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The effect of pre-ozonation on UF membrane fouling by the size fractioned sewage effluent

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ABSTRACT

The effect of pre-ozonation on fouling control is related with ozone-induced particle aggregation/destabilization or the structural changes of organic materials. To clarify the mechanism of pre-ozonation on fouling and further optimize the use of pre-ozonation in real full-scale UF membrane operation system, the actual sewage effluent (SE) was filtrated to remove specific foulants with sand filter, 1.2 µm and 0.45 µm filter. Then, UF membrane fouling caused by the remaining foulants after pre-ozonation was further investigated. As for the SE pre-filtered by sand filter, the results revealed that pre-ozonation only slightly alleviated the fouling of UF membrane. After pre-oxidation with the ozone concentration lower than 1.53 mgO_3/mg TOC, membrane flux dramatically decreased in the initial filtration stage, accompanying with an obvious increase of the irreversible fouling. With the increase of ozone concentration,the membrane flux was improved and the irreversible fouling was apparently decreased. Besides, the retention of total organic carbon by UF was strengthened with the increase of ozone concentration. As for the SE pre-filtered by the 1.2 µm or 0.45 µm filter, the effect of pre-ozonation on fouling control was obvious. Although a slight increase of the irreversible fouling was also observed under lower ozone concentration, the total fouling and the reversible fouling presented a continuously decrease with the increase of ozone concentration. SEM results revealed that the fouling alleviation by pre-ozonation was related to the aggregation of foulants. Pre-filtration before the hybrid process of pre-ozonation and UF is helpful for fouling alleviation and irreversible fouling control in processing the actual SE.

Keywords: Pre-ozonation; Ultrafiltration; Fouling; Sewage effluent

1. Introduction

Low-pressure membranes (LPMs) refer to that are operated at relatively low transfer membrane pressure (normally less than 0.1–0.2 Mpa). LPMs include microfiltration (MF) membranes and ultrafiltration (UF) membranes with pore sizes ranging from approximately 10–100 nm [1]. Recently, UF membranes are widely used for the treatment of natural waters and the reclamation of wastewater. Nevertheless, the sustainability of UF in water treatment is limited by its fouling. Membrane fouling results in a loss of membrane permeability due to an accumulation of aquatic constituents on the membrane surface or within the pores, including particulate matters, colloidal materials, organic macromolecules related with organic fouling, sparingly soluble inorganic compounds related with scaling, and microorganisms related with biofouling [2]. The operating conditions, the characteristics of membranes, and the water qualities all influence membrane fouling to a great extent [3–6].

Sewage effluent (SE) refers to the effluent from biological wastewater treatments process. The fouling of UF membrane in processing SE is more sophisticated because of its complicated aquatic constituents. The dissolved organic matter in SE was mainly constituted by the Effluent Organic Matter (EfOM), of which consists: 1) refractory natural organic matter (NOM) derived from drinking water,

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2) trace levels of synthetic organic compounds (SOC) produced during domestic use and disinfection by-products (DBPs) generated during the disinfection processes of water and wastewater treatment, and 3) soluble microbial products (SMPs) derived during the biological treatment process of wastewater [7]. Laabs et al. reported that the substances eluting in the biopolymer peak, which were identified as mostly organic colloids, polysaccharides, and proteins, were regarded as the major fouling-causing substances in EfOM [8]. Zheng et al. stated that the concentration of biopolymer, including mostly polysaccharide-like and protein-like substances, influenced the filterability of treated domestic wastewater proportionally [9]. Nguyen and Roddick reported that the major dissolved organic foulants were identified as proteins, polysaccharides, protein-like and polysaccharide-like materials, and humic substances (HS) [10]. Filloux et al. demonstrated that biopolymers in SE, normally regarded as polysaccharide-like and protein-like substances, contributed to a significant proportion of low-pressure membrane flux decline [11]. Our investigation also proved that the anthropogenic polysaccharide- and protein-like substances including polysaccharides, proteins, and colloids, as well as the humic substances were all the main potential foulants for UF membrane processing wastewater EfOM [12]. Besides the EfOM, it is important to note that the interactions between organic substances and the particles/colloids impact the combined membrane fouling behavior greatly. Some investigations revealed that there are existed a significant synergistic fouling effect between the model organic substances and the particles [13,14]. However, Kim et al. reported that the removal of particles and colloids resulted in an increased fouling, which was attributed to the increased contact of dissolved organic matter with the membrane [15]. Zheng et al. pre-filtered the treated domestic wastewater in series to particles, large colloids and dissolved substances. Their results revealed that colloids and dissolved organic substances contribute more to fouling than particulates [16]. As a result, it still needs to take a deep consideration about the necessity of removing all the particulate substances before membrane filtration in processing the actual SE.

Ozonation behave as a pretreatment method of membrane filtration, its effect on UF membrane fouling is complex. It was reviewed that the positive effect of pre-ozonation on membrane fouling derived from the substantial structural changes to the organic materials present in the feed water, including: (1) removal of the aromatic rings; (2) increasing the number of carboxylic functions; (3) decomposition of molecules into smaller fragments; and (4) higher propensity for complexation of humic substances with divalent ions [17]. Wang et al. reported that the apparent molecular weight distribution of organic substances had great influence on membrane resistances, which was influenced by the ozonation contact time greatly [18]. Nguyen and Roddick reported that fouling of the UF membrane by the activated sludge effluent was reduced after ozonation due to partial oxidation of the membrane foulants to give building block molecules, low molecular weight acids, and low molecular weight neutrals [10]. Liu et al. reported that the fluorescence peak intensities of the protein-like substances were obviously decreased as a result of preozonation, and both external and internal fouling could be effectively mitigated by the pre-ozonation [19]. Filloux et al. reported that ozonation induced a large reduction of the biopolymers and an important increase of the low MW humic substances, which alleviate flux reduction during MF and UF filtration tests [11]. Guo et al. demonstrated that the component transformation of SE after activated carbon catalytic ozonation pretreatment caused the alleviation of membrane fouling [20]. The negative impact of preozonation on membrane filtration process was also reported, such as increasing biofouling or permeat quality deterioration [21,22]. Besides the impact of ozonation on the structural of organic materials, ozonation acts as a coagulant aid through reactions related with natural particles [23]. The particle characteristics such as size, charge, and surface chemical stability were reported crucially affecting the morphology of cake layer formed on membrane surface that related with cake fouling [24,25]. As ozonation could alter the surface charge or zeta potential of particles in water and wastewater [26], the changes induced by ozonation may cause particle destabilization/aggregation, and further cause changes in the cake permeability in UF and therefore affect the membrane flux [27]. As Zhu et al. reported, pre-ozonation could change the average particle diameter as well as the particle size distribution, which influenced the porosity of gel layer and further caused the changes in the filtration performance of membrane [28]. Chang et al. reported that ozonation of digital textile printing wastewater led to aggregation of colloidal particles and decreased the cake resistance [29]. Nevertheless, Lee et al. did not find particle size increase with ozone treatment, and the impact of ozone on particle destabilization had little influence on the UF permeability [22]. Nguyen and Roddick also reported that although ozonation resulted in the breakdown of particles larger than 300 μm in the raw AS effluent. However, these changes had little influence on the UF permeability compared with the breakdown of dissolved EfOM [10].

As the actual SE possesses a complicated constitution, the effect of pre-ozonation on UF fouling by actual SE should be further clarified. Until now, almost no related research was designed to evaluate the impact of “ozone-induced particle aggregation/destabilization” or “ozonation-caused structural changes of the organic materials” on fouling control. Our experiment adopted a sequential filtration process to remove specific foulants from actual SE with sand filter, 1.2 μm and 0.45 μm filter. Then, the effect of pre-ozonation on membrane fouling caused by the remaining foulants was separately investigated. By monitoring the flux transformation, permeates quality, as well as the observation of foulants on membrane surface, the impact of pre-ozonation on fouling control by the size fractionated SE was evaluated. Then, the necessity of pre-filtration before the hybrid pre-ozonation and UF process could be estimated,which is helpful for optimizing the application of pre-ozonation in real full-scale UF membrane operation system.

2. Materials and methods

2.1. Feed water and size fractionation

The actual SE was collected from a pilot-scale sequential batch reactor (SBR) operated by the Key Laboratory of Water Pollution Control Center, Beijing University of Technology. The influent of the pilot-scale SBR is the domestic wastewater discharged from the residential districts. After collection, the SE was stored at 4°C before use. Then, the SE was filtrated to remove specific foulants with sand filter (normally with void size of several tens of micron), 1.2 µm (cellulose nitrate, Sartorius) and 0.45 µm filter (cellulose nitrate, Sartorius). Water qualities were analyzed and presented in Table 1.The size fractionation of SE was repeated for three times, and then the corresponding ozonation and UF experiments were conducted.

2.2. Ozonation procedure

The ozonation experiment was carried out in a semi-continuous flow reactor (Fig. 1a). The cylindrical reactor is made of glass with inside diameter of 50 mm, a length of 700 mm, and volume of 350 mL. O_3 was generated by a ozone generator (ZR-C-5, Beijing Zhong Rui Yi Jia Technology Co., Ltd., China) using pure oxygen as the feed gas. The oxidation reaction temperature was controlled at 20±1°C. Ozone was introduced into the reactor through a porous quartz aeration disc loaded at 20 mm height above the bottom. Ozone dosage was controlled through adjusting the feeding time of ozone gas, and the residual ozone in the off-gas was absorbed by the Potassium Iodide solution (KI). By using the iodinetry, gaseous ozone dosage (consumption of ozone) was calculated as the difference between the inlet ozone and the residual ozone in off-gas. After the feeding of ozone gas, water sample was continuously contacted with ozone for 1 min, and then pure N_2 was used to blow off the residual ozone. In the experiment, ozone concentration of 0.21, 0.53, 0.91, 1.21, 2.10, 3.01, 3.83 mgO_3/mg TOC (mg of gaseous O_3 per mg of dissolved organic matter) on fouling alleviation was evaluated.

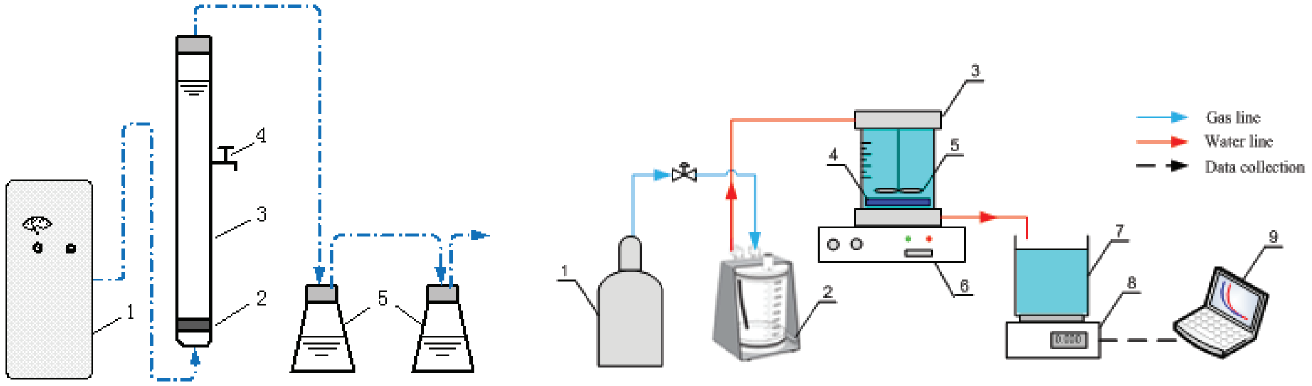
2.3. Ultrafiltration experiment

All ultrafiltration experiments were conducted at room temperature (20±1°C). The experiments were conducted in a 50 mL-stirring cell (Amicon 8050, Millipore, USA) and operated in down flow dead-end filtration mode, as shown in Fig. 1b. To avoid concentration polarization, the membrane filtration tests were conducted at stirring speed of 120 rpm. The flat sheet of a hydrophobic Polyethersulphone (PES) Membrane (PES-900C/D, Sepro, America) was used in the experiment, which had an effective filtration area of 13.4 cm^2. Up to 1 L of feed water could be supplied to the stirring cell by an attached feed reservoir. Nitrogen gas at a constant pressure of 0.1 MPa (measured using a pressure gauge and the variation of the pressure was controlled within 5% by a valve) was used to drive the feed solution through the membrane. Permeate flowed into glassware on the electronic balance that was connected to a computer. The weighting data were automatically recorded every thirty seconds. For each filtration test, a new membrane was placed at

Table 1
Water qualities of raw sewage effluent and after pre-filtration

	TOC (mg/L)	COD (mg/L)	UV_{254} (cm^{-1})	pH	TN (mg/L)	TP (mg/L)
Raw SE	8.65~10.02	30.6~54	0.15~0.21	7.54~8.04	18.10~25.85	2~5.42
Filtered by sand filter	6.16~8.05	ND	0.15~0.20	7.54~8.04	ND	ND
Filtered by 1.2 µm filter	5.82~7.50	ND	0.12~0.15	7.54~8.04	ND	ND
Filtered by 0.45 µm filter	5.78~7.51	ND	0.12~0.13	7.54~8.04	ND	ND

ND-not determined.



1. Ozone generator; 2.Quartz aeration disc;
3. ozonation reactor; 4.sampling point; 5. KI trap

a) Ozonation experiment

1. N2 pressure cylinder; 2. Liquid storage tank; 3. Filtration cell;
4. Membrane; 5. Stirrer; 6. Mangnetic stirrer; 7. Beaker; 8.Electronic balance;
9. Computer(for data collection)

b) Down flow dead-end UF scheme

Fig. 1. Schematic diagram of ozonation and UF.

the bottom of the cell with smooth side towards the bulk solution. To remove preservatives on new membranes, new membranes were soaked in 30% alcohol for 2 h and then rinsed and filtered with Milli-Q water until the TOC of the effluent approach zero. Immediately before the stirred cell test, the pure water flux of the membrane was determined by filtering pure water through the membrane until a stable permeating flux was reached. Only the membranes within 20% pure water flux variation were chosen for the experiment.

The pure water flux of each membrane was measured and named as J_0. Every UF experiment included filtrating 300 mL sewage effluent, backwashing by placing the reverse side of membrane upwards with 100 mL Milli-Q water and filtrating 200 mL Milli-Q water (used to calculate the fouling reversibility). The ending flux in the filtration of sewage effluent was named as J_e. The average flux in the filtration of Milli-Q water after backwashing was named as J_1. Then, reversible fouling (RF), physical irreversible fouling (IF) and total fouling (TF) could be calculated as follows:

$$IF = \frac{J_0 - J_1}{J_0} \tag{1}$$

$$RF = \frac{J_1 - J_e}{J_0} \tag{2}$$

$$TF = \frac{J_0 - J_e}{J_0} \tag{3}$$

2.4. Analytical methods

2.4.1. TOC and UV_{254}

Total organic carbon analyzer (Multi N/C 3000, analytik-jena, Germany) was used to determine the TOC. The non-purgeable organic carbon (NPOC) testing method was selected, which involved purging an acidified sample with carbon-free air prior to measurement. Then the total carbon in the sample was combusted into carbon dioxide and monitored by an NDIR detector. Total carbon standard substance using the potassium hydrogen phthalate was stored at 4°C for no longer than 1 month. UV_{254} absorption was used to identify the content of humic substances in water samples. The UV_{254} measurements were conducted using a spectrophotometer (UNICO2100, China) at a wavelength of 254 nm.

2.4.2. SEM

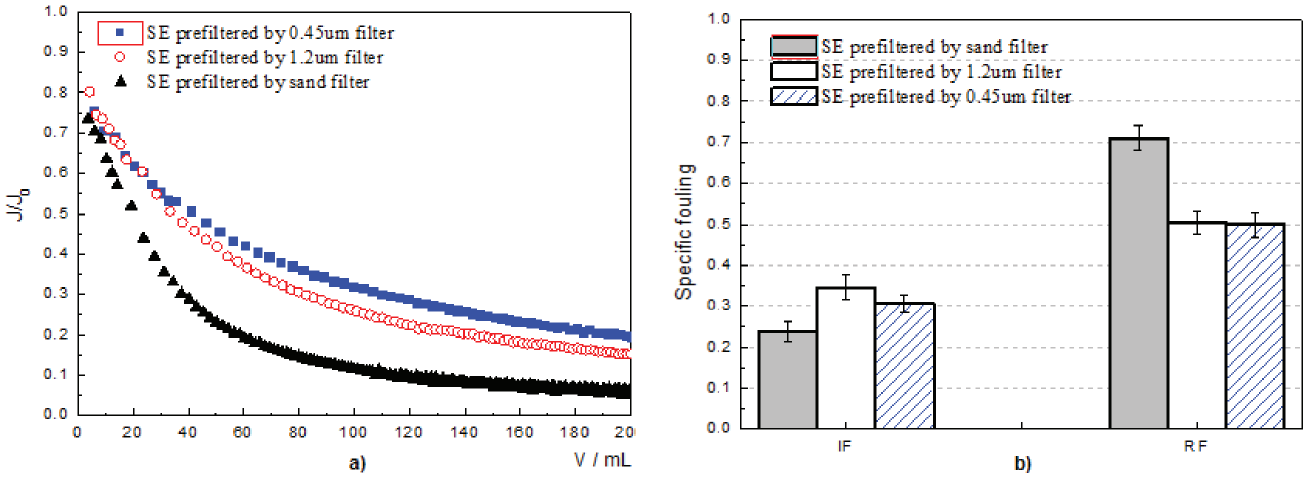
The surface of the new and fouled membranes samples were analyzed with a scanning electron microscope (SEM) (S-4300, Hitachi, Japan) at 15 keV. All specimens were dried for 24 h at 60°C before test.

3. Results

3.1. UF membrane fouling by the size fractioned SE

UF filterability is evaluated by the normalized flux, the ratio of membrane flux (J) to pure water flux (J_0). Fig. 3 displays the UF filterability contribution of the size fractioned SE. As that shown in Fig. 3a, the normalized flux declined to 5% of the initial flux in processing the SE pre-filtered by sand filter. After the removal of particles and large colloids by the 1.2 µm and 0.45 µm filter, the filterability of SE was slightly improved. The normalized flux improved to 18% and 25% of the initial flux, respectively. The result implies that the foulants with size smaller than 0.45 µm in SE still had a significant influence on the filterability of SE during the dead-end UF process. Qu et al. reported a similar result, they found that the flux decline of the extracellular organic matter (EOM) solution pre-filtered by 0.45 µm filter was still very serious, and the normalized flux decreased to 19% of its initial flux [30]. The result of Zheng et al. [9] also implied that the dissolved substances within the size of 0.45–0.026 µm had the most significant influence on the filterability of secondary effluent.

The fouling reversibility of the size fractioned SE is further shown in Fig. 3b. As illustrated, the SE pre-filtered by sand filter caused the greatest reversible fouling (0.7) but the least irreversible fouling (0.25). It was generally accepted that the reversible fouling is related to cake layer



a) b)

Fig. 3. UF filterability of the size fractioned SE: a) Flux curves b) Reversibility Temperature: 20±1°C; Pressure: 0.1 MPa±5%.

formation and the irreversible fouling is related to pore plugging. As for the SE pre-filtered by 1.2 µm filters, it could be found that the average irreversible fouling was increased from 0.25 to 0.35 while the average reversible fouling was decreased from 0.7 to 0.5. The further filtration by 0.45 µm filters slightly decreased the irreversible fouling to 0.3 but kept the reversible fouling unchanged. Although the flux curve results demonstrated that pre-filtration alleviated the UF fouling slightly, the reversibility results revealed that the removal of particulate substances by pre-filtration might induce the risk of increasing the irreversible fouling and deteriorate the UF membrane process. As Kim et al. reported, the removal of particles and colloids resulted in the increased contact of dissolved organic matter with the membrane, which increased membrane fouling [15]. Results of Zheng et al. also revealed that colloids and dissolved organic substances contributed more to fouling than particulates in treated domestic wastewater [16].

3.2. Impact of pre-ozonation on UF membrane fouling by the size fractioned SE

To optimize the use of pre-ozonation in real full-scale UF membrane operation system, the impact of pre-ozonation on UF membrane fouling by the size fractioned SE was investigated. The effect of ozone concentration (0.53, 0.91, 1.22, 1.53, 2.10, 2.71, 3.83 mgO_3/mg TOC) was also systematically evaluated. With ozone concentration lower than 1.53 mgO_3/mg TOC, membrane fouling of the SE pre-filtered by sand filter was aggravated after pre-ozonation. As shown in Fig. 4a, the normalized flux decreased dramatically at the beginning stage, which decreased to 17% of the initial flux after 50 mL of water samples were filtered. When ozone concentration was increased to above 1.53 mgO_3/mg TOC, although the flux displayed a slight fluctuation at ozone concentration of 2.71 mg O_3/mg TOC compared to ozone concentration at 2.10 mg O_3/mg TOC, membrane fouling of the SE pre-filtered by sand filter was generally alleviated after pre-ozonation. After the removal of particles and large colloids by the 1.2 µm and 0.45 µm filter, the fouling could be alleviated progressively with the increase of ozone concentration. As shown in Fig. 4c, membrane flux of the SE pre-filtered by 1.2 µm filter improved continuously from 15% to 60% of the initial flux with the increase of ozone concentration. Besides, membrane flux of the SE pre-filtered by 0.45 µm filter also continuously improved from 19% to 65% of the initial flux after pre-ozonation, as that shown in Fig. 4e.

The impact of pre-ozonation on fouling reversibility by the size fractioned SE is also demonstrated in Fig. 4. Fig. 4b shows that pre-ozonation with ozone concentration lower than 1.53 mgO_3/mg TOC decreased the reversible fouling but greatly increased the irreversible fouling by the SE pre-filtered by sand filter. With the continuously increase of ozone concentration to above 2.10 mgO_3/mg TOC, the total fouling and the irreversible fouling could be further decreased. Besides, as shown in Fig. 4d and Fig. 4f, after the SE was pre-filtered by 1.2 µm or 0.45 µm filter, the total fouling and reversible fouling were continuously decreased with the increase of ozone concentration. Although a slight increase of irreversible fouling was also observed after ozonation, the irreversible fouling was further decreased with the increase of ozone concentration. The results revealed that pre-filtration before the hybrid process of pre-ozonation and UF is helpful for fouling alleviation and irreversible fouling control in processing the actual SE.

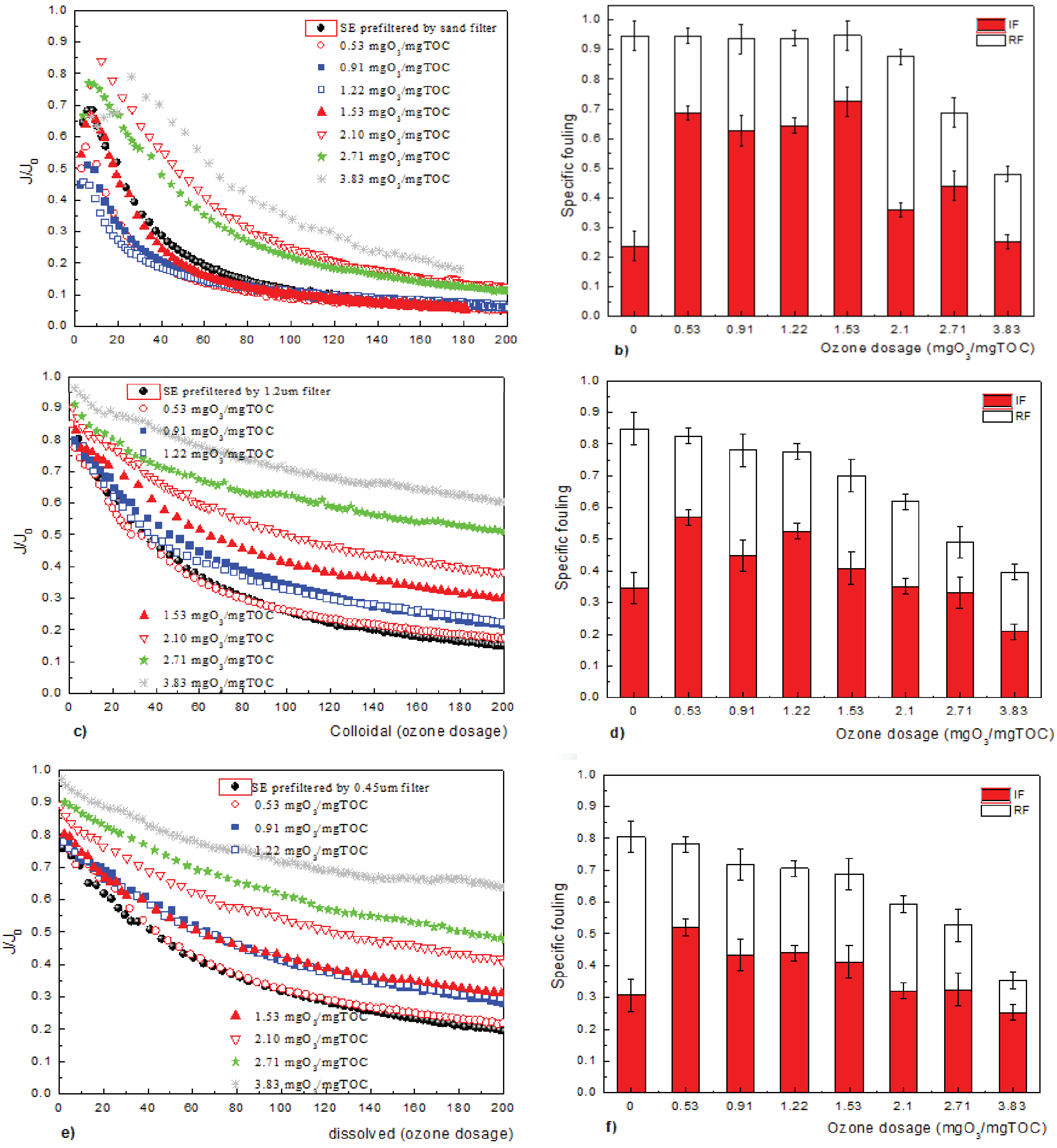
3.3. TOC and UV transformation of the size fractioned SE after pre-ozonation and ultrafiltration

TOC and UV_{254} transformation of the size fractioned SE after pre-ozonation and the corresponding ultrafiltration is shown in Fig. 5. As illustrated, TOC of the size fractioned SE gradually decreased with the increase of ozone concentration. A slight TOC flocculation of SE pre-filtered by 1.2 µm filter could be observed under lower ozone concentration. After the SE was pre-filtered by sand filter, 1.2 µm or 0.45 µm filter, UF further contributed to 5%, 2% and 5% TOC removal. After pre-ozonation, UF process further enhanced the average removal rate of TOC for the size fractionated SE. With the increase of ozone concentration to 3.83 mgO_3/mg TOC, the following UF contributed to 10%, 10% and 20% TOC removal for the SE pre-filtered by sand filter, 1.2 µm and 0.45 µm filter, respectively. The results implied that the retention effect of UF was strengthened with the increase of ozone concentration. Fig. 5 also demonstrates that pre-ozonation contributed to a significant UV_{254} decline of the size fractioned sewage effluent. When the ozone concentration increased to above 0.53 mgO_3/mg TOC, the decreasing speed of UV_{254} dropped gradually. UV_{254} was usually used to represent unsaturated organic matters in wastewater. After pre-ozonation, the further removal of UV_{254} by UF was limited. It revealed that ozonation effectively removed the unsaturated organic matters, while their further removal by ultrafiltration was negligible.

3.4. Morphology observation of the foulants on UF membrane surfaces

The surface of the virgin PES ultrafiltration membrane had a tight surface and no obvious porous structure could be observed, as shown in Fig. 6j. To understand the impact of preozonation on cake layer fouling, the surface of the fouled membranes samples without backwashing was analyzed with the SEM. Fig. 6 shows the SEM results of the UF membrane fouled by the size fractionated SE. As for the SE pre-filtered by sand filter, the UF membrane surface was completely covered with the foulants. As shown in Fig. 6a, a thicker layer of foulants was deposited on the membrane surface.

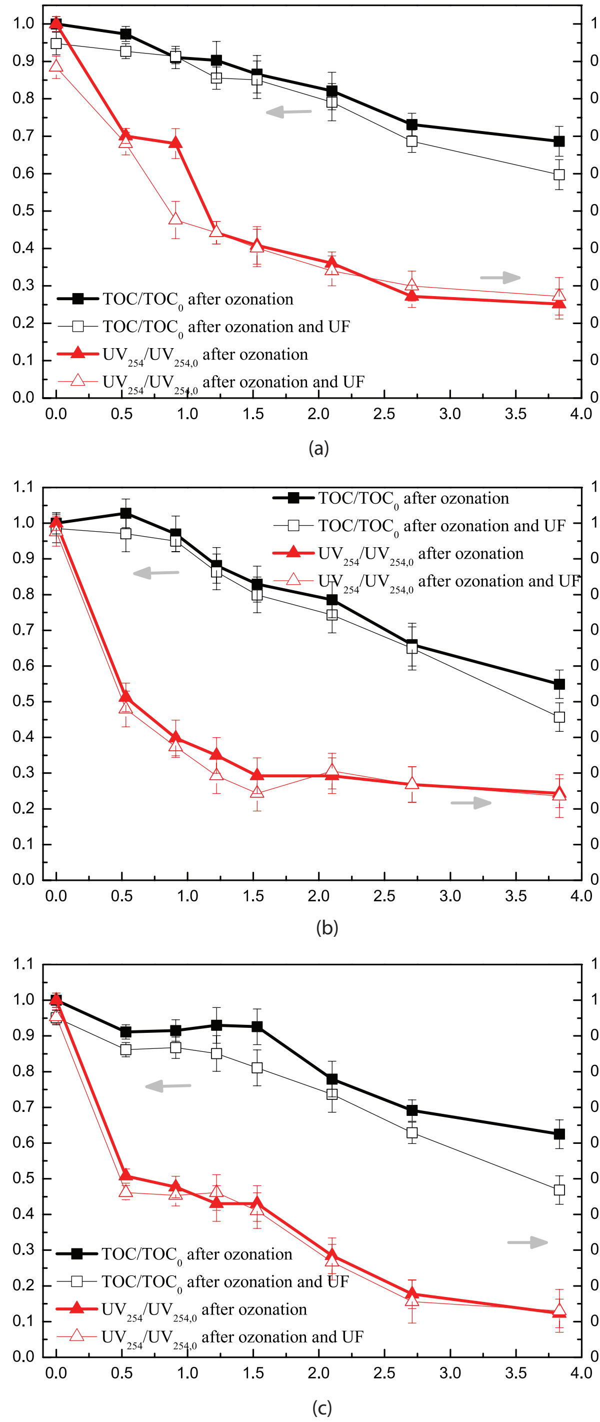
After pre-oxidation with ozone concentration of 0.21 mgO_3/mg TOC, aggregated foulants begin emerged on the membrane surface. The foulants layer seems compact and dense, and some sticky matters surrounded the aggregated foulants as shown in Fig. 6b. With the ozone concentration increased to 3.83 mgO_3/mg TOC, the aggregated foulants were more evenly deposited on the membrane surface. Comparing with that under lower ozone concentration, the foulants layer seems loose and had a large porosity. Besides, the border of aggregates was rel-



a) Flux curves – SE pre-filtered by sand filter; b) Reversibility – SE pre-filtered by sand filter; c) Flux curves – SE pre-filtered by 1.2 µm filter; d) Reversibility – SE pre-filtered by 1.2 µm filter; e) Flux curves – SE pre-filtered by 0.45 µm filter; f) Reversibility – SE pre-filtered by 0.45 µm filter, Temperature: 20±1°C; Pressure: 0.1 MPa±5%

Fig. 4. Impact of pre-ozonation on UF membrane fouling by the size fractioned SE.

atively clear and almost no sticky matter attached on the membrane surface as shown in Fig. 6c. After the SE was pre-filtered by 1.2 µm or 0.45 µm filter, ozonation also induced the aggregation of foulants on the surface of UF membrane. As shown in Fig. 6e and Fig. 6h, the aggregated foulants were evenly distributed on the membrane surface under ozone dosage of 0.21mgO$_3$/mg TOC, and a portion of clean virgin membrane can be visible. With the increase of ozone dosage, the size of aggregated foulants was further increased. As shown in Fig. 6f and Fig. 6i, larger aggregates depositing on the membrane surface could be found.



a) SE pre-filtered by sand filter; b) SE pre-filtered by 1.2 μm filter; c) SE pre-filtered by 0.45 μm filter

Fig. 5. TOC and UV_{254} of the size fractioned SE after pre-ozonation and ultrafiltration.

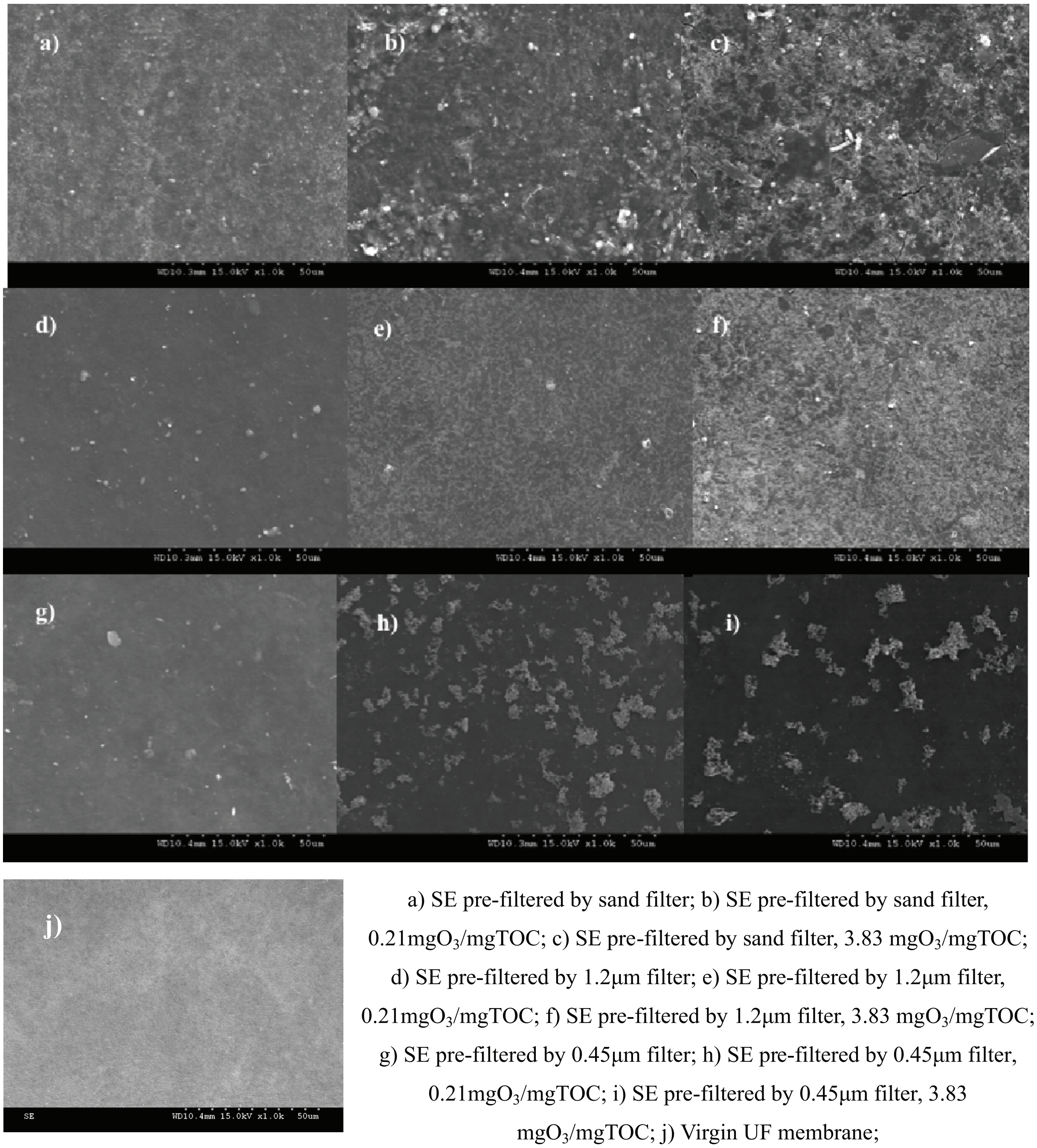
4. Discussion

Foulants that larger than the membrane are assumed to cause fouling by forming a cake on the membrane surface. According to filtration theory, the resistance of a cake layer R_c can be expressed using Darcy's law and the Carman-Kozeny equation [31].

$$R_c = (180(1-\varepsilon)/(d^2\varepsilon^3\rho_P))(m_p/A_m) \quad (4)$$

This equation shows that the cake layer resistance (reciprocal to cake permeability) is determined by particle characteristics such as the diameter d, the density ρ_P, the mass m_p, the membrane surface area A_m, and the cake porosity ε. The increase of diameter d and cake porosity ε all induces the decrease of cake layer resistance. Chang et al. reported that ozonation of the digital textile printing wastewater led to aggregation of colloidal particles, so that the cake resistance R_c after ozone and UF was lower than that of the control, suggesting that pre-ozonation is beneficial to not only flux enhancement but also to good permeate water quality [29]. Ozone assist in the destabilization and aggregation of particles by: (1) Increasing carboxylic acid content; (2) Reducing the molecular weight of adsorbed organics; (3) Bridging reactions among particles, and so on [26]. Our SEM results in Fig. 6 demonstrated that foulants were aggregated on membrane surface after pre-ozonation. As for the SE pre-filtered by sand filter, the aggregated foulants under lower ozone concentration displayed a compact and dense accumulation, as shown in Fig. 6b. Nevertheless, at high ozone concentration, the aggregated foulants changed to looser form with a higher porosity, as shown in Fig. 6c. Combining with the results shown in Fig. 4a, it was speculated that cake layer resistance was increased by the lower porosity under lower ozone concentration. At high ozone concentration, the increased cake porosity further induces the decrease of cake layer resistance. Zhu et al. also reported that pre-ozonation resulted in a more severe membrane fouling with 2 min ozone treatment, as a gel layer with a lower porosity caused by a wide particle size distribution was formed. Increasing the ozone treatment time to 15 min conducted a gel layer with a relatively high porosity, and improved the filtration performance of membrane [28]. The similar relationships between particle aggregation and hydraulic resistance were also shown in earlier flocculation studies using flocculation chemicals [32,33]. After the removal of particles and large colloids by the 1.2 μm and 0.45 μm filters, the aggregation of foulants after pre-ozonation was obvious, as shown in Fig. 6d~6f and Fig. 6g~6i. The higher porosity caused by aggregation decreased cake layer resistance. As that shown in Fig. 4, pre-ozonation continuously alleviated the decrease of membrane flux. No fluctuation was observed with the increase of ozone concentration.

Nevertheless, the membrane fouling mechanisms are not only the formation of the cake layer, but also the obstruction of the membrane pores (blockage or narrowing). As shown in Figs. 4b, 4d and 4f, the irreversible fouling of the size fractionated SE under low ozone dosage all increased apparently. It is speculated that the split fragments from the high MW materials after pre-ozonation could pass into the membrane pores and led to serious obstruction of the membrane pores. Buffle and Leppard stated that the risk of biofouling of the UF membrane and membranes further downstream was increased after preozonation [21]. Nevertheless, with the increase of ozone dosage, the irreversible fouling of the size fractionated SE was further decreased. Combined with the results of Fig. 5, it revealed that ozonation with



a) SE pre-filtered by sand filter; b) SE pre-filtered by sand filter, 0.21mgO$_3$/mgTOC; c) SE pre-filtered by sand filter, 3.83 mgO$_3$/mgTOC; d) SE pre-filtered by 1.2μm filter; e) SE pre-filtered by 1.2μm filter, 0.21mgO$_3$/mgTOC; f) SE pre-filtered by 1.2μm filter, 3.83 mgO$_3$/mgTOC; g) SE pre-filtered by 0.45μm filter; h) SE pre-filtered by 0.45μm filter, 0.21mgO$_3$/mgTOC; i) SE pre-filtered by 0.45μm filter, 3.83 mgO$_3$/mgTOC; j) Virgin UF membrane;

Fig. 6. SEM results of UF membrane surfaces fouled by the size fractionated SE.

high ozone concentration accelerated the TOC removal by UF membranes, especially the removal of saturated organic materials. It was speculated that the aggregation of foulants produced a barrier with a high porosity, as the SEM results demonstrated in Fig. 6. The loose aggregated barrier under high ozone dosage could act as a secondary membrane and prevent the smaller foulants from reaching the polymeric membrane surface or membrane pores, which resulted in a significant reduction of membrane pores' blocking. At the same time, the permeate quality was not deteriorated.

In most cases, the fouling behavior of membranes is dominated by the combination of cake layer as well as the obstruction of the membrane pores, occurring sequentially or simultaneously [12,13]. Although the removal of particulate substances might induce the risk of increasing the irreversible fouling (as discussed in Section 3.1), the impact of pre-ozonation on UF fouling by the actual SE is sophisticated as the ozonation impact the particle characteristics (aggregation/destabilization) and also cause the structural changes of the organic materials. The results of Fig. 4 demonstrated that there exist different impact of preozonation on UF fouling by the size fractionated SE. The interactions between the particulate substances and the colloids, dissolved organic substances could influence the effect of preozonation on fouling control. To deduce the filtration resistance, it is necessary to take pre-filtration method to remove particulate substances before the hybrid process of pre-ozonation and UF.

5. Conclusions

1. Pre-filtration slightly alleviated the fouling of UF membrane, the removal of particulate substances might induce the risk of increasing the irreversible fouling. Nevertheless, pre-filtration before the hybrid process of pre-ozonation and UF is helpful for fouling alleviation and irreversible fouling control in processing the actual SE.
2. As for the SE pre-filtered by sand filter, the impact of pre-ozonation on fouling control was limited. Pre-ozonation under lower ozone concentration increased the cake layer resistance as well as the irreversible fouling by pore blockage. After the removal of particles and large colloids by the 1.2 µm and 0.45 µm filter, the alleviation effect of pre-ozonation on UF membrane fouling was obvious.
3. The fouling alleviation by pre-ozonation is related with the aggregation of foulants. In the presence of particle substances, the aggregated foulants under lower ozone concentration displayed a compact and dense accumulation and increased the cake layer resistance. With the increase of ozone concentration, the aggregated foulants changed to looser form with a higher porosity, which could act as a secondary membrane and reduce the blocking of membrane pores.

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