rapid mixing for 1 min at 300 rpm, the coagulated water was analyzed via a spectrophotometric method for TEP, and the MFI-UF_{100kDa} of coagulated water was also determined to evaluate their fouling potential.

2.4 Ultrafiltration protocol

The UF setup used in this study is fully automated. There are two working phases: filtration and backwash. The duration of each phase and the order of phases can be controlled by a LabVIEW program. The UF system was operated at a constant flux mode with on-line transmembrane pressure (TMP) monitoring. The other water quality parameters, such as pH, turbidity, temperature, were measured via sampling, along with TEP reduction. Six types of feed water were prepared for the UF tests (Table 2). Experiments were conducted using two types of membranes: Multibore® PESM inside-out membranes with molecular weight cut-off (MWCO) of 100 kDa and 50 kDa. Each experiment contained 24 cycles, and one cycle included 30-min filtration and 1-min backwash. UF permeate was used for backwash. Experiments were carried out at constant flux of 130 L/(m²h) in filtration mode and 260 L/(m²h) in backwash mode.

Table 2: Different pretreated feed water for UF experiments

	Baseline (-)	TEP added mg xanthan gum eq./L	Coagulant dosed mg Fe/L
UF feed 1	Seawater	1.5	0
UF feed 2	Seawater	1.5	0.1
UF feed 3	Seawater	1.5	0.2
UF feed 4	Seawater	1.5	0.5
UF feed 5	Seawater	1.5	1.0
UF feed 6	Seawater	1.5	6.0

2.5 RO filtration protocol

A Sepa CF system (Sterlitech Inc.) was used for the SWRO membrane filtration in this study. The feed pressure of the filtration system was kept constant at 40 bar by a regulating valve, and the excessive feed water was by-passed back into the feed tank. Cross-flow velocity was kept constant at 0.1 m/s by adjusting the needle valve at the concentrate stream. Concentrate and permeate were both recycled back into the feed tank to keep the feed volume constant. The temperature of feed water was maintained at 20 °C by a thermostat.

1 µm microfiltration (MF) filter was used as a controller to compare the TEP removal efficiency by MF and UF commercial membranes. Since the 50 KDa UF membrane showed a better performance than the other membranes in the preliminary study, this membrane was used in the RO filtration tests. Permeate flux was recorded via a digital balance (TE6101, Sartorius) for 10 minutes at different time intervals, and the collected permeate was recycled back into feed tank after flux measurements. A new membrane was used for each experiment to ensure the identical initial condition of all tests. Before each experiment, the RO setup was cleaned by soaking with 1,000 mg/L NaOCl for one hour and forward flushing with Milli-Q water afterwards. After cleaning, the new membranes were pre-compacted under the experimental conditions for 36 hours, and then the clean water permeability of new membranes was determined to confirm the identical initial membrane permeability. Four types of feed water were prepared for the RO membranes filtration tests (Table 3). The duration of each experiment was 8 days.

Table 3: Different pretreated feed water for RO experiments

Baseline	TEP added	Coagulant dosed	Pre-filtration

	(-)	mg xanthan gum eq./L	mg Fe/L	(-)
RO feed 1	Seawater	1.5	0	MF (1.0 μ m)
RO feed 2	Seawater	1.5	0	UF 50 kDa
RO feed 3	Seawater	1.5	1	UF 50 kDa
RO feed 4	Seawater	1.5	6	UF 50 kDa

2.6 TEP quantification

Particulate and colloidal TEP were measured with a modified spectrophotometric method, reported by Passow and Alldredge (Passow and Alldredge 1995). This method applied alcian blue 8GX as a staining dye. Both particulate TEP ($> 0.4 \mu\text{m}$) and colloidal TEP ($0.1\text{-}0.4 \mu\text{m}$) were quantified with this modified method. Briefly, the water sample was firstly filtered through a $0.4 \mu\text{m}$ polycarbonate filter at a low and constant pressure to avoid deformable particulate TEP being pushed through the filter. Particulate TEP retained on the filter are then stained with pre-filtered ($0.2 \mu\text{m}$) Alcian blue solution made from acetate buffer (pH 4). Secondly, the $0.4 \mu\text{m}$ permeate was filtered again on a $0.1 \mu\text{m}$ polycarbonate filter, and the retained colloidal TEP on $0.1 \mu\text{m}$ filter was stained with Alcian blue solution as well. Afterwards the filters were gently rinsed with clean water to remove excess dye, and then soaked with 80% sulfuric acid for 2 h to dissolve the dye bound to the particles. Finally, absorbance of Alcian blue in the sulfuric acid solution is measured at 750 nm.

In this method, xanthan gum was used as a model compound of TEP for calibration. A 100 mL xanthan gum standard solution of 100 mg/L was prepared. 10 mL of the xanthan gum standard solution was filtered on a $0.4 \mu\text{m}$ filter and the TOC of xanthan gum solution before and after filtration were determined with a TOC analyzer (SHIMADZU). The $\text{TOC}_{0.4\text{retained}}$ could then be calculated by subtracting $\text{TOC}_{\text{before}0.4}$ and $\text{TOC}_{\text{after}0.4}$. The particulate TEP concentrations of different amounts of xanthan gum solution (0, 0.5, 1, 2, 3 mL) were measured with the procedure described above. A linear relationship with a R^2 of 0.99 was observed as follow:

$$UV_{750} = 0.024 \times V_{\text{gum}} + 0.138 \quad (1)$$

$$178 \quad \text{Particulate TEP} = \frac{V_{\text{gum}} \times \frac{\text{TOC}_{0.4 \text{ retained}}}{0.45}}{V_{\text{sample}}} \quad (2)$$

179 where V_{gum} is the volume of xanthan gum standard solution, V_{sample} is the volume of sample to be
 180 analyzed, and 0.45 is the fractional percentage weight of organic carbon in xanthan gum.

181 In terms of the 0.1 μm calibration, the $\text{TOC}_{0.1 \text{ retained}}$ was also determined by measuring the
 182 $\text{TOC}_{\text{after}0.1}$, and then subtracting $\text{TOC}_{\text{after}0.4}$ and $\text{TOC}_{\text{after}0.1}$. The colloidal TEP concentrations of
 183 different amounts of xanthan gum 0.4 μm permeate (0, 0.5, 1, 2, 3 mL) were measured with the
 184 procedure described above. A linear relationship with a R^2 of 0.99 was observed as follow:

$$185 \quad UV_{750} = 0.1 \times V_{\text{gum}0.4} + 0.0 \quad (3)$$

$$186 \quad \text{Colloidal TEP} = \frac{V_{\text{gum}0.4} \times \frac{\text{TOC}_{0.1 \text{ retained}}}{0.45}}{V_{\text{sample}}} \quad (4)$$

187 where $V_{\text{gum}0.4}$ is the volume of xanthan gum standard solution after 0.4 μm filtration.

188 When the 0.1 and 0.4 μm calibration was established, the TEP concentration of samples
 189 could be expressed as micrograms of xanthan gum equivalent (Xeq.) per liter of water.

190

191 2.7 MFI-UF_{100kDa}

192 The Modified Fouling Index (MFI) was originally defined as an index of the fouling potential of
 193 RO feed water (Schipper and Verdouw 1980) for filtration at constant pressure using
 194 membranes with 0.45 mm pore size as:

$$195 \quad MFI = \frac{\eta l}{2 \Delta P A^2} \quad (5)$$

196 where ΔP is the reference pressure value of 2 bar, η is the reference viscosity at 20°C and A is
 197 the reference filtration area of $13.8 \times 10^{-4} \text{ m}^2$.

MFI was further developed into MFI-UF for filtration at constant flux, using ultrafiltration membranes (Boerlage et al., 2004). In constant flux mode, 'I' is the slope of the linear region in a plot of ΔP versus time and is a characteristic of the cake/gel filtration mechanism.

MFI-UF and 'I' represent bulk properties of particles in feed water and therefore reflect variations in water quality characteristics. As such, these parameters can be used to assess the fouling potential of feed water. In this study MFI-UF measured at constant flux through 50 kDa and 100 kDa UF membranes is used as a tool to assess the fouling potential of BOM in the absence or presence of coagulant.

2.8 Liquid Chromatography - Organic Carbon Detection (LC-OCD)

An LC-OCD analysis instrument (DOC-LABOR Dr. Huber) was used in this study to quantify the amount of TEP precursors and investigate their molecular weight distribution (Huber et al., 2011). This instrument consists of three detectors: Organic Carbon (OCD), UV at 254 nm (UVD), and organic nitrogen (OND). The principle of this apparatus is available online at www.doc-labor.de. Water samples were pre-filtered with a 0.45 μm GMF filter (Whatman) prior to LC-OCD analysis. Before analyzing actual samples, a 2,000 μL aliquot of 0.1 mol/L NaOH was injected into the separation column (Toyopearl TSK HW50S, TOSOH Bioscience GmbH, Stuttgart, Germany) for cleaning, lasting for 260 minutes. Following the NaOH cleaning, a 2,000 μL aliquot of the sample was injected for analysis. Afterwards, different fractions of organics were eluted from the column at different retention times. The total retention time used in the sample analyses was 180 minutes.

2.9 Particle size distribution

Particles in (feed and permeate) water samples were characterized according to particle size distribution (PSD) using the Nano Sizer LM20 instrument manufactured by Malvern (Radić et al., 2004). It is used to analyze the range of nano particles typically between 10-1,000 nm depending on particle material. All samples were analyzed in duplicate.

3. Results and discussion

3.1 Optimal pH for seawater coagulation

Raw Red Sea water and Red Sea water with added TEP were coagulated under different conditions, including different FeCl_3 dosages at different pH levels. FeCl_3 showed a maximum DOC reduction at 6.0 mg Fe/L dosage for both seawater and seawater with TEP. At a constant coagulant dosage of 4 mg Fe/L, it was found that pH 5.0 was the optimal value in terms of DOC reduction (Supplementary Fig. S1). Therefore, in this study, feed waters were adjusted to pH 5.0 before coagulation in UF experiments.

3.2 Impact of ferric dosage on the transformation of TEPs

Table 4 shows the particulate and colloidal TEP concentrations of different coagulated waters, respectively. As shown in the Table 4, the particulate TEP concentration increased with an increase in ferric dosage, indicating the positive effect of ferric on forming particulate TEP larger than 0.4 μm . That was probably because the TEP are negatively charged acidic polysaccharides and/or proteins; the presence of cationic coagulant species substantially reduced the electrical double layer on the negatively charged TEP, and thus lowered the repulsion force between them for agglomeration. Consequently, they formed larger particles during coagulation. On the other

hand, it is interesting to note that the colloidal TEP concentration reduced with the increase of ferric coagulant dosage (Fig. 2), which was the opposite of the particulate TEP's variation. This indicated that the colloidal TEPs aggregated under the assistance of coagulant and formed particulate TEP.

However, the increase of coagulant dose from 1.0 mg Fe/L to 6.0 mg Fe/L did not further reduce the colloidal TEP in seawater. Therefore, from an economic point of view, 1.0 mg Fe/L dosage could be defined as an optimal level in terms of maximizing transformation of colloidal TEP (0.1-0.4 μm) to particulate TEP (>0.4 μm).

Table 4: P-TEP and C-TEP concentration after coagulation and UF.

	Feed		50kDa UF permeate		100kDa UF permeate	
	P-TEP mg/L	C-TEP mg/L	P-TEP mg/L	C-TEP mg/L	P-TEP mg/L	C-TEP mg/L
UF feed 1	1.208	0.639	0.001	0.009	0.001	0.009
UF feed 2	1.247	0.314	0.003	0.005	0.003	0.005
UF feed 3	1.272	0.191	0.004	0.002	0.005	0.001
UF feed 4	1.369	0.113	0.005	0.002	0.005	0.001
UF feed 5	1.601	0.030	0.009	0.002	0.009	0.001
UF feed 6	1.636	0.026	0.014	0.002	0.010	0.001

The fractionated organic concentrations of different UF feed waters detected by LC-OCD is shown in Figure 1. Since all samples were pre-filtered with 0.45 μm before being analyzed by LC-OCD, the detected organics can be considered as DOC, including not only biopolymers but also humic substances and low molecular weight acids and neutrals. Previous studies have shown that TEP precursors are mainly composed of polysaccharides and proteins and characterized as biopolymers in LC-OCD chromatograms (Li et al. 2015). As shown in Figure 1, by increasing the coagulant dosage from 0.1 mg Fe/L to 1.0 mg Fe/L, more biopolymers were removed from the feed water. That is because more particulate TEP were formed by the increase of coagulant dosage and were removed during sample pre-filtration. The further increase of coagulant up to

6.0 mg Fe/L was not effective in further removal of biopolymers. However, 6.0 mg Fe/L coagulant dosage removed 260 $\mu\text{g/L}$ more humic substances than the 1 mg Fe/L. Considering the equal removal of biopolymers (TEP precursors), if TEP precursors played a dominant role in RO membrane fouling, a similar RO fouling potential would be exhibited for water treated by either 1.0 or 6.0 mg Fe/L. On the other hand, if humic substance also play a critical role in the RO membrane fouling, 6.0 mg Fe/L should show less fouling than 1.0 mg Fe/L due to more humic substance removal during coagulation. The impact of improved humic substance removal by increasing ferric coagulant dosage up to 6.0 mg Fe/L was evaluated in RO filtration tests (Section 3.6).

Figure 1: Concentrations of different organic matter fractions in UF feed waters.

Regarding the removal of particulate TEP, conventional pre-filtration such as dual media filtration is probably sufficient due to the relatively large size of particulate TEP ($>0.4\mu\text{m}$). However, the colloidal TEP would be difficult to completely remove from the seawater. If these colloidal TEP pass through SWRO pre-treatment, they can deposit/accumulate on the RO

membrane surface and form a fouling layer (Li et al., 2016). Because of TEP's sticky and lectin-like property (Li et al., 2015), if colloidal TEP is formed on the membrane surface, bacteria will attach and grow on it, leading to a further biofilm formation. Therefore, it is also crucial to remove the colloidal TEP as much as possible before the pre-treated seawater enters the SWRO system. The addition of ferric chloride at pH 5.0 substantially shifted the colloidal TEP into particulate TEP, providing easier removal by subsequent membrane filtration. TEPs are composed of polysaccharides and proteins (Li et al., 2015), and they have been reported to be major foulants on UF membranes (Li 2011, van de Ven et al., 2008). When UF is combined with coagulation, the transformation from colloidal to particulate TEP also has the potential to reduce UF membrane fouling.

3.3 Performance of UF membranes

The particulate and colloidal TEP concentrations in UF permeate are also displayed in Table 4. It shows that both UF membranes with 50 kDa and 100 kDa MWCO, respectively, were very effective in removing particulate and colloidal TEP. After UF filtration, almost no particulate TEP appeared in the UF permeate. Although a small amount of colloidal TEP was detected in the UF permeate when the UF feed water was not coagulated or coagulated with a very small dose only (0.1 mg Fe/L), with an increase in coagulant dosage, the colloidal TEP concentration in UF permeate approached zero as well. Since the efficient removal of particulate and colloidal TEP by UF membranes has been achieved, coagulation was not necessary in terms of improving TEP removal by UF membranes, which indicates that UF is a good pretreatment for removing particulate and colloidal TEP before SWRO. Moreover, 50 kDa and 100 kDa membranes did not show significant difference in terms of particulate and colloidal TEP removal efficiency.

Figure 2 shows the TOC concentration of different UF feed water and its corresponding permeates. The TOC concentration of UF feed water decreased with the increase of coagulant dosage. Theoretically, the TOC concentration should be constant for all coagulated water. However, the samples after coagulation contained more big particles, and thus settled down to the bottom of the TOC vials during the analysis process (30 min for each sample). The settlement at the bottom of TOC vials could not be taken by the analyzer for analysis, and consequently the TOC concentration of coagulated UF feed water was underestimated. The higher the coagulant dose, the more big particles formed in seawater and the less TOC concentration will be observed. However, because the UF feed water was kept agitated by magnetic stirring during the UF membrane filtration experiments; the TOC loading for different UF experiments was constant. From Figure 2, we see that the TOC was also significantly reduced after UF membrane filtration, which is consistent with the reduction of TEP substances. Comparing to the identical removal efficiency of TEP, the 50 kDa UF membrane exhibited a slightly higher TOC removal than 100 kDa membrane, likely due to the smaller pore size of the 50 kDa UF membrane enabling more organic carbon rejection. Both particulate ($>0.4\ \mu\text{m}$) and colloidal TEP ($0.1\text{-}0.4\ \mu\text{m}$) are larger than the pore sizes of both 50 kDa and 100 kDa membranes, which confirms the high removal efficiently. Therefore, the 50 kDa and 100 kDa membranes could not be differentiated by TEP removal.

On the other hand, as shown in Figure 3, the feed water turbidity increased from 1 NTU up to 11.5 NTU due to the greater amount of flocs formed by increasing the coagulant dosage. The increase of turbidity after adding coagulants is reasonable given that more coagulant should aggregate more particles. One study reported that a higher coagulant dosage caused a higher turbidity while increasing the removal efficiency by UF (Dong et al., 2014). Although there was

324 a slight increase of turbidity in UF permeate when the coagulant dosage was high, that may have
 325 been due to the presence of unreacted ferric in water and its role in the formation of aggregates
 326 from low molecular weight organics during the UF treatment. However, after UF membrane
 327 filtration in our study, permeate turbidities were substantially reduced to 0.5–1.0 NTU for both
 328 UF membranes.

329
 330 Figure 2: TOC concentration of different coagulated UF feed and corresponding 50 kDa and 100
 331 kDa UF permeates.

Figure 3: Turbidity of different coagulated UF feed and corresponding 50 kDa and 100 kDa UF permeates.

3.4 Fouling potential of different UF feeds (MFI-UF)

Although coagulation seems not necessary for improving TEP removal by UF membranes, it can play an important role in UF fouling control. Figure 4 shows the MFI-UF of different coagulated water on 50 kDa and 100 kDa UF membranes. As shown in the figure, UF feed 1 (seawater with TEP) exhibited the highest MFI-UF value (about, 2300 and 3,750 s/L^2 for 50 kDa and 100 kDa UF membranes, respectively) among all UF feed waters, indicating its higher fouling potential. However, the MFI-UF for both 50 kDa and 100 kDa membranes decreased with an increase in coagulant dosage.

This reduction trend is consistent with the reduction of colloidal TEP in coagulated waters. It indicates that the removal of colloidal TEP substantially reduces UF membrane fouling potential. That is probably because the size of colloidal TEP is smaller than particulate TEP, and thus it can

form a more compact fouling layer on the membrane surface and is easier to block membrane pores than particulate TEP. When the coagulant dosage increased, more colloidal TEP was transformed into particulate TEP, increasing the porosity of the fouling layer. Consequently, the fouling potential was reduced. The reduction of MFI-UF with the increase of coagulant dosage was greater for the 100 kDa membrane than the 50 kDa membrane, indicating a higher improvement by coagulation on fouling control of the 100 kDa UF membrane.

Figure 4: MFI-UF of 50 kDa and 100 kDa UF membranes for different coagulated UF feed water.

3.5 UF membrane fouling

Figure 5 shows the normalized TMP as a function of time for different feed water filtered through 100 kDa and 50 kDa UF membranes during the first and last 4 cycles of experiments.

For both UF membranes, the increase in TMP was reduced by increments of Fe^{3+} dosage. Although the improvement by the coagulant was not very obvious within the first 4-cycle operation, the benefit of coagulation was clearly exhibited at the end of experiments. When there was no coagulation applied, the normalized (fractional) TMP increased up to around 2.5 and 4.9 for 50 and 100 kDa UF membranes, respectively.

The higher normalized TMP increase observed for the 100 kDa membrane than that of the 50 kDa membrane suggested that the former membrane was more exposed to fouling than the latter membrane. Moreover, Figure 6 shows that not only the total fouling but also the hydraulically irreversible fouling of the 100 kDa membrane was higher than for the 50 kDa UF membranes, likely due to the penetration of particles in the larger membrane pores. The particles size distribution of different feed water is shown in Figure 7. The particle size of the main portion of organics in UF feed 1 was around 20-30 nm. On the other hand, the pore size of 100 kDa UF membranes is around 20 nm according to a previous study by (Gille and Czolkoss 2005). Therefore, the particle size was in the range of the 100 kDa membrane pore size. When UF feed 1 was treated, pore blocking might occur for the 100 kDa membranes. The 50 kDa membrane pores are tighter, so most of the particles in UF feed 1 having larger sizes than the pores of the 50 kDa membranes do not penetrate the membrane structure. In this case, a cake layer filtration was likely the main fouling mechanism for the 50 kDa membranes (Ghaffour 2004, Jermann et al., 2007, Li et al., 2011). It has been reported that fouling caused by pore blocking is normally more serious than cake layer (Li et al., 2011). The porosity of a cake layer varies according to the particle size of foulants forming the cake layer (Jermann et al., 2007). The larger particles are, the higher the porosity of cake layer, and thus less fouling on the membranes. Since the particle size after 0.1 mg Fe/L coagulation is larger than 100 nm, which is greater than the pore size of

the membrane (20 nm), the same cake layer could be expected on both UF membranes and thus similar fouling could be observed. However, it is interesting to see that both membranes showed different fouling behavior even after coagulation with 0.1 (UF feed 2) and 0.2 mg Fe/L (UF feed 3). That is probably because the pores of UF membranes are asymmetric, and the pore diameter is not uniform from the top to the bottom. According to the SEM images of the 100 kDa membrane (Supplementary Fig. S2), some of the surface openings on the membrane surface are much larger than 100 nm. That could be the reason why after 0.1 and 0.2 mg Fe/L coagulation, the fouling on the 100 kDa UF membrane was still high compared to the 50 kDa membrane.

Figure 5: TMP as a function of time for different UF feeds through (a) 100 kDa in first 4 cycles; (b) 100 kDa in last 4 cycles; (c) 50 kDa in first 4 cycles; (d) 50 kDa in last 4 cycles.

Figure 6: Hydraulically reversible and irreversible fouling on 50 KDa and 100 kDa UF membranes for different feed water.

Figure 7: Particles size distribution of different UF feed water.

By adding coagulant to the feed, the increase in normalized TMP was substantially reduced for both 50 kDa and 100 kDa UF membranes (as shown in Figure 5). The reduction of

normalized TMP was more prominent for the 100 kDa membrane than the 50 kDa membrane, which was consistent with the results of MFI-UF. When the coagulant was increased up to 0.5 mg Fe/L, the normalized TMP (TMP/TMP_0) for the 100 kDa membranes could be maintained at a constant low value (between 1.25-1.5). Further increments of Fe^{3+} dosage did not improve the fouling control in UF. A similar trend was observed for the 50 kDa UF membrane as well, but the minimal required Fe^{3+} dosage (0.2 mg Fe/L) to obtain good fouling control for the 50 kDa UF membrane was lower than the 100k Da membrane. The reduction of fouling by increasing coagulant dosage is probably because of an increase of particle size in the UF feed water. Figure 7 shows the shift of particle size of different UF feed waters. It can be seen that the particle size increased from 20-30 nm to 0.6-5.0 μm with a coagulant dosage of 6 mg Fe/L. The cake layer formed by larger particles could be more porous and less compact, leading to lower filtration resistance and thus lower fouling.

The minimal coagulant dosage is related with the pore size of the UF membranes and the particle size in feed water. When the coagulant dosage is sufficient to aggregate the colloidal organics into particles with a larger size than the membrane pore size, then it is considered the minimal dosage required for this specific feed water. In general, coagulation can significantly reduce TEP fouling on UF membranes, but the minimal dosage may be case-specific.

3.6 Impact of pretreatments on SWRO performance

Figure 8 shows the normalized flux decline of different feed waters: seawater + TEP after MF (1 μm), seawater + TEP after 50 kDa UF, seawater + TEP after 1.0 mg Fe/L coagulation and 50 kDa UF, and seawater + TEP after 6.0 mg Fe/L coagulation and 50 kDa UF. As shown in the figure, when seawater + TEP after MF was treated by SWRO, normalized flux decreased from

100% to around 49% after eight-day filtration. RO membranes experienced a fast flux decline at the first ten hours (from 100% to around 80%). The flux decline was likely caused by the adsorption of particulate and colloidal TEP smaller than 1 μm on the RO membranes, and indicated formation of a fouling layer on the surface of RO membranes.

However, the TMP for seawater + TEP solution treated by 50 kDa UF filtration only decreased from 100% to 85% within the same time period. Although coagulation could slightly further reduce the flux decline, the improvement is not significant to promote the incorporation of coagulation pretreatment. This indicated that UF was a good pre-treatment choice to remove TEP/TEP precursors, and that coagulation could make it only slightly better. However, the main benefit of coagulation was to reduce the fouling in the UF pretreatment (as explained in section 3.5), which is an important fouling control strategy.

Figure 9 shows the amount of particulate and colloidal TEP deposited on the RO membrane surfaces during different experiments. It can be observed that about 33 $\mu\text{g}/\text{cm}^2$ particulate TEP and 7 $\mu\text{g}/\text{cm}^2$ colloidal TEP deposited on the RO membranes when the RO feed water was only pre-filtered with the 1 μm MF. After UF pretreatment, both particulate TEP and colloidal TEP deposition on RO membranes were significantly reduced. Deposition of P-TEP was reduced from 33 to 11 $\mu\text{g}/\text{cm}^2$ for all the three conditions with UF as pretreatment. Moreover, the deposition of colloidal TEP decreased from 7 $\mu\text{g}/\text{cm}^2$ to around 2 $\mu\text{g}/\text{cm}^2$. When 1 mg Fe/L coagulation was combined with 50 kDa UF, the deposition of colloidal TEP was further reduced to around 1 $\mu\text{g}/\text{cm}^2$. When 6 mg Fe/L coagulation was used, there was almost no colloidal TEP deposition, but the deposition of particulate TEP was still similar to the other conditions. Although 6 mg Fe/L coagulation led to less colloidal TEP deposition on the membrane surface, its fouling on the RO membrane was similar to the 1 mg Fe/L coagulation dose. That is probably

because, compared to colloidal TEP, RO membrane fouling is correlated more with the amount of particulate TEP having a larger size, which covered more surface area of the membrane and contributed to more filtration resistance. Moreover, the different in amount of colloidal TEP between 1 and 6 mg Fe/L coagulation was less than $1 \mu\text{g}/\text{cm}^2$, which is much less than the amount of particulate TEP ($11 \mu\text{g}/\text{cm}^2$).

Particulate and colloidal TEP could be removed by UF pretreatment as discussed in section 3.2, so the deposited TEP on the RO membrane was likely from the aggregation of TEP precursors in RO feed that were then deposited on the membrane, or from the clusters of accumulated TEP precursors (Li et al., 2016).

The results of deposited TEP substances on the RO membranes are consistent with the decline of normalized flux under different pretreatment conditions. It can be supported that 50 kDa UF membranes provide high quality RO feed and the improvement by additional coagulation on RO performance is limited. Considering the cost of increasing coagulant dosage and its corresponding benefits, the coagulant dose should be based on the optimal value for UF fouling control.

It has been believed that the higher coagulant dosage is, the more organics are removed, and thus the less fouling for RO membranes. Our results have shown that when UF is applied as pretreatment of SWRO membranes, the further improvement of coagulation in terms of SWRO fouling control is marginal. However, considering the whole treatment scheme, coagulation is still necessary because of its efficiency in reducing UF fouling. In this case, the only judgement for the minimal coagulant dosage should be the minimal requirement for reducing UF fouling.

Figure 8: Normalized flux declines of RO tests with different feed water, and (b) TEP on fouled RO membranes.

Figure 9: TEP foulants on fouled RO membranes.

4. Conclusions

The impact of coagulation on the transformation between colloidal and particulate TEP in seawater, and the effectiveness of combined pretreatment with coagulation and UF on minimizing TEP fouling of SWRO membranes was first systematically investigated in this study.

The colloidal TEP was transformed into particulate TEP with an increase in ferric dosage up to about 1 mg Fe/L. However, further increase of ferric dosage could only slightly improve the transformation. UF pretreatment alone could successfully remove particulate and colloidal TEP, but suffered from serious TEP fouling. The 50 kDa UF membrane showed less fouling than the 100 kDa membrane because of its tighter pore size, minimizing the occurrence of pore blockage. By incorporating coagulation, fouling of both UF membranes (50 kDa and 100 kDa multibore inside-out PESM membranes) could be controlled at a low level. The critical coagulant dosages were 0.5 and 0.2 mg Fe/L for the 100 kDa and 50 kDa membranes, respectively. UF pretreatment successfully reduced the TEP fouling on SWRO membranes via TEP removal. Although higher coagulant dosage could increase the removal of humic substance, it did not further improve subsequent RO membrane fouling control, which is in contrast with the original expectation: the higher coagulant dosage is, the better RO membrane fouling control will be due to a higher DOC removal. In other words, TEP plays a more important role than humic substance in RO membrane fouling.

This study exhibited the benefits of the use of a combined coagulation-UF process as pretreatment for TEP removal and consequent SWRO membrane fouling control; mainly providing optimal operational conditions for the coagulation-UF-SWRO treatment scheme.

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Supplementary Figure S1: FeCl_3 coagulation optimization for (a) dose scan at ambient pH and (b) pH scan at 4 mg Fe^{3+} /L dosage.

Supplementary Figure S2: SEM images of virgin 100kDa (left) and 50kDa UF membranes (right).

Figure 8: Normalized flux declines of RO tests with different feed water.

Figure 9: TEP foulants on fouled RO membranes.

Highlights

- This study investigated TEP removal efficiency by coagulation-UF pretreatment.
- The effectiveness of combined pretreatment on minimizing UF and SWRO membranes fouling is presented.
- The impact of coagulation on the transformation between colloidal and particulate TEP is studied.
- Pretreated seawater quality was extensively analyzed.
- A critical coagulant dosage was set for each membrane.