Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1169222

57 (2016) 27113–27124
December

Taylor & Francis
Taylor & Francis Group

Impact of AC/O_3 pretreatment on ultrafiltration processing sewage effluent for fouling alleviation

Jin Guo*, Liying Wang, Jie Shi, Yuqi Guan, Kailun Wang, Hong Liu, Jianhong Liu, Baogui Wang

School of Environment and Energy Engineering, Beijing University of Technology, 100124 Beijing, China, emails: guojin@bjut.edu.cn (J. Guo), wlybjgy@163.com (L. Wang), shijie_bjut@163.com (J. Shi), environ_gyq@126.com (Y. Guan), wang350880576@163.com (K. Wang), liuhong1103@163.com (H. Liu), 15001245908@163.com (J. Liu), baogui19@163.com (B. Wang)

Received 13 December 2015; Accepted 6 March 2016

ABSTRACT

To resolve membrane fouling in the ultrafiltration process of sewage effluent, the impact of activated carbon catalytic ozonation (AC/O_3) on fouling control was investigated. The influence of initial pH on AC/O_3 for fouling alleviation was further explored. The results revealed that AC/O_3 pretreatment greatly mitigated the membrane fouling. The total fouling, reversible fouling, and irreversible fouling were all decreased. The initial pH influenced the alleviation effect of AC/O_3 on fouling control obviously, although it only slightly impacted the AC adsorption pretreatment on fouling alleviation. Besides, there was no obvious impact of pH on the ultrafiltration process. Compared with the adjustment of initial pH during ultrafiltration and the pretreatment methods such as AC adsorption and preozonation, AC/O_3 displayed the greatest effect on both fouling alleviation and permeate quality improvement under all pH conditions. It was the component transformation of sewage effluent after AC/O_3 pretreatment that caused the alleviation of membrane fouling. With the increase in initial pH, the high-MW biopolymers as well as humic substances in the effluent organic matter could be preferentially removed by AC/O_3, which mitigated the flux decline during the ultrafiltration process and decreased the reversible and irreversible fouling.

Keywords: Ozonation; Activated carbon; Ultrafiltration; Membrane fouling; pH

1. Introduction

Among low-pressure membranes (LPMs), ultrafiltration (UF) is widely used for the treatment and reclamation of wastewater. Although UF has many advantages, the sustainability of UF is limited by membrane fouling, which results in loss of membrane permeability due to the accumulation of aquatic constituents on the membrane surface or within the pores [1]. Similar to natural organic matter (NOM) in drinking water, effluent organic matter (EfOM) also has a significant humic-like content, and is considered the major foulant that causes organic fouling during wastewater reclamation [2,3]. Except for the background NOM originating from drinking water, EfOM is also composed of soluble microbial products (SMP), disinfection byproducts generated during the disinfection processes of water and wastewater treatment, along with natural and synthetic organic chemicals [4]. As a result, diverse ultrafiltration performance of

---

*Corresponding author.

EfOM and NOM was expected, although their characteristics overlap extensively.

Studies show that colloids and dissolved organic substances contribute more to membrane fouling than particulates in treated domestic wastewater [5]. Laabs et al. reported that the substances eluting in the biopolymer peak, which were identified as mostly organic colloids, polysaccharides, and proteins using size exclusion chromatography combined with online dissolved organic carbon and UV_{254} detectors, were retained completely by the UF membrane and were regarded as the major fouling-causing substances in EfOM [6]. 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 [7]. Filloux et al. also demonstrated that biopolymers in sewage effluent, normally regarded as polysaccharide-like and protein-like substances, contributed to a significant proportion of LPM flux decline [8]. Our recent research further revealed that the 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 [9].

To reduce membrane fouling and/or increase the removal of certain aquatic contaminants, integration of pretreatment with UF has been widely employed. In principle, pretreatment of source water can impact membrane filtration in three ways: altering contaminant size distributions, changing mutual affinities of contaminants or their affinities to membrane surfaces, and suppressing undesirable microbial growth or removing biodegradable contaminants [1]. Among the pretreatment methods, preozonation could result in a significant decrease in membrane fouling, although only a minor DOC removal was achieved. Studies conducted with ozone-resistant polyvinylidene fluoride (PVDF) [10–12], polysulfone (PS) membrane materials [13], and ceramic membrane [14–17] showed that using preozonation all enhanced the permeate flux and reduced membrane fouling. As reviewed by Geluwe et al. [18], ozone causes substantial structural changes to the organic materials present in the feed water, including the following: (1) removal of the aromatic rings, which decreases the adsorption of organic materials by hydrophobic interactions; (2) increasing the number of carboxylic functions, which improves the repulsion of organic materials by the negative membrane surface; (3) decomposition of molecules into smaller fragments; and (4) higher propensity for the complexation of humic substances with divalent ions, which caused the visible fouling alleviation.

Activated carbon catalytic ozonation (AC/O_3), as an effective advanced oxidation process, since its first application by Jans and Hoigne [19], has been extensively investigated to remove toxic and/or low biodegradable organic compounds from water. With the more rigorous demand of reclaimed water, the use of AC/O_3 for pretreating sewage effluent became applicable. Although AC/O_3 has a better oxidant ability than O_3, as a pretreatment method, its impact on the ultrafiltration process was rarely reported. Besides, the environmental pH influences both the AC/O_3 process and the membrane filtration process. In the case of AC/O_3, solution pH may affect the ozone decomposition and the surface property of the catalyst, as well as the dissociation of organic pollutants in aqueous solution [20–22]. At the same time, solution pH also influences the surface property of membrane and impacts the ultrafiltration process [23]. As a result, the influence of pH value on AC/O_3 for fouling alleviation is valuable for further exploration. Until now, no systematic investigation has been done concerning this aspect.

In this study, the transformation of UF membrane flux, the reversible and irreversible fouling after AC/O_3 pretreatment was investigated. The influence of environmental pH on AC/O_3 for fouling alleviation was also studied. To explore the mechanism, the environmental pH adjustment and its impacts on AC adsorption and ozonation for fouling alleviation were further systematically compared with that on AC/O_3. Furthermore, the water quality and structural information of multi-component organic substances in sewage effluent after these pretreatment methods were characterized.

2. Materials and methods

2.1. Feed water

Sewage effluent was collected from the 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. The sewage effluent was filtrated by 0.45-μm membrane and then stored at 4°C before use. Water qualities of the filtered sewage effluent are presented in Table 1.

2.2. Granular activated carbon

Granular activated carbon (GAC) was produced by Xinhua Coal Co., Ltd (China) through activation of

Table 1
Water qualities of the sewage effluent

DOC (mg/L)	COD (mg/L)	UV_{254} (cm^{-1})	pH	TN (mg/L)	TP (mg/L)
6.65–9.02	30.6–54	0.15–0.21	7.54–7.94	18.10–25.85	2–5.42

bituminous coal with steam. The GAC with a size of 16–20 mesh was used in the experiment. According to the pretreatment methods described by Alvarez et al. [21], the GAC was boiled in ultrapure water for 1 h, washed repeatedly with ultrapure water, dried at 110℃ for 12 h, and stored in a desiccator at room temperature until use. The pH of point of zero charge (pH_{pzc}) of the GAC was determined using the mass titration method described by Noh and Schwarz [24] with some alterations. Firstly, $NaNO_3$ solutions (0.01 M) of pH 3, 6, and 11 were prepared with HNO_3 (0.1 M) and NaOH (0.1 M). Then, 40 mL of $NaNO_3$ solution with different initial pH (3, 6, and 11) and increasing amounts of carbon sample (w/w = 0.1, 0.5, 1.0, 2.5, 5.0, 7.5, 10%) were added to 50-mL Erlenmeyer flasks. Finally, the equilibrium pH was measured after 24 h of shaking at 25 ± 0.1℃. The pH_{pzc} of the GAC was determined as 9.0.

2.3. Activated carbon catalytic ozonation (AC/O_3) procedure

The activated carbon catalytic ozonation experiments were carried out in a semi-continuous flow reactor (Fig. 1). The cylindrical reactor is made of glass with an inside diameter of 50 mm, a length of 700 mm, and volume of 350 mL. O_3 was generated by an ozone generator (ZR-C-5, Beijing Zhong Rui Yi Jia Technology Co., Ltd, China) that used pure oxygen as the feed gas. The oxidation reaction temperature was controlled at 20 ± 1℃. Ozone was introduced into the reactor through a porous quartz aeration disk loaded at 20 mm height above the bottom. In the catalytic ozonation experiment, the filtered sewage effluent was first added into the reactor, then ozone was introduced into the reactor immediately after 2 g/L GAC being dosed into the sewage effluent. The initial pH value of the sewage effluent was adjusted by H_2SO_4 (0.1 M) and NaOH (0.1 M). Ozone dosage was controlled by adjusting the feeding time of the ozone gas, and the ozone in the off-gas was absorbed by the KI solution. Then the oxidized sample was used as the feed water for ultrafiltration experiment. To make a comparison, the ozonation experiment was performed in the same reactor, while no GAC was added under the same conditions. In the GAC adsorption test, pure oxygen was fed into the reactor column under the same operation condition of ozonation.

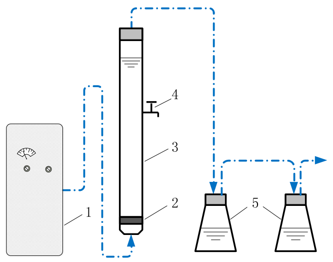

Fig. 1. Schematic diagram of AC/O_3 treatment system.
Notes: (1) ozone generator, (2) quartz aeration disk, (3) ozonation reactor, (4) sampling point, and (5) KI trap.

2.4. Ultrafiltration experiment

All ultrafiltration experiments were conducted at room temperature (20 ± 1℃). The experiments were conducted in a 50-mL stirring cell (Amicon 8050, Millipore, USA) and operated in a down-flow dead-end filtration mode, as shown in Fig. 2.

To avoid concentration polarization, the membrane filtration tests were conducted at a stirring speed of 120 rpm. The flat sheets of 20 kDa polysulfone ultrafiltration membranes (PS20, Sepro, USA) were 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 gage and the variation of

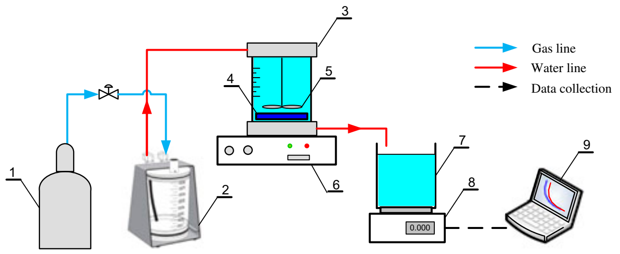

Fig. 2. The down-flow dead-end ultrafiltration scheme.
Notes: (1) N_2 pressure cylinder, (2) liquid storage tank, (3) filtration cell, (4) membrane, (5) magnetic stirrer, (6) magnetic stirrer, (7) beaker, (8) electronic balance, and (9) computer (for data collection).

the pressure was controlled within 5% by a valve) was used to drive the feed solution through the membrane. Permeate flowed into the glassware on the electronic balance that was connected to a computer. The weighting data were automatically recorded every 30 s. For each filtration test, a new membrane was placed at the bottom of the cell with the smooth side toward the bulk solution. To remove preservatives on new membranes, they were soaked in 30% alcohol for 2 h and then rinsed and filtered with Milli-Q water until the DOC 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 of sewage effluent, backwashing by placing the reverse side of membrane upward with 100 mL of Milli-Q water, and filtrating 200 mL of Milli-Q water (used to calculate the fouling reversibility). The final 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), irreversible fouling (IF), and total fouling (TF) could be calculated as follows:

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

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

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

2.5. Analytical methods

2.5.1. DOC, UV_{254}, and pH

Total organic carbon analyzer (Multi N/C 3000, Analytik-Jena, Germany) was used to determine the DOC. 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. The 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. The pH was tested using pHS-25 (Shanghai Precision & Scientific Instrument Co., Ltd, China).

2.5.2. Zeta potential of membrane

An electrokinetic analyzer (SurPASS, Anton Paar) was used to measure the zeta potentials of the ultrafiltration membrane. In the process of measuring the zeta potentials, 10 drops of KCl solution (10 mg/L) was added to 600 mL of pure water to obtain an electrolyte solution with KCl solution concentration of 1.0 mol/L. The operation pressure was maintained at 0.05 MPa. In order to measure the zeta potentials of the membranes under various pH conditions, the pH value of the electrolyte solution was accordingly adjusted to pH of 3.0, 4.5, 7.54, and 9.0 with 2 mol/L HCl and 0.5 mol/L NaOH.

2.5.3. EEM

EEM spectra were measured by a 1-cm cuvette using a luminescence spectrometer (F-7000, Hitachi). EEM spectra were collected with subsequent scanning emission spectra from 300 to 550 nm at 1.0 nm increments by varying the excitation wavelength from 200 to 400 nm at 5 nm increments. Excitation and emission slits were maintained at 5 nm and the scanning speed was set at 1,200 nm/min for all the measurements. The *X*-axis represents the emission spectra from 300 to 550 nm, whereas the *Y*-axis is the excitation wavelength from 200 to 400 nm. The spectrum of Milli-Q water was recorded as the blank. The result is a three-dimension spectrum in which fluorescence intensity is represented as a function of excitation and emission wavelengths.

3. Results

3.1. AC/O_3 pretreatment for fouling alleviation

The impact of AC/O_3 pretreatment on membrane permeability was evaluated by the normalized/specific permeates flux (the ratio of membrane flux J to pure water flux J_0). With the addition of 2 g/L GAC, the influence of ozone dosage from 0.48 to 2.5 mg (O_3)/mg (DOC) (mg of gaseous O_3 per mg of dissolved organic matter) on fouling alleviation was evaluated. As shown in Fig. 3(a), the flux decline caused by the prefiltered (0.45 μm filter) sewage effluent was serious. The normalized flux decreased to 20% of its initial flux after 200 mL of the water sample penetrating through the UF membrane. Under an ozone dosage of 0.48 mg (O_3)/mg (DOC) combining with

2 g/L GAC, AC/O_3 pretreatment mitigated the decline of membrane flux. With the increase in ozone dosage, even less flux decline was observed. The final normalized flux accounted for nearly 50% of the initial value.

Except for the flux curves, the DOC and UV_{254} transformation was also investigated. After AC/O_3 pretreatment with an ozone dosage of 0.48 mg (O_3)/mg (DOC) combining with 2 g/L GAC, a 20% reduction of DOC was observed. Nevertheless, the degradation speed of DOC was decreased with the increase in ozone dosage. Following AC/O_3 pretreatment, there was a further 20% DOC removal by ultrafiltration. The removal might be caused by the adsorption of the PS membrane used in the experiment, which had a weaker anti-fouling capacity. The UV_{254} after AC/O_3 pretreatment also decreased noticeably, while no further decrease could be observed after ultrafiltration, which revealed that the aromatic fractions in EfOM were degraded, especially by the oxidation process. With the increase in ozone dosage to above 1 mg (O_3)/mg (DOC), the decreasing speed of UV_{254} was mitigated.

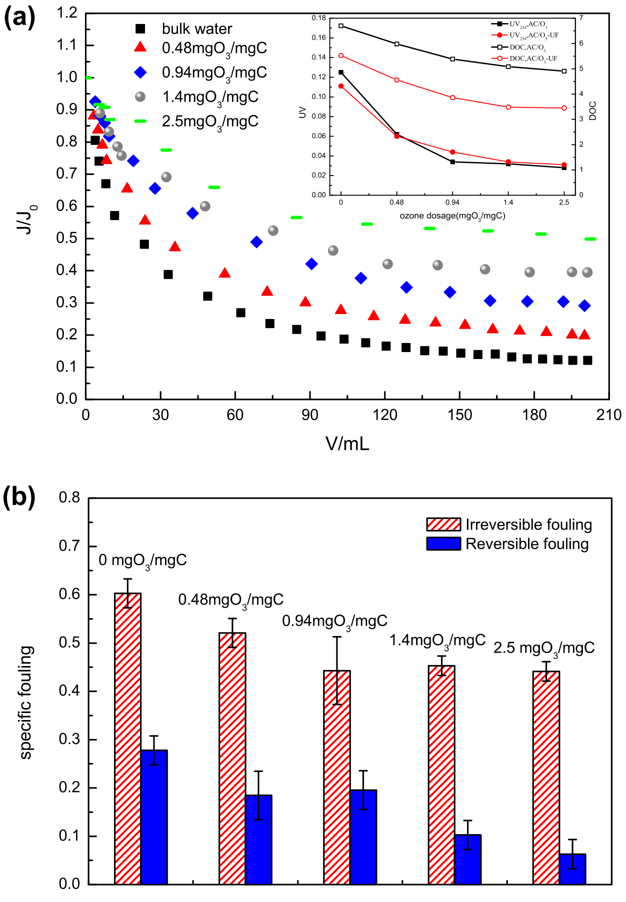

Fig. 3. Effect of AC/O_3 pretreatment on membrane fouling: (a) normalized flux curve and (b) specific fouling.

The effect of AC/O_3 pretreatment on reversible and irreversible fouling of membrane was further calculated, and the corresponding results are demonstrated in Fig. 3(b). As it is shown, the sewage effluent caused severe fouling even though it had been filtered by a 0.45-μm filter, the total fouling (the sum of irreversible and reversible fouling) accounted for about 0.9. Compared with the reversible fouling, it was demonstrated that EfOM caused more severe irreversible fouling (contributed to about 0.6). Qu et al. [25] reported that algal EOM, which had some affinity with the SMP in EfOM, caused more severe reversible fouling. On one hand, the polyethersulfone (PES) membrane used by Qu et al. was looser (100 kDa) than the PS membrane in our experiment (20 kDa). Furthermore, the PES membrane has a hydrophilic character, which could mitigate the irreversible attaching of organic materials in membrane pores. The results further revealed the weaker anti-fouling capacity of the PS membrane used in our experiment. In spite of this, AC/O_3 pretreatment effectively mitigated the total fouling. As shown in Fig. 3(b), the reversible fouling after AC/O_3 pretreatment was prominently lowered. With the increase in ozone dosage, the irreversible fouling was also decreased.

3.2. Impact of pH on AC/O$_3$ pretreatment for fouling alleviation

With an ozone dosage of 2.0 mg (O_3)/mg (DOC) combining with 2 g/L GAC, the impact of initial pH on AC/O_3 pretreatment for fouling alleviation was investigated. As shown in Fig. 4(a), with the initial pH increasing from 3.0 to 9.0, the decline of specific permeates flux was gradually mitigated. The final specific permeates flux increased from 20 to 80% after 200 mL of water samples penetrating through the UF membrane. Fig. 4(b) further demonstrated that both the reversible and irreversible fouling was decreased by AC/O_3 pretreatment. With the increase in initial pH, the reversible fouling decreased and even vanished, especially under neutral and alkaline conditions (pH of 7.54 and 9.0), and the irreversible fouling diminished noticeably. Karnik et al. [15] investigated the effects of oxidation on permeates flux of a ceramic membrane operating with continuous ozonation. It was reported that the flux improved at lower pH, as the dissolved ozone concentration increased with decreasing pH [15]. Different from their continuous ultrafiltration process, our results were obtained from a dead-end ultrafiltration

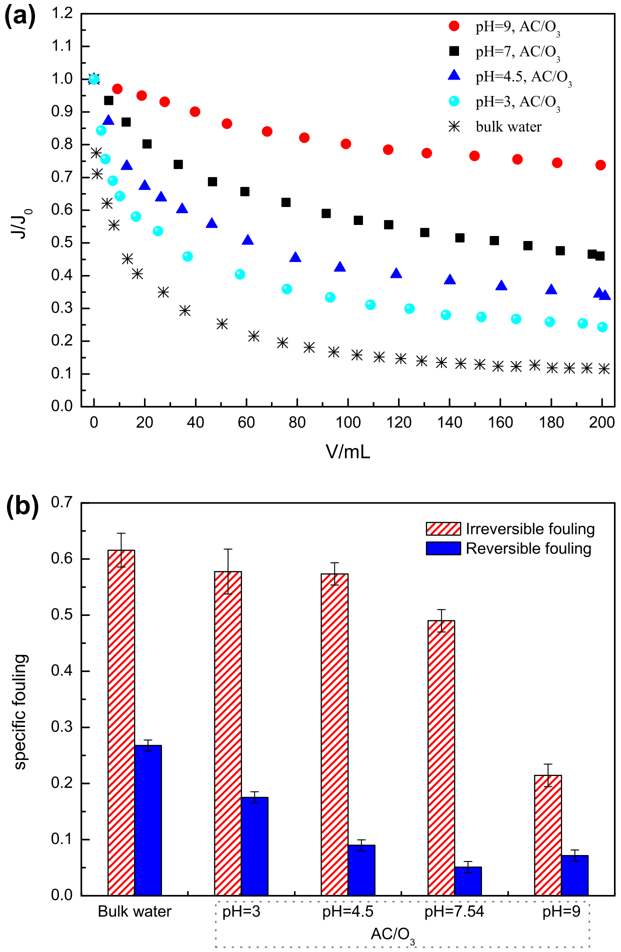

Fig. 4. Impact of pH value on AC/O_3 pretreatment for fouling alleviation: (a) normalized flux curve and (b) specific fouling.

process. The ozone dosage used in our hybrid AC/O_3–UF process is normally lower than that used in a ceramic membrane system. Under a different initial pH, a constant ozone dosage was kept by adjusting the feeding time of ozone gas. As a result, the influence of pH on AC/O_3 pretreatment for fouling alleviation mainly originated from the catalytic ozonation process itself and other factors.

As stated, pH influenced ozone decomposition, the surface property of the catalyst, and the dissociation of organic pollutants in aqueous solution as well [19–21]. Besides that, pH also had an impact on the AC adsorption and ozonation process. Moreover, the surface property of the membrane and the ultrafiltration process was impacted by pH [22]. To evaluate all these factors, the impact of initial pH on all pretreatment methods for fouling alleviation was investigated, including the direct influence of pH on the ultrafiltration process, and its indirect influence on AC and ozone pretreatment for fouling alleviation. As shown in Fig. 5(a), the adjustment of the pH value had no obvious impact on the ultrafiltration process except for a slight alleviation effect under alkaline conditions. With the increase in pH from 3.0 to 9.0, the specific permeates flux was slightly improved. At the same time, the reversible fouling was slightly increased, while the irreversible fouling was decreased with the increase in pH, as shown in Fig. 5(b). The influence of pH on AC adsorption for fouling alleviation is also shown in Fig. 5(c). It was observed that the alleviation effect of AC pretreatment on membrane fouling was negligible, and the specific permeates flux slightly changed under different initial pH. Despite this, it was found that the reversible fouling was slightly decreased with the increase in pH, while the irreversible fouling was increased with the increase in pH, as shown in Fig. 5(d). The influence of initial pH on preozonation for fouling alleviation is also shown in Fig. 5(e). With the increase in pH, a prominent reduction in membrane fouling was observed, and the final specific permeates flux increased from 20 to 70% of the initial value. Furthermore, as shown in Fig. 5(f), the reversible fouling and irreversible fouling were all clearly decreased by preozonation. Among the pretreatment methods, the AC/O_3, which was similar to preozonation, had the obvious mitigating effect on membrane fouling. In addition, the impact of initial pH for fouling alleviation was obvious.

Under different initial pH, the fouling alleviation effects of the above pretreatment methods are also compared in Fig. 5. As demonstrated, AC/O_3 displayed the best mitigating effect on membrane fouling under all initial pH. The alleviation effects were enhanced in the order of pH adjustment, AC adsorption, preozonation, and AC/O_3 preoxidation. Under acidic conditions of pH 3 and 4.5, the final specific permeates flux after AC/O_3 pretreatment was about 10 and 12% higher than that after preozonation, and was around 15 and 20% higher than that after pH adjustment or AC adsorption. Preoxidation displayed more prominent mitigating effects comparing with AC adsorption or pH adjustment. With the increase in pH, the superiority of preoxidation was strengthened. Under the neutral condition (pH 7.54), the effect of preozonation and AC/O_3 pretreatment on membrane fouling was similar. The final specific permeates flux achieved to about 50% of the initial value. Under alkaline condition (pH 9.0), the final specific permeates flux after AC/O_3 pretreatment was 80% of the initial value, which was 10% higher than that after preozonation. Although AC/O_3 pretreatment under basic conditions alleviated the membrane fouling to a great extent, it would be a trade-off between flux, fouling,

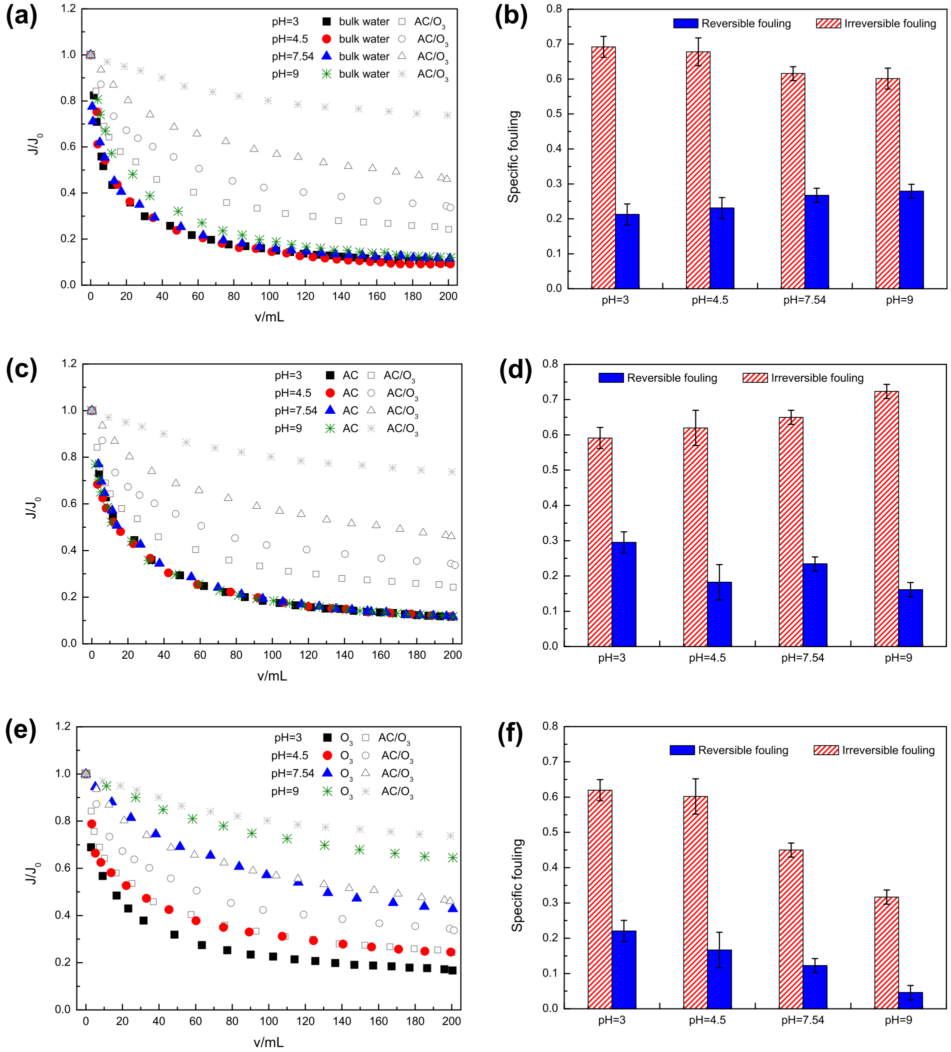

Fig. 5. Impact of pH on pretreatment methods for fouling alleviation: (a) normalized flux curve—pH adjustment, (b) specific fouling—pH adjustment, (c) normalized flux curve—AC adsorption, (d) specific fouling—AC adsorption, (e) normalized flux curve—ozonation, and (f) specific fouling—ozonation.

and chemical usage for pH adjustment when choosing the pH for the application of AC/O_3 pretreatment. Through the above comparison, it was revealed that the impact of pH on AC/O_3 pretreatment for fouling alleviation was mainly derived from the oxidation process itself.

3.3. Water quality analysis after pretreatment under different initial pH

To further verify the influence of pH on pretreatment methods for fouling alleviation, water quality (characterized with DOC, UV) and structural information (characterized with the EEM) of multi-component organic substances were further analyzed. Fig. 6 demonstrated the transformation of DOC and UV after pretreatment and their corresponding permeates from UF under different initial pH value. As shown in Fig. 6, the pH adjustment caused only a little fluctuation of DOC and UV. As for the AC adsorption, there also existed a slight transformation of DOC and UV. Nevertheless, DOC and UV decreased noticeably after preozonation with the increase in initial pH. The transformation of DOC and UV after AC/O_3 pretreatment was similar with preozonation. As the removal rate of UV was always higher than that of DOC, it revealed that the aromatic substances in sewage effluent were prone to be removed by preoxidation process. It seems that the increase in initial pH promoted their degradation in the oxidation process. Among the

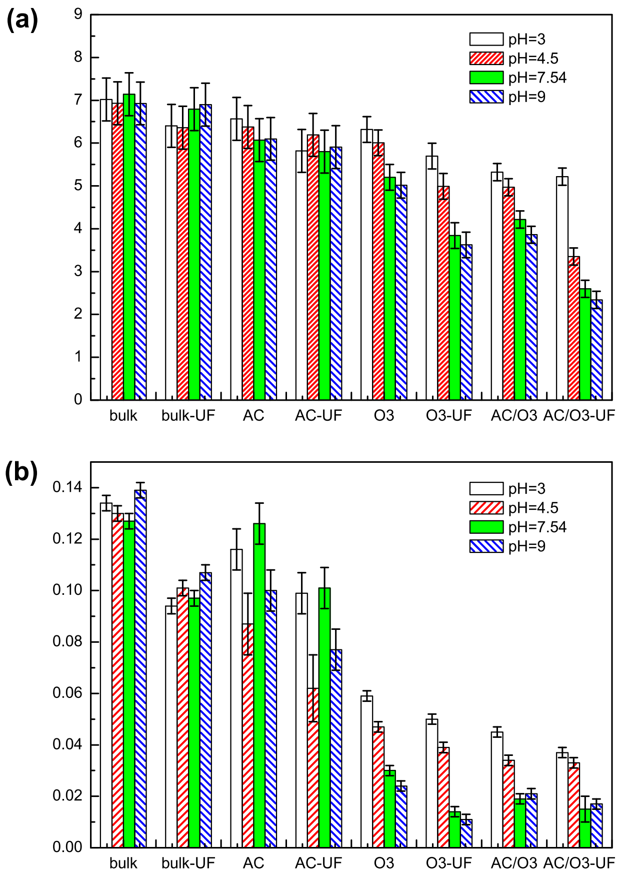

Fig. 6. (a) DOC and (b) UV transformation after pretreatments under different initial pH.

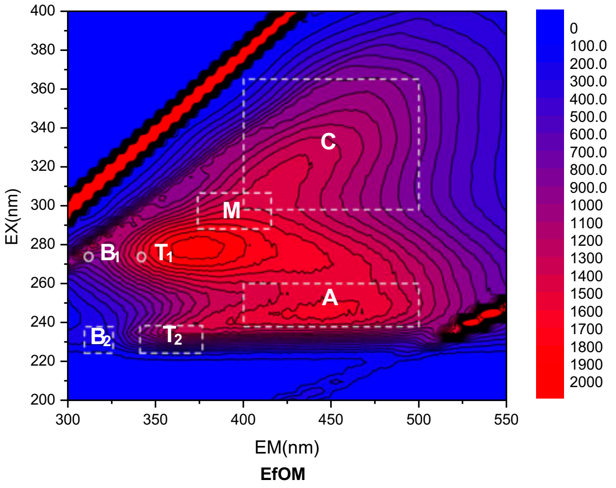

Fig. 7. EEM spectra of bulk sewage effluent after filtrating with 0.45-μm filter.

pretreatment methods, AC/O_3 displayed the best effect on water quality improvement under all pH conditions. Besides, further decrease in DOC and UV by UF could be found after all pretreatment methods.

The structural information of multi-component organic substances after pretreatments was further characterized with the EEM. Fig. 7 presented the fluorescence EEM of bulk sewage effluent after filtrating with a 0.45-μm filter. Peak A (Ex: 237–260 nm, Em: 400–500 nm) and peak C (Ex: 300–370 nm, Em: 400–500 nm) were related to humic-like substances, peak B (B_1: Ex: 275 nm, Em: 310 nm; B_2: Ex: 225–237 nm, Em: 309–321 nm) was related to tyrosine-like substances, peak T (T_1: Ex: 275 nm, Em: 340 nm; T_2: Ex: 225–237 nm, Em: 340–381 nm) was related to tryptophan-like substances, and peak M (Ex: 312 nm, Em: 380–420 nm) was related to marine humic substances associating with algae activity. As shown in Fig. 7, the fluorescence EEM of bulk sewage effluent was rich in tryptophan-like fluorescence (peak T_1), a 20–30 nm shift to a longer emission wavelength could be observed. Furthermore, relatively weaker peaks A and C, which reflected the humic-like fluorescence, could be observed.

The intensity transformation of EEM after pretreatments under different initial pH is further demonstrated in Table 2. As shown, there were no prominent transformations of EEM intensity after pH adjustment and AC adsorption. However, the EEM intensity decreased prominently after preozonation and AC/O_3 pretreatment. Besides, the intensity of peak T, peak A, and peak C all decreased prominently with the increase in the initial pH value. The unsaturated bonds in humic substances could be transformed to oxygenated saturated bonds by O_3 that facilitated their efficient decomposition. Besides, O_3 caused denaturation of proteins and the aromatic amino acids tryptophan, tyrosine, and phenylalanine could be oxidized. As a similar oxidation process, we speculated that the tryptophan-like and the humic-like substances in EfOM were preferably degraded by AC/O_3 pretreatment. Compared with preozonation, especially when the oxidation dosage increased above 1 mg (O_3)/mg (DOC), AC/O_3 displayed a more prominent effect on the decrease in fluorescence intensity of peak T, peak A, and peak C. The results revealed that the characteristics or constituents of sewage effluent were greatly changed by AC/O_3.

4. Discussion

As we know, EfOM has a significant humic substance content derived from drinking water. It was reported that membrane fouling caused by the humic substances was more severe at low pH, as the membrane was most positively charged under the

Table 2
Intensity transformation of EEM after pretreatment under different initial pH

	Peak T1 (Ex: 275–280 nm, Em: 360–384 nm)						Peak A (Ex: 245–255 nm, Em: 423–449 nm)						Peak C (Ex: 325–330 nm, Em: 402–418 nm)					
pH	SE	AC adsorption (2 g/L)	O_3 (0.48 mg O_3/mg DOC)	O_3 (1.4 mg O_3/mg DOC)	AC/O_3 (0.48 mg O_3/mg DOC, 2 g/L AC)	AC/O_3 (1.4 mg O_3/mg DOC, 2 g/L AC)	SE	AC adsorption (2 g/L)	O_3 (0.48 mg O_3/mg DOC)	O_3 (1.4 mg O_3/mg DOC)	AC/O_3 (0.48 mg O_3/mg DOC, 2 g/L AC)	AC/O_3 (1.4 mg O_3/mg DOC, 2 g/L AC)	SE	AC adsorption (2 g/L)	O_3 (0.48 mg O_3/mg DOC)	O_3 (1.4 mg O_3/mg DOC)	AC/O_3 (0.48 mg O_3/mg DOC, 2 g/L AC)	AC/O_3 (1.4 mg O_3/mg DOC, 2 g/L AC)
3	267.32	258.50	127.6	101.7	127.1	58.44	254.23	236.4	142.5	84.15	123.7	68.14	301.06	281.52	97.81	58.67	87.17	45.60
4.5	288.13	265.61	63.15	32.28	64.29	20.76	263.15	243.6	77.07	46.89	89.14	26.38	309.45	282.34	74.39	41.36	68.48	21.64
7.54	312.14	278.23	38.29	24.57	39.86	21.53	248.40	228.5	63.29	29.02	56.25	20.87	311.7	301.71	52.63	23.73	50.93	19.33
9	331.45	304.45	36.62	22.82	39.42	19.32	256.12	246.3	51.02	28.41	50.29	14.34	303.68	286.86	50.02	21.89	50.07	18.28

acidic condition, which resulted in a strong HA–membrane attraction [23]. Moreover, a greater mass of humic acid molecule aggregates was seen depositing at low pH and increasing the hydraulic resistance of membrane [26]. With the increase in pH value, the membrane is negatively charged and humic acid molecules are negatively charged due to deprotonization, then membrane fouling was decreased [27]. Although EfOM possesses the humic characteristic, the results of Fig. 5 revealed that there is no obvious impact of pH on UF except for a slight alleviation effect under alkaline condition. The zeta potential of the UF membrane used in our experiment was further detected as a function of solution pH. As shown in Fig. 8, it was noted that the surface of the UF membrane had positive charges of 20 mW under pH 3 and weak negative charges of −5 mV under pH 4.5. Under neutral pH value, the surface of the UF membrane had a negative charge of −60 mV. After ultrafiltrating sewage effluent for 200 mL, the surface charge of the UF membrane was completely changed to negative at all determined pH values. Combined with the results of Fig. 5(a), it revealed that the electrostatic repulsion between the less charged EfOM macromolecules and the positive/less negative membrane (20 mW to −5 mV) was relatively weak under an acidic condition. Moreover, the hydrophobic character of EfOM promoted its adsorption onto the UF membrane. With the increase in pH, the increase in EfOM deprotonization and the more negative charges (−60 mV) of the membrane induced an increased electrostatic repulsion between the EfOM in solution and the clean membrane, which alleviated the fouling. As shown in Fig. 5(b), the irreversible fouling (related to pore plugging) was decreased with the increase in pH,

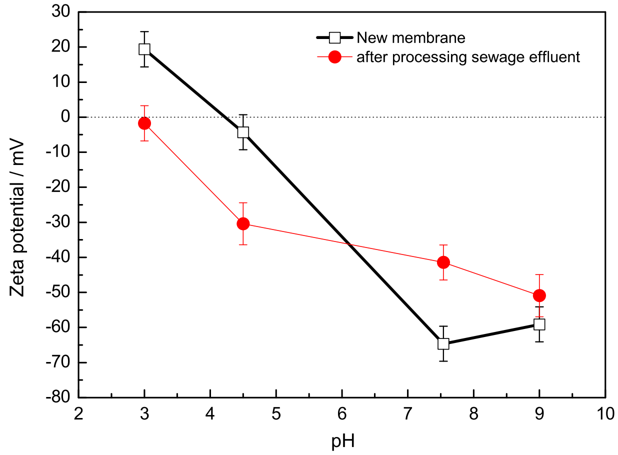

Fig. 8. Zeta potential of membrane before and after processing sewage effluent.

although reversible fouling (related to cake fouling) was slightly increased. However, pH adjustment of the sewage effluent had a weaker impact on membrane fouling compared with humic substances. On one hand, the adjustment of pH caused only a little fluctuation of DOC and UV, as shown in Fig. 6. On the other hand, EfOM in sewage effluent had a more complicated composition, and no obvious structural transformation of multi-component organic substances occurred after pH adjustment, as shown in Table 2. As a result, the adjustment of pH had minor influence on fouling alleviation when compared with oxidation pretreatment.

It was reported that the effect of AC on membrane fouling was determined by the function of the membrane characteristics, the diversity of raw water, as well as the concrete operation of pretreatment [28]. As a result, contradictory results such as improvements of permeate flux, similar flux behavior or exacerbated flux decline after AC adsorption were all reported [29–32]. As shown in Fig. 5(c) and (d), AC adsorption had almost no alleviation effect on membrane fouling, while the irreversible fouling increased with the increase in pH. Generally, the role of non-electrostatic interactions (hydrophobicity reaction) for the adsorption of EfOM on the AC surface was important under acidic condition, and the electrostatic repulsion between EfOM and the AC surface was enhanced when pH increased above the pH_{pzc} of AC (determined as 9.0). The decreased adsorption by AC led to a larger amount of these substances being adsorbed on the membrane, and further increased the proportion of internal fouling. However, 2 g/L GAC used in our experiment could not effectively remove the foulants. As Fig. 6 demonstrated, the DOC and UV removal after AC pretreatment were limited. Moreover, the EEM results in Table 2 further proved that no obvious structural transformation of multi-component organic substances occurred after AC adsorption under different initial pH. This is similar to Filloux et al. [8], who reported that the biopolymers in sewage effluent could not be significantly removed after AC adsorption compared with oxidation pretreatment, as it was hydrophilic in nature and unable to penetrate into the micropores of AC. Consequently, AC adsorption had only a minor influence on fouling alleviation.

Normally, biopolymers (mostly macro-polysaccharide-like and protein-like molecules) in sewage effluent were identified as major foulants affecting the filterability of water in dead-end UF [6–9]. 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, and the higher the biopolymer concentration in the feed water, the lower the filterability of the water sample [7]. Besides the biopolymers, the humic-like substances were also another main foulant in the ultrafiltration process [9]. It was reported that ozonation could break the high-MW biopolymers to a great extent and alleviated flux reduction during MF and UF [8]. Ozonation was also reported to decrease the membrane fouling by humic substances, as it decreased the adsorption of humic substances by hydrophobic interactions and/or decomposed the molecules into smaller fragments [18]. Among the pretreatment methods, AC/O_3 pretreatment had the obvious mitigating effect on membrane fouling and the best effect on water quality improvement under all pH conditions, as stated in Sections 3.2 and 3.3. As for the AC/O_3 pretreatment, it was a very complex system with potential adsorption by the AC, oxidation of organics by the direct and indirect pathways for ozonation (i.e. latter via hydroxyl radicals) and thus different oxidation products. The impact of initial pH on AC/O_3 for fouling alleviation was obvious. It was speculated that the adsorption process of EfOM would not dominate the reactions between EfOM and AC/O_3, as the adsorption of EfOM by AC decreased with the increase in pH. We speculated that the catalytic reaction essentially occurred in the bulk liquid with the increase in pH, as the improvement of OH^- concentration with the increase in pH contributed to the degradation of ozone molecular and resulted in an increase in the concentration of the $\cdot OH$ or other radical species. As expected, the characteristics or compositions of sewage effluent were changed greatly by AC/O_3. The aromatic substances in sewage effluent were prone to be removed with the increase in pH after AC/O_3 pretreatment, as shown in Fig. 6. Moreover, Table 2 further demonstrated that humic-like substances related to peak A, peak C and tryptophan-like substances related with peak T all degraded prominently after AC/O_3 pretreatment. The increase in initial pH further promoted the degradation of humic-like and tryptophan-like substances. It proved that the preferential removal of high-MW biopolymers as well as humic substances in EfOM by AC/O_3 with the increase in initial pH value alleviated the membrane fouling.

Liu et al. also reported that both external (related to reversible fouling) and internal (related to irreversible fouling) fouling could be effectively mitigated by the preozonation [33]. As they reported, the breakdown of protein-like substances and structural change of humic-like substances were observed in external foulants from EEM fluorescence spectra due to pre-ozonation, although the effect was relatively weaker for the internal foulants. Nguyen and Roddick [34] reported that ozonation could hydraulically reduce irreversible fouling of the membrane. They speculated that the reduction of irreversible fouling was attributed to the removal of the aromatic rings, and led to a smaller amount of these substances being adsorbed on the membrane and further reduced the proportion of internal fouling. In our experiment (as demonstrated in Fig. 4(b)), with the increase in initial pH, the reversible fouling was reduced and even vanished under neutral and alkaline conditions, and the irreversible fouling diminished noticeably after AC/O_3 pretreatment. Nevertheless, ozonation and hydroxyl-mediated breakdown of organic matter might increase the biodegradability of the treated organic matter. The implications for biofouling of the UF membrane in long-term use still need further investigation.

5. Conclusions

(1) Compared with the adjustment of pH value and pretreatment methods such as AC adsorption and preozonation, AC/O_3 displayed the greatest impact on fouling alleviation and the best effect on water quality improvement under all pH conditions. No obvious impact of pH on ultrafiltration process was observed. AC adsorption pretreatment had almost no alleviation effect on membrane fouling regardless of the initial pH.

(2) AC/O_3 pretreatment clearly mitigated the membrane fouling. After AC/O_3 pretreatment, the total fouling, the reversible fouling (related to cake fouling) and irreversible fouling (related to pore plugging) were all decreased. The impact of initial pH on AC/O_3 for fouling alleviation was prominent. With the increase in initial pH, the reversible fouling was reduced and even vanished, and the irreversible fouling was diminished to a great extent after AC/O_3 pretreatment.

(3) It was the component transformation of sewage effluent after AC/O_3 pretreatment that caused the alleviation of membrane fouling. With the increase in initial pH, the high-MW biopolymers as well as the humic substances in EfOM were preferentially removed by AC/O_3, which mitigated the flux decline during the ultrafiltration process and decreased the reversible and irreversible fouling.

Acknowledgments

This work was supported by the Beijing Nova Programme China (Grant No. Z1511000003150139), the National Natural Science Foundation of China (Grant No. 51478009), the Cultivation Plan for the Top Young Talents of Beijing (2013–2015), the Beijing Municipal Commission of Education (Grant No. KM201310005011), the Basic Research Funds offered by the Beijing University of Technology, and the Organization Department of Municipal Party Committee (Outstanding Young Team, Grant No. Q0004018201502/003).

References

[1] H. Huang, K. Schwab, J.G. Jacangelo, Pretreatment for low pressure membranes in water treatment: A review, Environ. Sci. Technol. 43 (2009) 3011-3019.
[2] C. Jarusutthirak, G. Amy, J.-P. Croué, Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes, Desalination 145 (2002) 247–255.
[3] H.K. Shon, S. Vigneswaran, I.S. Kim, J. Cho, H.H. Ngo, The effect of pretreatment to ultrafiltration of biologically treated sewage effluent: A detailed effluent organic matter (EfOM) characterization, Water Res. 38 (2004) 1933–1939.
[4] H.K. Shon, S. Vigneswaran, S.A. Snyder, Effluent organic matter (EfOM) in wastewater: Constituents, effects and treatment, Crit. Rev. Environ. Sci. Technol. 36 (2006) 327–374.
[5] K.N. Bourgeous, J.L. Darby, G. Tchobanoglous, Ultrafiltration of wastewater: Effects of particles, mode of operation, and backwash effectiveness, Water Res. 35 (2001) 77–90.
[6] C.N. Laabs, G.L. Amy, M. Jekel, Understanding the size and character of fouling-causing substances from effluent organic matter (EfOM) in low-pressure membrane filtration, Environ. Sci. Technol. 40 (2006) 4495–4499.
[7] X. Zheng, M. Ernst, M. Jekel, Identification and quantification of major organic foulants in treated domestic wastewater affecting filterability in dead-end ultrafiltration, Water Res. 43 (2009) 238–244.
[8] E. Filloux, H. Gallard, J.P. Croue, Identification of effluent organic matter fractions responsible for low-pressure membrane fouling, Water Res. 46 (2012) 5531–5540.
[9] J. Guo, H. Liu, J.H. Liu, L.Y. Wang, Ultrafiltration performance of EfOM and NOM under different MWCO membranes: Comparison with fluorescence spectroscopy and gel filtration chromatography, Desalination 344 (2014) 129–136.
[10] S. Lee, K. Lee, W.M. Wan, Y.S. Choi, Comparison of membrane permeability and a fouling mechanism by pre-ozonation followed by membrane filtration and residual ozone in membrane cells, Desalination 178 (2005) 287–294.
[11] S.H. You, D.H. Tseng, W.C. Hsu, Effect and mechanism of ultrafiltration membrane fouling removal by ozonation, Desalination 202 (2007) 224–230.

[12] S.V. Geluwe, C. Vinckier, L. Braeken, B.V. derBruggen, Ozone oxidation of nanofiltration concentrates alleviates membrane fouling in drinking water industry, J. Membr. Sci. 378 (2011) 128–137.

[13] Y.G. Park, Effect of ozonation for reducing membrane-fouling in the UF membrane, Desalination 147 (2002) 43–48.

[14] J. Kim, S.H.R. Davies, M.J. Baumann, V.V. Tarabara, S.J. Masten, Effect of ozone dosage and hydrodynamic conditions on the permeate flux in a hybrid ozonation-ceramic ultrafiltration system treating natural waters, J. Membr. Sci. 311 (2008) 165–172.

[15] B.S. Karnik, S.H.R. Davies, K.C. Chen, D.R. Jaglowski, M.J. Baumann, S.J. Masten, Effects of ozonation on the permeate flux of nanocrystalline ceramic membranes, Water Res. 39 (2005) 728–734.

[16] S.G. Lehman, L. Liu, Application of ceramic membranes with pre-ozonation for treatment of secondary wastewater effluent, Water Res. 43 (2009) 2020–2028.

[17] B. Schlichter, V. Mavrov, H. Chmiel, Study of a hybrid process combining ozonation and microfiltration/ultrafiltration for drinking water production from surface water, Desalination 168 (2004) 307–317.

[18] S.V. Geluwe, L. Braeken, B.V. derBruggen, Ozone oxidation for the alleviation of membrane fouling by natural organic matter: A review, Water Res. 45 (2011) 3551–3570.

[19] U. Jans, J. Hoigné, Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH-radicals, Ozone: Sci. Eng. 20 (1998) 67–90.

[20] J. Ma, M.H. Sui, T. Zhang, C.Y. Guan, Effect of pH on MnO_x/GAC catalyzed ozonation for degradation of nitrobenzene, Water Res. 39 (2005) 779–786.

[21] P.M. Alvárez, J.F. García-Araya, F.J. Beltrán, I. Giráldez, J. Jaramillo, V. Gómez-Serrano, The influence of various factors on aqueous ozone decomposition by granular activated carbons and the development of a mechanistic approach, Carbon 44 (2006) 3102–3112.

[22.] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Ozone decomposition in water catalyzed by activated carbon: Influence of chemical and textural properties, Ind. Eng. Chem. Res. 45 (2006) 2715–2721.

[23] I. Sutzkover-Gutman, D. Hasson, R. Semiat, Humic substances fouling in ultrafiltration processes, Desalination 261 (2010) 218–231.

[24] J.S. Noh, J.A. Schwarz, Effect of HNO_3 treatment on the surface acidity of activated carbons, Carbon 28 (1990) 675–682.

[25] F.S. Qu, H. Liang, Z.Z. Wang, H. Wang, H.R. Yu, G.B. Li, Ultrafiltration membrane fouling by extracellular organic matters (EOM) of *Microcystis aeruginosa* in stationary phase: Influences of interfacial characteristics of foulants and fouling mechanisms, Water Res. 46 (2012) 1490–1500.

[26] W. Yuan, A. Zydney, Humic acid fouling during ultrafiltration, Environ. Sci. Technol. 34 (2000) 5043–5050.

[27] M. Kulovaara, S. Metsämuuronen, M. Nyström, Effects of aquatic humic substances on a hydrophobic ultrafiltration membrane, Chemosphere 38 (1999) 3485–3496.

[28] M. Campinas, M.J. Rosa, Assessing PAC contribution to the NOM fouling control in PAC/UF systems, Water Res. 44 (2010) 1636–1644.

[29] C. Stoquart, P. Servais, P.R. Bérubé, B. Barbeau, Hybrid membrane processes using activated carbon treatment for drinking water: A review, J. Membr. Sci. 411–412 (2012) 1–12.

[30] J. Lohwacharin, K. Oguma, S. Takizawa, Use of carbon black nanoparticles to mitigate membrane fouling in ultrafiltration of river water, Sep. Purif. Technol. 72 (2010) 61–69.

[31] S.K. Kang, K.H. Choo, Why does a mineral oxide adsorbent control fouling better than powdered activated carbon in hybrid ultrafiltration water treatment? J. Membr. Sci. 355 (2010) 69–77.

[32] M. Remy, V. Potier, H. Temmink, W. Rulkens, Why low powdered activated carbon addition reduces membrane fouling in MBRs, Water Res. 44 (2010) 861–867.

[33] T. Liu, Z.L. Chen, W.Z. Yu, S.J. You, Characterization of organic membrane foulants in a submerged membrane bioreactor with pre-ozonation using three-dimensional excitation–emission matrix fluorescence spectroscopy, Water Res. 45 (2011) 2111–2121.

[34] S.T. Nguyen, F.A. Roddick, Effects of ozonation and biological activated carbon filtration on membrane fouling in ultrafiltration of an activated sludge effluent, J. Membr. Sci. 363 (2010) 271–277.