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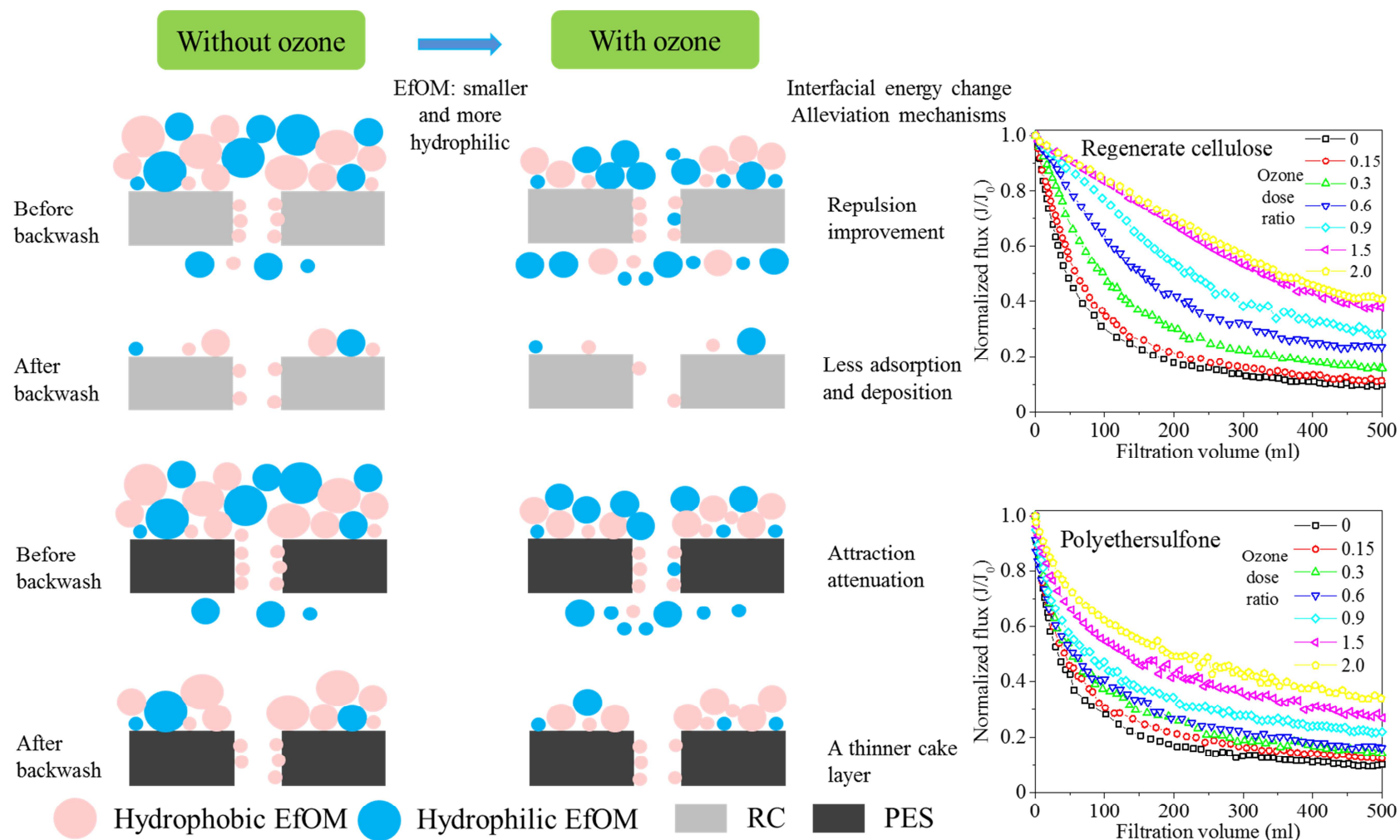
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Reducing ultrafiltration membrane fouling during potable water reuse using pre-ozonation

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ABSTRACT

Wastewater reclamation has increasingly become popular to secure potable water supply. Low-pressure membrane processes such as microfiltration (MF) and ultrafiltration (UF) play imperative roles as a barrier of macromolecules for such purpose, but are often limited by membrane fouling. Effluent organic matter (EfOM), including biopolymers and particulates, in secondary wastewater effluents have been known to be major foulants in low-pressure membrane processes. Hence, the primary aim of this study was to investigate the effects of pre-ozonation as a pre-treatment for UF on the membrane fouling caused by EfOM in secondary wastewater effluents for hydrophilic regenerated cellulose (RC) and hydrophobic polyethersulfone (PES) UF membranes. It was found that greater fouling reduction was achieved by pre-ozonation for the hydrophilic RC membrane than the hydrophobic PES membrane at increasing ozone doses. In addition, the physicochemical property changes of EfOM, including biopolymer fractions, by pre-ozonation were systemically investigated. The classical pore blocking model and the extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theories were employed to scrutinize the fouling alleviation mechanism by pre-ozonation. As a result, the overarching mechanisms of fouling reduction were attributed to the following key reasons: (1) Ozone degraded macromolecules such as biopolymers like proteins and polysaccharides into smaller fractions, thereby increasing free energy of cohesion of EfOM and rendering them more hydrophilic and stable; (2) pre-ozonation augmented the interfacial free energy of adhesion between foulants and the RC/PES membranes, leading to the increase of repulsions and/or the decrease of attractions; and (3) pre-ozonation prolonged the transition from pore blocking to cake filtration that was a dominant fouling mechanism, thereby reducing fouling.

1. INTRODUCTION

Membrane technology in wastewater treatment continues gaining popularity as a result of increasingly stringent discharge criteria and incremental demand for water reclamation (Van Geluwe et al. 2011). Ultrafiltration (UF) works as an effective barrier to remove particles, colloids, micro-organisms and other organic matter on the basis of size (steric) exclusion (Jarusutthirak and Amy 2006, Peter-Varbanets et al. 2011, Zheng et al. 2010b). However, despite the various advantages of UF technology, an inevitable impediment limiting for membrane performance is membrane fouling, which causes a reduction in permeate flux, an increasing filtration resistances and more frequent physical/chemical cleaning (Chang et al. 2015, Porcelli and Judd 2010). Consequently, membrane fouling leads to higher operating costs and shorter membrane life span.

In secondary wastewater effluents, effluent organic matter (EfOM) ubiquitously exists and has been found to be responsible for membrane fouling (Zheng et al. 2014). Particularly, high-molecular weight fractions of EfOM are known to be major foulants. In previous research, such fractions (e.g., molecular weight cut-off > 10 kDa) were identified as biopolymers consisting of polysaccharide-like/protein-like substances using liquid chromatography with organic carbon detector (LC-OCD) combined with fluorescence (Her et al. 2003). The primary EfOM fouling mechanism due to biopolymer is the gel/cake layer formation and pore blockage since such fractions can be retained by membrane based on size exclusion mechanism, causing both reversible and irreversible UF membrane fouling (Filloux et al. 2012, Jarusutthirak et al. 2002, Laabs et al. 2006, Lee et al. 2006). In addition to size, physico-chemical properties of EfOM plays significant roles in membrane fouling. For instance, Zheng et al. (2014) isolated various fractions of EfOM using XAD resin and demonstrated hydrophobic acids might be the most crucial

fractions for the biopolymer fouling. Additionally, proteinaceous EfOM could constitute to a more tightly-bound foulant layer, leading to another important fouling potential (Henderson et al. 2011).

Ozone has been used as an oxidative disinfectant for decades (Shannon et al. 2008). Recently, strong oxidative characteristics of ozone can extend its use to various water treatment applications (von Gunten 2003). For instance, pre-ozonation was proved to be a promising option for mitigating membrane fouling (Cheng et al. 2016, Lehman and Liu 2009, Zhu et al. 2010). In addition, ozone could improve the biodegradability of organic matter; therefore, it would be feasible to integrate ozonation with biological activated carbon filtration as a combined pre-treatment prior to a membrane process to reduce membrane fouling property (Nguyen and Roddick 2010, Siembida-Losch et al. 2015). Furthermore, ozone was demonstrated as an efficient and practical pre-treatment to ameliorate UF membrane fouling in a long-term operation of a pilot-scale system (Lehman and Liu 2009). Previously, three overarching mechanisms of fouling alleviation by pre-ozonation were proposed: (1) decomposition from high molecular weight compounds (biopolymers) into low fractions (Filloux et al. 2012, Lee et al. 2005, Nguyen and Roddick 2010), (2) the increase of hydrophilic nature of EfOM (Van Geluwe et al. 2011, Zhu et al. 2010) and (3) biofouling decrease through microbial disinfection (Yu et al. 2016).

Despite of the existing explanations of fouling reduction mechanisms, other influential factors such as the type of the membrane (Lee et al. 2006, Qu et al. 2014), solution chemistry (Jones and O'Melia 2001) and operating conditions (Kim et al. 2008) are also of importance to scrutinize the fouling reduction by ozonation. Particularly, the interactive force between foulant and membrane surfaces would vary with respect to membrane type (hydrophilic versus hydrophobic) and physicochemical properties of foulants. Recently, extended Derjaguin- Landau- Verwey-

Overbeek (XDLVO) theory was demonstrated to evaluate the membrane-foulant interactions and to predict membrane fouling caused by soluble microbial products (Chen et al. 2012, Wang et al. 2013). Therefore, investigation on the interactions between ozonated EfOM and membrane surface using both the hydrophilic and hydrophobic membrane could contribute to better illuminating the alleviation mechanisms behind the fouling reduction by pre-ozonation, which has yet been reported.

The primary aim of this study is to investigate the impacts of pre-ozonation of secondary wastewater effluent on the extent of hydrophilic and hydrophobic membrane fouling amelioration by pre-ozonation for secondary effluent reclamation. To this end, fouling propensity test under large-range of ozone dose with or without MF pre-treatment was conducted using a flat sheet membrane system. To gain a comprehensive understanding about the effects of pre-ozonation on EfOM fouling behavior, physicochemical properties of EfOM before and after pre-ozonation was systematically assessed by various characterization methods. For instance, classical pore blocking and cake filtration model were employed in attempts to illustrate possible alteration of fouling mechanism by pre-ozonation. Furthermore, the interfacial free energy of adhesion between membrane-foulant and foulant-foulant under different O_3 : dissolved organic carbon (DOC) ratio ($\text{mg } O_3 / \text{mg DOC}$) was calculated using XDLVO theory. The associated interactions between ozonated EfOM and hydrophilic/hydrophobic membrane surface shed light on the elucidation of membrane fouling alleviation mechanisms by pre-ozonation.

2. MATERIALS AND METHODS

2.1 Sample preparation

The biologically treated wastewater secondary effluents before chlorination process from Tres Rio wastewater treatment plant in Tuscon, AZ, U.S.A. were used in this study. During the experimental period, DOC of the secondary effluent (SE) was 6.54-6.62 mg/L with an UV absorbance at 254 nm close to 0.098 (cm^{-1}). The pH of the SE solution was consistently 7.6-7.8. The borosilicate glass filters with 0.7 μm pore size (Whatman, USA) were used to pre-filter the SE before UF experiments to remove the large particles, which gained insight into the effect of pre-filtration on the pre-ozonation and UF process.

2.2 Ozone preparation and experiments setup

Ozone stock solution was prepared by diffusing ozone gas through DI water at 1°C. A concentrated stock solution of dissolved ozone at ~50–60 mg/L was generated using a bench-scale ozone generator (Modular 8HC ozone generator, Xylem Wedeco, Germany). The stock solution was then added into the SE solutions to achieve the desired O_3/DOC ratio from 0 to 2.0 (mg O_3 /mg DOC). The indigo ozone residual method (Rakness et al. 2010) was employed to measure the dissolved ozone concentration and ensure residual ozone in the ozonated SE below the detection limit.

2.3 Dead-end ultrafiltration experiments

Two types of flat-sheet UF membranes with the same molecular weight cut-off (MWCO) of 100 kDa (i.e., a polyethersulfone (PES) membrane (PBHK06210, EMD Millipore Corp., USA) and a regenerated cellulose (RC) membrane (PLHK06210, EMD Millipore Corp., USA) were utilized in this study. The pure water contact angles of the PES and RC membrane were

67.4±2.9° and 22.0±1.1°, respectively. The effective membrane surface of these two types of UF membrane was 28.7 cm². The main characteristics of the membranes were described with details in previous literature (Yang et al. 2014). The PES membrane and the RC membrane exhibit hydrophobic and hydrophilic natures, respectively. Prior to the filtration tests, each virgin membrane was soaked in ultrapure water for 24 h and the water was replaced at least three times during the soaking process. Then, each membrane was rinsed thoroughly by filtering at least 2 L of ultrapure water to remove organic residues and wetting agents on the membrane.

The UF tests were conducted in a filtration cell (Amicon 5123, Millipore, USA) under a room temperature of 23 ± 1 °C. Nitrogen gas with a constant pressure of 14 psi was applied to drive the SE through the membrane in dead-end filtration mode. The volume of filtrate was measured using an electronic balance and automatically recorded every five seconds and converted to flux. Filtration experiment was stopped when 500 mL of permeate was produced. The membrane was then turned over (top-side down) and ultrapure water was passed through the same filter apparatus to backwash the fouled membranes. Each filtration experiment was conducted in triplicate. The methods of flux curves and fouling reversibility were described in detail in the next section.

2.4 Membrane fouling resistance calculations

To evaluate the influence of pre-ozonation on membrane fouling resistances, the resistance-in-series model (Chiang and Cheryan 1986) was employed in this study, as shown in the following equation:

$$R_t = R_m + R_r + R_{ir} = \frac{\Delta P}{\mu J} \quad (1)$$

Where R_t , R_m , R_r and R_{ir} are the total hydraulic resistance (m⁻¹), the intrinsic membrane resistances (m⁻¹), hydraulic reversible resistance (m⁻¹) and hydraulically irreversible resistance (m⁻¹),

respectively; ΔP is trans-membrane pressure; μ is absolute viscosity of the feed water (Pa s) and J is the permeate flux (L/ (m² h)).

R_m was calculated by filtration of 200 ml ultrapure water via Eq. (2) and the average of permeate flux was recorded as J_0 . Then, the feed water of 500 ml non-ozonated or ozonated SE was filtered through the membrane, and the final flux was monitored as J_1 . After that, 50ml ultrapure water was used to backwash the fouled membrane under the pressure of 6 psi in order to determine the irreversible resistance. The membrane was reserved again, and the constant flux J_2 of 200ml ultrapure water was achieved. The R_t , R_r and R_{ir} were calculated using Eqs. (3), (4) and (5), respectively.

$$R_m = \frac{\Delta P}{\mu J_0} \quad (2)$$

$$R_t = \frac{\Delta P}{\mu J_1} \quad (3)$$

$$R_r = \frac{\Delta P}{\mu J_1} - \frac{\Delta P}{\mu J_2} \quad (4)$$

$$R_{ir} = \frac{\Delta P}{\mu J_2} - \frac{\Delta P}{\mu J_0} \quad (5)$$

2.5 Interaction energy analysis

Based on the theory of XDLVO theory, foulant-foulant interaction energy of cohesion (ΔG_{131}) and foulant-membrane interaction energy of adhesion (ΔG_{132}) were quantified to interpret membrane fouling alleviation mechanism caused by pre-ozonation (Chen et al. 2012, Subhi et al. 2012). The interfacial free energy of cohesion respects the interaction free energy per unit area when two surfaces of the same material are immersed in aqueous environment and brought into contact (Chang et al. 2015). Additionally, the interfacial free energy of adhesion per unit area

signifies the affinity between the foulant and the membrane surface (Wang et al. 2013). The detailed presentation of the method can be found in previous literature (Li et al. 2014b) and the Supplementary material. The surface tension parameters of the foulants and RC/ PES membrane surfaces were determined by three probe liquids with known surface tension characteristics. In this study, diiodomethane (Sigma-Aldrich, USA), glycerol (Sigma-Aldrich, USA) and ultrapure water. The contact angles were measured using a contact angle goniometer (Ramé-Hart model 250 Instrument Co., Ltd., USA) according to the standard sessile drop method.

The probe liquids with a 2 μL volume were dropped on the pre-dried membrane surfaces using a microsyringe. At least six measurements were conducted at randomly selected locations for each membrane sample.

2.6 Fouling mechanism analysis

The fouling mechanism was observed to alter from initial pore blocking to cake layer formation, during ultrafiltration of biopolymer-containing secondary effluent (Zheng et al. 2010a). Therefore, it is invaluable to assess the fouling mechanism change caused by pre-ozonation. In order to affirm this, graphical analysis of classical pore blocking model was employed using the following equation:

$$\frac{d^2t}{dV^2} = k \left(\frac{dt}{dV} \right)^n \quad (6)$$

Where t is the filtration time (s), V is the cumulative volume (m^3), k is the fouling coefficient. The classical pore blocking model can be expressed by the fouling behavior index n with dimensionless number: $n=2$ for complete pore blocking, $n=1.5$ for standard pore blocking, $n=1.0$ for intermediate pore blocking and $n=0$ for cake layer formation (Huang et al. 2008). The value of n can be obtained graphically (Park et al. 2017). The derivatives for experimental flux data were widely

used to identify fouling mechanism by the logarithmical plot of d^2t/dV^2 against dt/dV (Byun et al. 2011, Lee et al. 2013, Zheng et al. 2009a), which can be calculated as follows:

$$\frac{dt}{dV} = \frac{1}{JA} \quad (7)$$

$$\frac{d^2t}{dV^2} = -\frac{1}{J^3 A^2} \frac{dJ}{dt} = \frac{1}{A} \frac{d(1/J)}{dV} \quad (8)$$

Where A is the membrane surface area (m^2) and J is the filtrate flux (m/s).

2.7 Analytical methods

Dissolved organic carbon (DOC) concentrations were determined by a Shimadzu Total Organic Carbon (TOC) Analyzer (Shimadzu Corp., Japan). UV spectra and fluorescence excitation-emission matrices (FEEMs) were measured by a fluorescence spectrophotometer (Aqualog, Horiba, USA). Normalized total fluorescence (TF) and regional integration methods was employed in this study as previous work described (Chen et al. 2003). Apparent molecular weight (AMW) fractionation of dissolved organic matter was conducted by RC membranes with nominal molecular weight cutoffs of 3k, 10k, 30k and 100k Da. The protein content in the SE solution was measured by a modified Bradford method, called the Pierce™ Coomassie Plus (Bradford) (ThermoFisher, USA) with bovine serum albumin (BSA) (Jackson ImmunoResearch, Laboratories, INC) as the standard (Yu et al. 2014). Polysaccharides were also calculated using the phenol-sulfuric method, and glucose (Sigmaaldrich, USA) was used for the calibration (DuBois et al. 1956). In addition, a scanning electron microscope (SEM, Hitachi S-4800, Japan) was used to observe the surface morphology of fouled membrane, with sputter coated with platinum until a reduction in charging was observed (Hummer 6.2, Anatech, USA).

3. RESULTS AND DISCUSSIONS

3.1 Flux curves

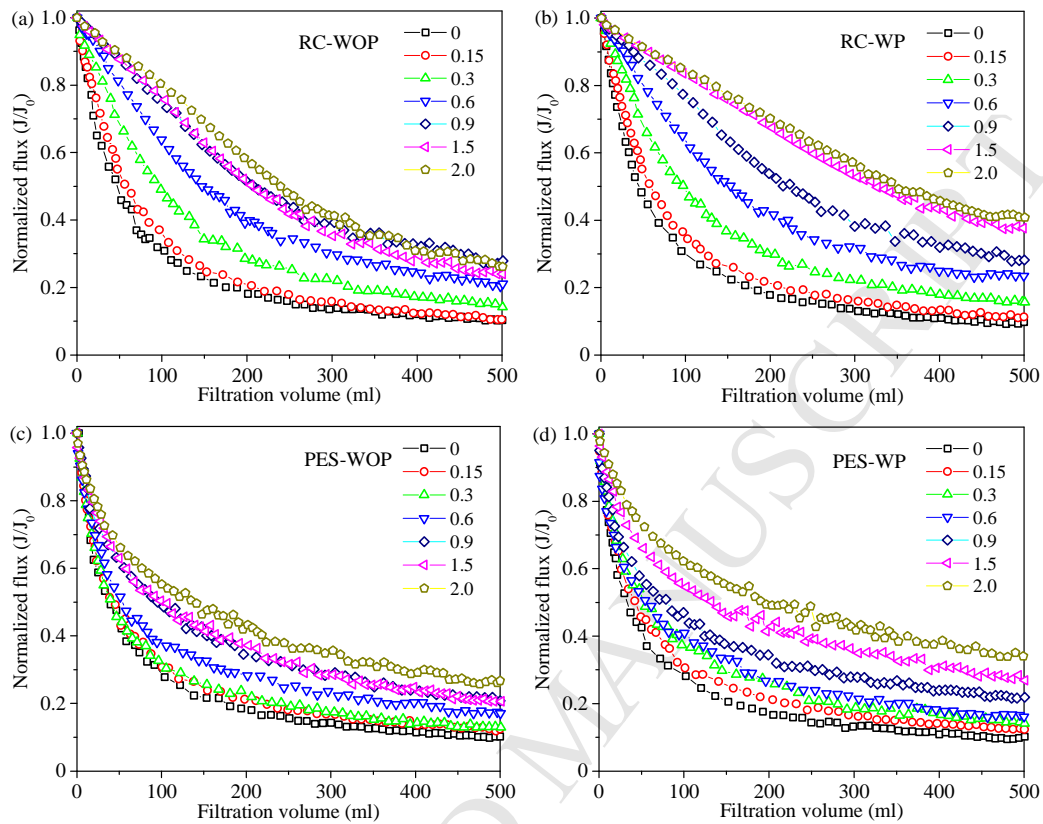


Fig.1 Effect of O_3 :DOC ratio on normalized flux decline during the UF of secondary effluent: (a) RC membrane without 0.7 μ m pre-filter (RC-WOP), (b) RC membrane with 0.7 μ m pre-filter (RC-WP), (c) PES membrane without 0.7 μ m pre-filter (PES-WOP), (d) PES membrane with 0.7 μ m pre-filter (PES-WP). WOP: without pre-filtration, WP: with pre-filtration

Fig. 1 illustrates the impacts of pre-ozonation on the flux for the hydrophilic RC and hydrophobic PES membranes. It was shown that increasing O_3 :DOC ratio dramatically alleviated permeate flux decline for the both RC and PES membranes, which is consistent with the results during the microfiltration of pre-ozonated and coagulated SE (Lehman and Liu 2009). Interestingly, the feed water without ozonation caused the similar trend of normalized flux decline

for the both RC and PES membranes while the ozonated SE ($\text{mg O}_3/\text{mg DOC}$ ratio > 0.3) caused greater flux enhancement for the RC membrane than the PES membrane at the corresponding filtration time. Since molecular weight alteration of EfOM by ozonation and resulting EfOM fractions were expected to have similar extent of size exclusion, the different extent of flux enhancement by ozonation was likely due to the difference of physico-chemical properties between the hydrophobic membrane and hydrophilic membrane, which will be further elucidated based on XDLVO theory in Section 3.6. By comparing the flux curves between feed waters with and without pre-filtration (Fig. 1(a) versus Fig. 1(b) and Fig. 1(c) versus Fig. 1(d)), the ozone exhibited greater extent of flux enhancement as increasing $\text{O}_3\text{:DOC}$ ratio for the both RC and PES membranes with pre-filtration. This was possibly because particulate matter ($>0.7\ \mu\text{m}$) consumed ozone more rapidly than smaller fractions of EfOM, therefore reducing the overall efficacy of ozone for EfOM degradation. In addition to physico-chemical property, size change of EfOM can be an important factor of fouling reduction by pre-ozonation since the size of foulant relative to membrane pore size is a critical parameter governing the membrane fouling mechanisms (Lin et al. 2009, Wang et al. 2007). Therefore, the effects of pre-ozonation on the EfOM removal and the molecular weight distribution will be presented in the subsequent section to further explain the fouling behavior of RC and PES membranes.

3.2 Effects of pre-ozonation on EfOM removal and MW alteration

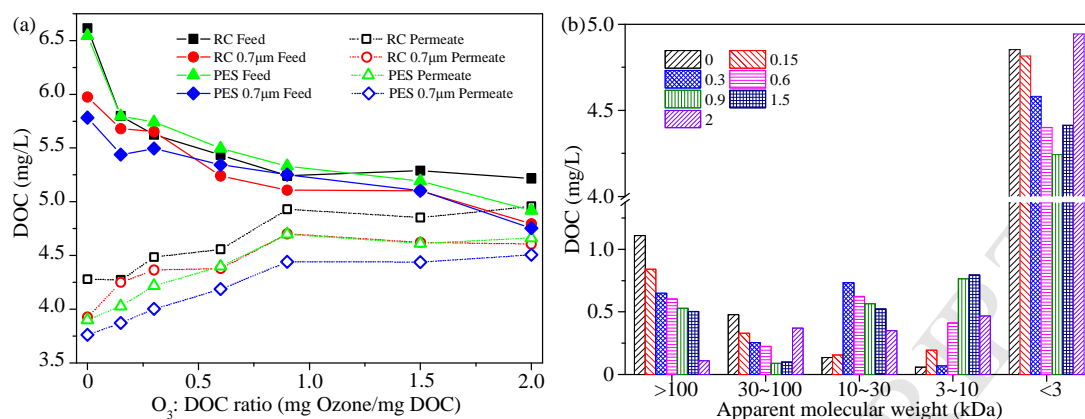


Fig. 2 Effect of pre-ozonation on the DOC values of feed and filtrate of RC and PES membrane with or without 0.7 µm pre-filter (a) and apparent molecular weight (AMW) composition of EfOM after prefiltration with 0.7 µm filter under various O₃:DOC ratio (b).

The DOC concentrations of the feedwater and the permeate for the RC and PES membrane are shown in Fig. 2(a). It was observed that the increased O₃:DOC ratio reduced the DOC values of SE (i.e., feed water), but increased those of UF filtrates, indicating that the amount of EfOM retained by UF membranes was reduced by pre-ozonation. The DOC values of feed water of RC membrane descended from 6.0 to 4.8 mg/L with pre-filtration, however, those of RC membrane permeate increased from 3.9 to 4.6 mg/L, when ozone dose ratio increased from 0 to 2.0 mg O₃/mg DOC. This result was consistent with the effect of pre-ozonation on the UF membrane fouling study previously conducted with a natural water source and model organic foulant (Cheng et al. 2016). It was found that the DOC concentrations of humic acid (HA), sodium alginate (SA), BSA and surface river water UF permeate were augmented with the increase of ozone dose. This phenomenon was ascribed to that ozone decomposed the macromolecules into smaller molecules that penetrated through the membrane pores. Furthermore, ozonation resulted in the greater extent of EfOM penetration through the RC membrane than the PES membrane.

In order to scrutinize alteration of molecular weight of EfOM by ozonation, AMW distribution of EfOM under various O₃:DOC ratio was demonstrated in Fig. 2(b). The cumulative

molecular weight distribution of biopolymer against various O_3 :DOC ratio was also shown in Fig. S1(b). The EfOM in the raw water exhibited a bimodal distribution of DOC with a majority of EfOM having a MW less than 3 kDa and greater than 30 kDa. The DOC value of the large molecules with the AMW greater than 100 kDa decreased at the elevated ozone dose, which was consistent with the results by Zhu et al (2010). Similar results were also reported that colloidal EfOM or biopolymer fraction detected with LC-OCD was degraded by ozone (Filloux et al. 2012, Lehman and Liu 2009). The EfOM with 30k–100kDa of AMW displayed the similar decreasing trend of DOC, but substantial DOC increase was found at 2.0 of O_3 :DOC ratio. In contrast, the formation of smaller molecules was found for 3–30 kDa of AMW. Even if the fouling behavior is a result of mixture effects of various sizes of molecules, the subsequent decreasing trend of DOC for high molecular-weight EfOM (AMW>100kDa) and the extent of fouling as increasing ozone dose, it would be reasonable to postulate that the macromolecule and its degradation by ozonation play important roles in fouling reduction. It was widely proved that the reduction of macromolecules particularly biopolymer fraction by ozonation played a key role in the membrane fouling mitigation (Filloux et al. 2012, Lehman and Liu 2009, Nguyen and Roddick 2010). Therefore, the reduction of biopolymers such as protein and polysaccharide will be investigated in the following section.

3.3 Biopolymer and fluorescent organic matter reduction by pre-ozonation

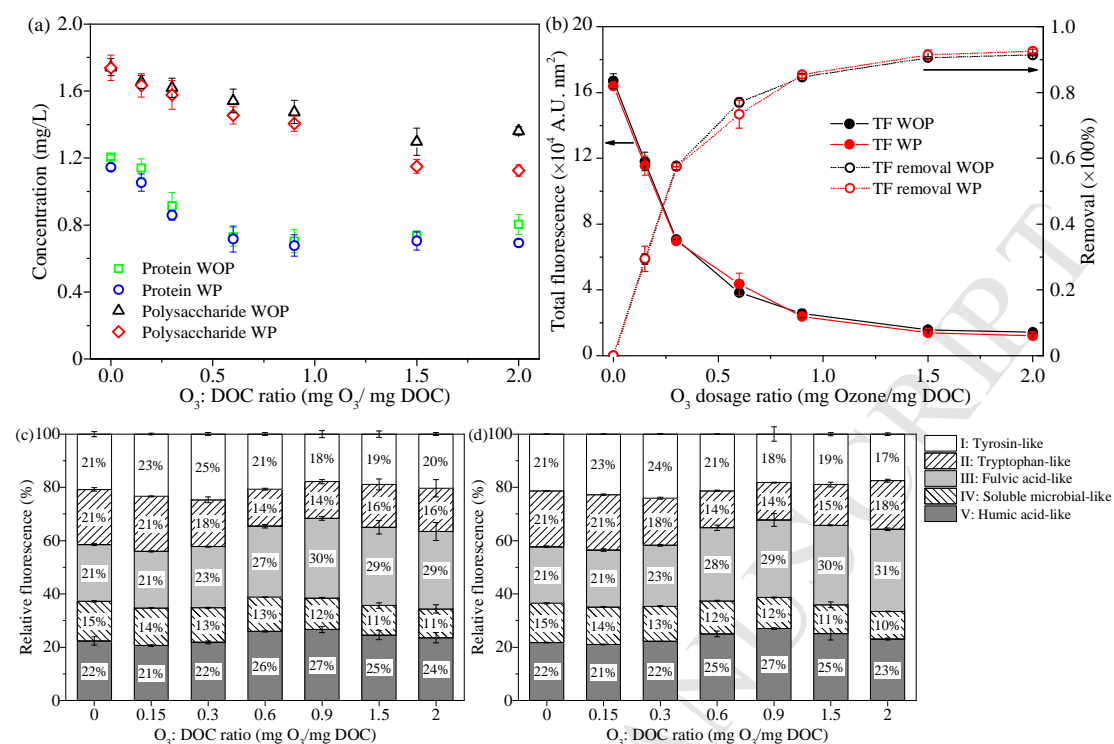


Fig. 3 Effect of pre-ozonation at various O_3 :DOC ratio on protein and polysaccharide removal (a), total fluorescence removal (b), relative fluorescence integrated in each operationally-defined excitation/emission wavelength region without 0.7 μm filter pre-filtration (c) and with 0.7 μm filter pre-filtration (d). WOP: without pre-filtration, WP: with pre-filtration.

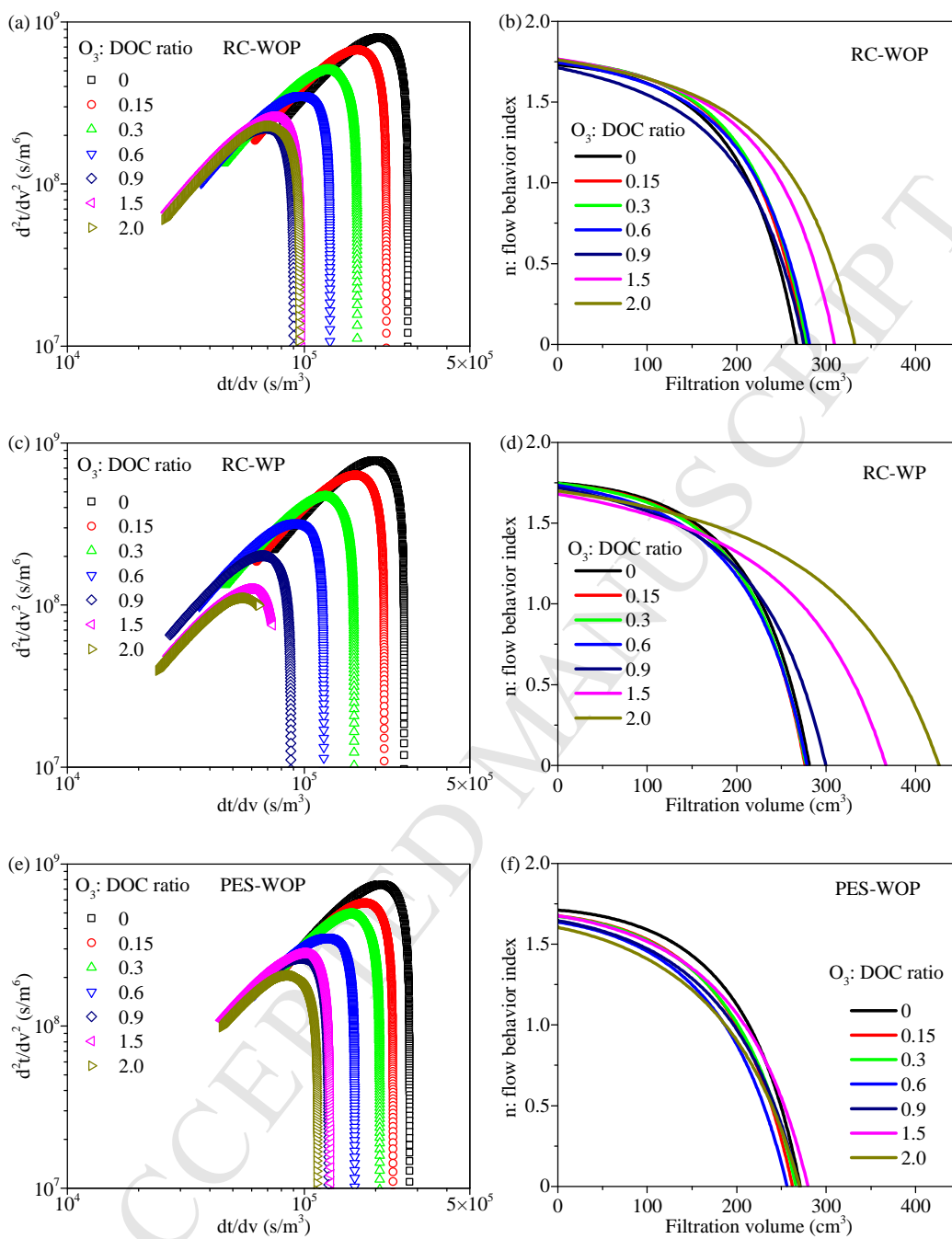
Proteins and polysaccharides were identified to be the major constituents of macromolecules (i.e. biopolymer or colloid) in the algal organic matter (Lee et al. 2006) and secondary effluent (Zheng et al. 2009b). Moreover, it was testified that they were highly responsible for the membrane fouling (Fonseca et al. 2007, Siembida-Losch et al. 2015). Fig. 3(a) shows proteins and polysaccharides concentrations in the SE under different O_3 :DOC ratio with or without pre-filtration. Proteins were detected at lower concentrations than the polysaccharides in the SE. However, they were more readily oxidized by ozone than the polysaccharides. About 41% of

proteins were removed under an O_3 :DOC ratio of 0.9 mg O_3 /mg DOC with pre-filtration while only 19% of polysaccharides were reduced. It was presumably ascribed to that aromatic amino acidic fractions of proteins (Cataldo 2003) reacted with O_3 with a greater rate than glycosidic linkages of polysaccharides (Wang et al. 1999). Pre-filtration with 0.7 μ m filter enhanced the reduction of polysaccharides during the ozonation process, especially at the high O_3 :DOC ratio, resulting in the greater extent of flux decline alleviation (Fig. 1). However, pre-filtration exerted minor influence on the decrease of proteins. Interestingly, the removal of proteins and polysaccharides was slightly deteriorated at 2.0 O_3 :DOC ratio without pre-filtration. This phenomenon was likely caused by that protein and polysaccharide could be released from microorganisms that can be rejected by 0.7 μ m pre-filter at a such high concentration since ozone have a potential to decrease membrane integrity of bacteria cells (Czekalski et al. 2016).

The hydrophobic interaction of extracellular polymeric substances (EPS) including polysaccharides and polymers with membranes plays a major role in the adsorptive deposition of foulants (Su et al. 2014). In order to identify the impacts of hydrophobicity of NOM, fluorescence spectroscopy was employed quantitatively and qualitatively in this study. According to Chen et al., integrated fluorescence (i.e., TF) exhibited positive correlation with hydrophobicity of NOM (Chen et al. 2003). Fig. 3(b) shows the significant reduction of the normalized TF as increasing O_3 :DOC ratio: over 81% reduction at O_3 :DOC ratio greater than 0.9 mg O_3 /mg DOC. Based on the regionally integrated fluorescence intensities under the five specific excitation-emission regions in Fig. 3(c and d), aromatic proteins, i.e. tyrosine-like (Region 1) and tryptophan-like (Region 2), and SMP-like matter (Region 4) were attenuated to the greater extent compared to fulvic-like (Region 3) and humic-like (Region 5). This result is in accordance with the observations

by Zhu et al. (2010) and Park et al. (2017) during the ozonation process of secondary effluent and the surface water brine from a nanofiltration system, respectively. The greater removal of fluorophores at Region 1, 2 and 4 was attributed to their large size fractions (AMW>10k Da) observed from size-exclusion chromatography with a fluorescence detector, which had greater reactivity with ozone (Park et al. 2017). Ozone preferentially reacts with electron-rich moieties such as aromatic rings of NOM particularly with large molecule weight (Westerhoff et al. 1999). Consequently, pre-ozonation can reduce the hydrophobicity of EfOM through cleavage of the aromatic rings and carbon-carbon double bonds, thereby reducing fouling potential of EfOM. Later in this article, the change of the EfOM hydrophobicity caused by ozonation was further demonstrated based on the XDLVO theory.

3.4 Fouling alleviation mechanisms by pre-ozonation



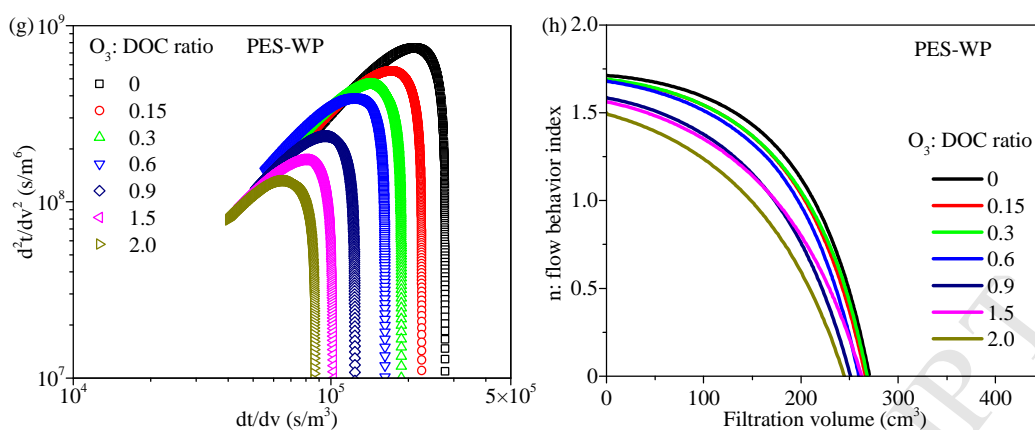


Fig. 4 Characteristic curves reflecting fouling alleviation mechanism by pre-ozonation at different O₃:DOC ratios for secondary effluent fouling: (a) RC-WOP: RC membrane without 0.7 μm pre-filter, (c) RC-WP: RC membrane with 0.7 μm pre-filter, (e) PES-WOP: PES membrane without 0.7 μm pre-filter, (g) PES-WP: PES membrane with 0.7 μm pre-filter and the respective n flow behavior index against filtration volume (b), (d), (f) and (h).

To gain an insight into the influences of pre-ozonation on the fouling mechanisms for the hydrophilic and hydrophobic membranes, characteristic curves based on the classical pore blockage-cake filtration model were calculated and shown in Fig 4 (a, c, e and g). It is noted that larger values of both dt/dV and d^2t/dV^2 were caused by lower initial flux and yielded by the faster flux decline (higher value of dt/dV means longer filtration time for larger filtrate volume) (Lee et al. 2013). Ozonation noticeably reduced the values of both dt/dV and d^2t/dV^2 in the characteristic curves as increasing O₃:DOC ratio for the both hydrophilic and hydrophobic membranes. This finding clearly demonstrated that pre-ozonation altered the fouling mechanisms. It was confirmed that the biopolymer in the SEs loaded to membranes surface played a key role on the transition of fouling mechanism from complete pore blocking to cake filtration according to mechanistic interpretation (Zheng et al. 2009a). Consequently, ozone decomposed the macromolecules

including biopolymers of EfOM as discussed earlier, resulting in a significant change of membrane fouling mechanisms.

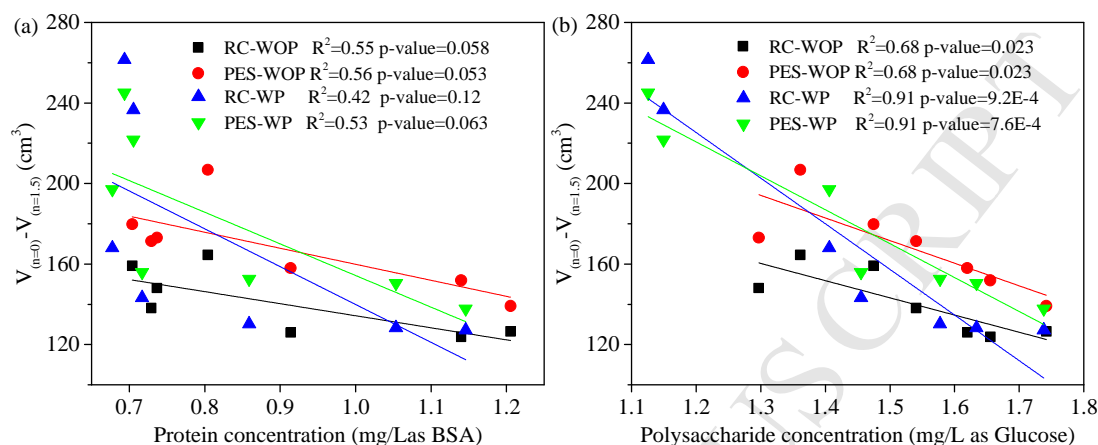


Fig. 5. The linear correlation of the filtration volume required for the transition from standard pore blocking to cake filtration ($V_{(n=0)} - V_{(n=1.5)}$) with protein concentration (a) and polysaccharide concentration (b). RC-WOP: RC membrane without 0.7 μ m pre-filter; RC-WP: RC membrane with 0.7 μ m pre-filter; PES-WOP: PES membrane without 0.7 μ m pre-filter; PES-WP: PES membrane with 0.7 μ m pre-filter. WOP: without pre-filtration, WP: with pre-filtration

The plots of flow behavior index n in Fig 4(b, d, f and h) provides a clear graphical demonstration of the effects of pre-ozonation on pore blockage, cake filtration, and the transition of these mechanisms. All the curves in Fig. 4(b and d) exhibited the initial n values close to 1.7, which indicates the dominance of standard or complete blocking mechanisms for the early flux decline. It was shown that more filtration volume was required for transition from pore blocking mechanism to cake filtration mechanism for RC membranes. Interestingly, the volume required for the transition from standard pore blocking to cake filtration ($V_{(n=0)} - V_{(n=1.5)}$), named “transition volume” hereinafter) was statistically correlated with the concentration of polysaccharide whereas

polysaccharide concentration was statistically significant (i.e., p -values < 0.05) (Fig. 5), indicating that polysaccharide played significant roles in the fouling mechanism transition. This finding is in agreement with previous research that polysaccharide is a major foulant of intermediate fouling layer that affects the formation of consecutive cake layer formation (Metzger et al. 2007). The hydrophobic PES membrane exhibited the smaller transition volume than the hydrophilic RC membrane (Table S1). This infers that hydrophobic membrane filtration of ozonated SE seemed more likely to be governed by cake layer mechanisms with earlier development of cake layer compared to the raw SE.

3.5 Reversibility of membrane fouling

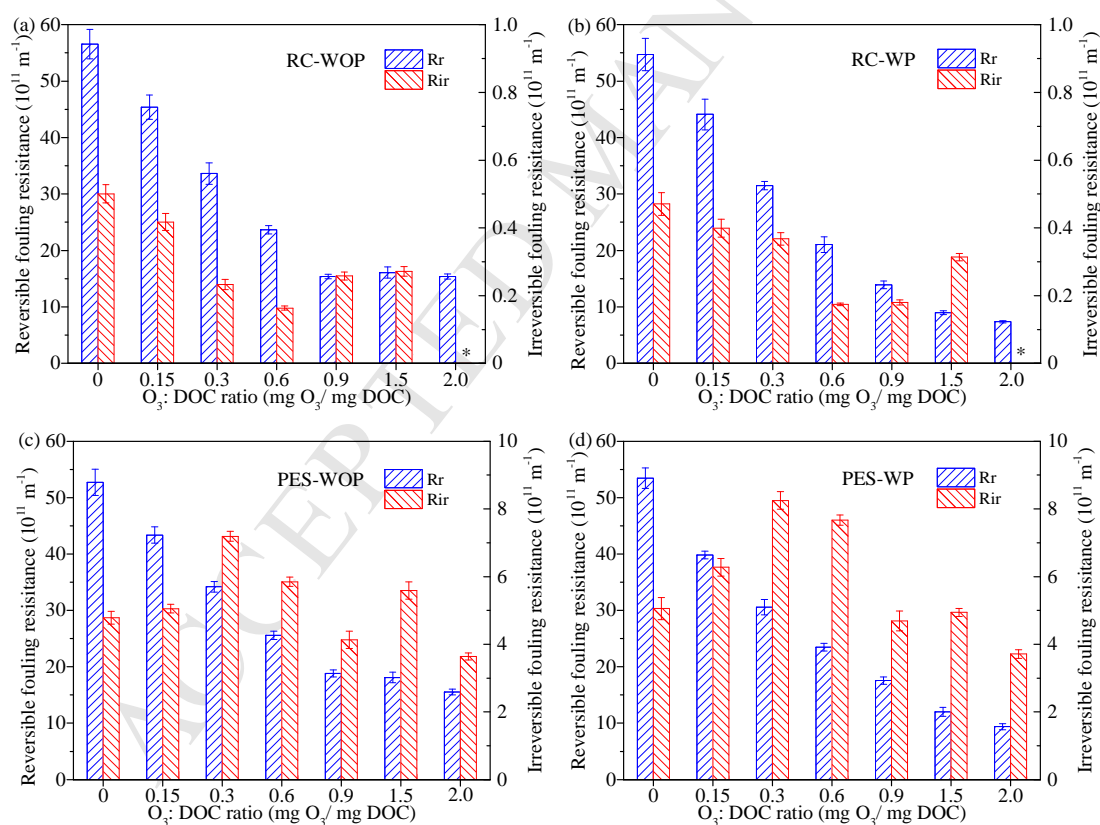


Fig. 6 Effect of O_3 :DOC ratio on UF fouling resistances: (a) RC membrane without 0.7 μm pre-filter (RC-WOP), (b) RC membrane with 0.7 μm pre-filter (RC-WP), (c) PES membrane without 0.7 μm pre-filter (PES-WOP), (d) PES membrane with 0.7 μm pre-filter (PES-WP). Note

that the irreversible fouling resistance marked with asterisk was slightly below zero.

Reversibility of RC and PES membrane fouling during UF of original secondary effluent and ozonated secondary effluent was compared and shown in Fig. 6. It was shown that increasing O_3 :DOC ratio reduced the reversible fouling resistances for RC and PES membranes with or without pre-filtration. The irreversible resistance of RC membrane decreased after pre-ozonation compared to that of the control, and it was completely removed at 2.0 ozone dose ratio. The change in fouling propensity caused by pre-ozonation can be closely related to the change of EfOM physicochemical characteristics. The removal of biopolymers and the reduction of hydrophobicity of EfOM both benefited the membrane fouling propensity. The attachment of foulant on the RC membrane was limited due to the improvement of hydrophilic nature of EfOM, which induced the alleviation of RC (hydrophilic membrane) fouling resistances. Generally, the membrane fouling resistances were better alleviated by pre-ozonation for the RC membranes compared to the PES membranes. This observation was agreed with previous studies for the UF of model organic matter and extracellular organic matter (EOM) from algae (Li et al. 2014a, Qu et al. 2014). It was reported that hydrophobic membrane sustained severer reversible and irreversible fouling than hydrophilic membrane during the filtration of HA, SA, BSA and EOM. The hydrophobic interactions between ozonated EfOM and hydrophobic PES membrane surfaces, leading to hydrophobic adsorption of EfOM on the membrane. Interestingly, PES membranes showed higher irreversible fouling resistance at 0.15–0.6 O_3 :DOC rations compared to the control. This effect of hydrophobic interaction change by ozonation on the extent of fouling was further scrutinized by interfacial energy analysis in the following section.

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3.6 Interaction Energy Analysis

Table 1. Free energy of cohesion (mJ/m^2) of the EfOM after pre-ozonation at various O_3 :DOC ratio

with pre-filtration

O_3 : DOC ratio	γ^{LW}	γ^+	γ^-	γ^{AB}	γ^{TOT}	$\Delta G_{131}^{\text{LW}}$	$\Delta G_{131}^{\text{AB}}$	ΔG_{131}
0	41.53	0.01	19.74	0.63	42.16	-6.30	-12.09	-18.40
0.15	45.44	0.57	22.39	7.15	52.59	-8.58	-5.45	-14.04
0.3	44.68	0.15	13.52	2.84	47.52	-8.12	-25.59	-33.72
0.6	41.94	0.54	30.03	8.08	50.01	-6.53	7.42	0.89
0.9	46.63	2.10	47.92	20.07	66.70	-9.33	26.97	17.64
1.5	45.35	0.75	32.55	9.89	55.24	-8.53	10.97	2.44
2.0	46.60	2.85	64.03	27.04	73.64	-9.31	39.67	30.37

Table 2 Free energy of adhesion (mJ/m^2) between EfOM and RC and PES membranes after

pre-ozonation at different O_3 :DOC ratios with pre-filtration

O_3 : DOC ratio	$\Delta G_{132}^{\text{LW}}$	$\Delta G_{132}^{\text{AB}}$	ΔG_{132}	O_3 : DOC Ratio	$\Delta G_{132}^{\text{LW}}$	$\Delta G_{132}^{\text{AB}}$	ΔG_{132}
RC 0	-7.43	13.77	6.34	PES 0	-8.09	-10.93	-19.02
RC 0.15	-8.67	13.68	5.01	PES 0.15	-9.44	-7.72	-17.16
RC 0.3	-8.44	5.86	-2.57	PES 0.3	-9.18	-16.90	-26.08
RC 0.6	-7.56	20.29	12.73	PES 0.6	-8.23	-1.54	-9.77
RC 0.9	-9.04	30.19	21.15	PES 0.9	-9.84	11.27	1.43
RC 1.5	-8.64	21.77	13.13	PES 1.5	-9.41	0.48	-8.93

RC 2.0	-9.03	38.71	29.69	PES 2.0	-9.83	20.50	10.68
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Table 1 lists the surface energy parameters and the interfacial free energy of cohesion of non-ozonated and ozonated EfOM. The surface tension parameters and free energy of cohesion for the RC and PES membranes are shown in Table S2. The values of electron donor components (γ^-) were gradually elevated with increasing O₃:DOC ratio as a result of the increase of carboxylate of EfOM during the pre-ozonation process (Zhu et al. 2010). Carboxylic acidic groups of organics can be fully deprotonated and mainly negatively charged in a neutral pH (Wang et al. 2013). Hence, the produced carboxylic acidic groups can enhance electron donating capacity, thereby increasing hydrophilicity (equivalently, increasing γ^-). Pre-ozonation increased the acid-base interaction energy (ΔG_{131}^{AB} and ΔG_{132}^{AB}), which indicates that acid–base interaction played a more important role than Lifshitz-van der Waals interaction did in the ozone-control regime. Moreover, the ΔG_{131} values presented an ascending trend from -18.40 mJ/m² to 30.37 mJ/m² along with the increase in O₃:DOC ratio. A negative value for ΔG_{131} indicates thermodynamic instability (i.e. attractive to each other) whereas a positive value indicates thermodynamic stability for repelling each other. The increase in the ΔG_{131} values indicated that pre-ozonation transformed the hydrophobic nature of EfOM into the hydrophilic, which were expected to lessen the hydrophobic adsorption between the foulant and membranes, which is in an agreement with our results regarding normalized TF (Section 3.3).

The analysis of interactions energy between membrane and EfOM can provide fundamental insights into the mechanisms of the fouling alleviated by pre-ozonation. The values of the interfacial free energy of adhesion between the membranes and the foulant (ΔG_{132}) are displayed in Table 2. The values of ΔG_{132} between RC/PES membrane and raw EfOM were 6.34 and -19.02

mJ/m², respectively. The positive ΔG_{132} indicates repulsive interactions between raw EfOM and RC membrane whereas the attractive interactions was expected for PES membrane (i.e., negative ΔG_{132}). The similar observation was reported that the values of ΔG_{132} for another type of hydrophilic membrane such as cellulose acetate and hydrophobic PES membrane when investigating their interactions with HA with Ca²⁺ (Chang et al. 2015). The value of ΔG_{132} between RC membranes and EfOM was reduced from 6.34 mJ/m² to -2.57 mJ/m² at low O₃:DOC ratio from 0 to 0.3. However, ΔG_{132} turned into an increasing trend from 12.73 to 29.69 mJ/m² when O₃:DOC increased from 0.6 to 2.0, indicating the increased repulsive interactions between the EfOM and RC membranes. The repulsive interactions between RC membranes and foulant were enhanced at high O₃:DOC ratio, resulting in the reduction of both hydraulically reversible and irreversible membrane fouling (Fig. 6). Subhi et al. (2012) reported similar results that higher foulant deposition on the membranes was attributed to the reduction of repulsions between model organic foulant or wastewater organic matter and membrane surfaces. The attachment or deposition potential of foulant was determined by interfacial free energy of adhesion between foulant and membrane (short-range non-electrostatic interactions).

The interfacial free energy of adhesion of PES membranes exhibited lower values than those of RC membranes with respect to non-ozonated and ozonated EfOM (Table 2). It was indicated that the PES membranes had larger attractive or less repulsive interactions with the EfOM compared to RC membranes. Consequently, EfOM had a greater attachment affinity to the PES membranes than RC membranes after pre-ozonation, causing greater foulant adsorption on the PES membrane surface. This finding was consistent with lower flux or higher total membrane fouling resistances for PES membranes in Fig. 6. Pre-ozonated EfOMs were still characterized to

be hydrophobic at low O_3 :DOC ratio (<0.6) (i.e., negative values of ΔG_{131} in Table 1). Additionally, hydrophobic substances demonstrated strong attraction with hydrophobic membrane (Chen et al. 2012). As a result, PES membranes sustained severe irreversible membrane fouling at the O_3 :DOC ratio from 0.15 to 0.6, due to relatively low ΔG_{132} . The irreversible attachment of foulant to the hydrophobic membrane surface was further promoted due to their attractions. At O_3 :DOC ratio (0.9–2.0), the irreversible membrane fouling was mitigated to some extent compared to the control (i.e., no ozonated SE) due to the improvement of repulsive interactions between EfOM and PES membranes. In summary, the fouling alleviation caused by pre-ozonation was governed by increase in repulsive interactions and decrease in attractive interactions between EfOM and membrane surfaces in Table 2. This observation was evinced by the fact that the RC and PES membrane after pre-ozonation displayed a more loose and porous deposit layer over the membrane surface compared to the control as SEM images shown in Fig. S3.

4. Conclusion

The characteristics of secondary wastewater effluent organic matter (EfOM) pre-treated by ozonation were systematically investigated. The effects of pre-ozonation on membrane fouling alleviation were studied based on classical pore blockage-cake filtration model and interfacial interaction energy assessment. The primary findings were summarized as follows:

- (1) Ozonation reduced fouling potential of SE for both hydrophilic RC and hydrophobic PES membranes. Greater extent of fouling potential reduction was found for the hydrophilic membrane.
- (2) The removal of polysaccharide and proteins were enhanced with O_3 :DOC ratio increase. It was

found that the reduction in polysaccharide concentration by pre-ozonation was statistically correlated with the increase in the filtration volume required for the transition from pore blocking to cake filtration that is a dominant flux decline mechanism.

(3) The extent of reversible fouling was gradually reduced as increasing O_3 :DOC ratio while irreversible fouling did not show clear increasing/decreasing trend as increasing O_3 :DOC ratio.

(4) Ozonation decomposed macromolecule into smaller fragments and increased the interfacial free energy of cohesion of EfOM, which mitigated flux decline for both RC and PES membranes.

(5) Pre-zonation improved the interfacial free energy of adhesion between EfOM and RC/PES membranes. Therefore, the increase of repulsions or the decrease of attractions contributed to the membrane fouling alleviation.

Appendix A. Supplementary data

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Highlights

- Ozonation reduced membrane fouling for both hydrophilic and hydrophobic membranes
- Ozonation was more efficacious for hydrophilic membrane fouling reduction
- Transition from pore blocking to cake filtration was retarded by ozonation
- Polysaccharide was statistically related to such transition retardation
- XDLVO theory elucidated fouling mechanism by explaining adhesion/cohesion energies