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Control of dissolved organic matter fouling ultrafiltration membrane treating a WWTP secondary effluent via multi-pretreatments

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ABSTRACT

Dissolved organic matter (DOM) has been regarded as a major organic foulant resulting in UF membrane fouling in wastewater reclamation. This study investigated the effects of multi-pretreatments, including coagulation, adsorption, and pre-oxidation, of a WWTP secondary effluent via adding $Al_2(SO_4)_3$/diatomite composite, $FeCl_3$, GAC, and O_3 to control DOM fouling UF membrane. Results showed the membrane fluxes increased by 18.1, 8.1, 5.3, and 0.1% and membrane resistances decreased by 58.9, 28.9, 17.8, and 2.2%, when the optimal adding dosages of $Al_2(SO_4)_3$/diatomite composite, $FeCl_3$, GAC, and O_3 were 400, 80, 80, and 6 mg L^{-1}, respectively. The tests of a series of UF membranes with different pore sizes demonstrated that DOM of 10,000–30,000 Dalton MW in the secondary effluent was dramatically reduced by adding $Al_2(SO_4)_3$/diatomite composite, $FeCl_3$, and GAC. This fractionation was mainly protein-like substances characterized by 3DEEM fluorescence spectroscopy. Additionally, adding $Al_2(SO_4)_3$/diatomite composite was available for removing humic acid-like substances simultaneously. Although O_3 addition effectively oxidized protein-like and humic acid-like substances, it could induce the increase in DOM of <4,000 Dalton MW up to 80.1% and triggered the UF membrane fouling. Combination of MW distribution, SEM and 3DEEM, the DOM fractionation of <6,000 Dalton MW, mainly humic acid-like substances, easily caused UF membrane fouling. Consequently, compared with adsorption and pre-oxidation, the coagulation of $Al_2(SO_4)_3$/diatomite composite, the first time used for the pretreatment of DOM, was proved to be the best additive for controlling UF membrane fouling.

Keywords: Secondary effluent; DOM; Membrane fouling; MW distribution; 3DEEM

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1. Introduction

Currently, the reuse of a secondary WWTP effluent is one of the key issues in water resource management worldwide, as the dual economic benefits, including increasingly stringent discharge standards and increased water reclamation demand, can be expected. For instance, the secondary effluents of urban WWTPs have been reused for agriculture irrigations in some regions of Spain and Greece, with faint influence on local environments and crops [1]. In some countries of Middle East, such as Kuwait and Saudi Arabia, and in Egypt of North Africa, the proportions of water supply via reusing municipal wastewater annually

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increased [2]. However, as a prerequisite to reuse the secondary effluents from WWTPs, an advanced tertiary treatment is necessary due to the high residual DOM, nutrients (nitrogen, phosphorus, potassium, etc.), turbidity, and suspended solids (SS) [3].

In wastewater reclamation, UF has been regarded as a promising membrane separation technology due to simplicity of operation, low membrane costs, and excluding material transformations during treatments [4]. It can effectively remove both macro- and microparticles driven by the pressure [5]. However, the wide application of UF membrane in wastewater treatment is considerably limited by the irreversible membrane fouling, which increases the operating cost and shortens membrane life [6]. Extensive studies have been undertaken for more insights into UF membrane fouling, and the DOM, including protein-like and humic acid-like substances, has been generally considered as the major culprit responsible for membrane fouling [4,7,8].

To overcome the problem of membrane fouling, various control measures have been introduced. One is the optimization of operation conditions, including running under the critical flux, rinsing, and chemical cleaning, etc. [9]. Another is the pretreatment of inflows of UF systems, including coagulation, adsorption, and pre-oxidation [10]. Recently, the pretreatments have received much more attention, since the membrane fouling can be prevented or controlled from the source. For instance, Gamage et al. [11] found that aluminum salts can reduce the accumulation of hydrophobic foulants and consequent membrane fouling via complexing hydrophilic molecules in a PVDF membrane system. Not only aluminum-based but also ferric-based coagulants or other iron salts are commonly used for mitigating the membrane fouling. Dong et al. [9] pretreated the inflows of UF system with the PFC. Results displayed that the fouling degree varied with the species of Fe(III), the removal effect of dissolved organic matter (DOM) was better with the higher alkalinity. For adsorption, powdered activated carbon (PAC) is the most common type of commercially available absorbent and has been widely applied in UF systems. It can adsorb a significant proportion of humic-like substances and efficiently control the membrane fouling [4]. Other measures such as pre-oxidation have also been applied for controlling membrane fouling, using O_3 or chemicals to oxidize organic contaminants of the cake layer into fragmentations [12].

Most of aforementioned studies employed one or two pretreatment methods, while there has been lack of sufficient investigation on the comparisons in mitigating membrane fouling and the underlying mechanisms are still unclear. Therefore, the main objective of this study was to obtain the comprehensive understanding of the effects of multi-pretreatments, including coagulation, adsorption, and pre-oxidation, of a WWTP secondary effluent by addition of $Al_2(SO_4)_3$/diatomite composite, $FeCl_3$, GAC, and O_3 to control DOM fouling UF membrane. The DOM characteristics and dynamics were systematically compared after these multi-pretreatments. Additionally, to the best of our knowledge, there are no report for using the cheap and easily available $Al_2(SO_4)_3$/diatomite composite as coagulants for controlling membrane fouling in UF systems. The findings of this study can provide the detailed insights for economic and effective running of UF membrane systems for wastewater reclamation and for the management strategies of water resource.

2. Materials and methods

2.1. Water source

The raw water from the secondary settling tank of a local wastewater plant with the anaerobic–anoxic–oxic process in Wuhu, China, was randomly sampled for the experiments. The influent flow to the wastewater plant was mainly domestic sewage wastes from surrounding universities and residential quarters. The water quality data of the secondary settling tank are presented in Table 1.

2.2. Experimental setup

A bench-scale UF membrane system, as displayed in Fig. 1, was setup for the experiments in current study. The setup consisted of three parts, i.e. filtration cell (SCM-300, Shanghai SINAP Membrane Tech Co., Ltd, Shanghai, China), pressure-supply system, and effluent section. The cell placed on a magnetic stirrer and connected to the pressure-supply system, with a constant value of 0.2MP controlled by a pressure gage. The filtration test was performed in a dead-end mode at room temperature (13–20℃). Permeate was collected in a measuring cylinder to measure the UF membrane flux. The poly-ethersulfone (PES) UF membranes (Shanghai SINAP Membrane Tech Co., Ltd, Shanghai, China) with different molecular weight cut-offs (MWCOs) of 4,000, 6,000, 10,000, 20,000, and 30,000 Dalton were used in this study. All of the ultrafiltration units were conducted to treat the raw water as mentioned above with the volume of 300 ml.

Table 1
The water quality of the effluents from the secondary settling tank of a wastewater plant in Wuhu, China (n = 5)

	DOC (mg L^{-1})	UV_{254} (cm^{-1})	COD (mg L^{-1})	TN (mg L^{-1})	TP (mg L^{-1})	pH
Min	55.26	0.096	20.2	5.1	0.4	7.03
Max	80.32	0.168	41.3	10.0	1.2	7.86
Average	70.37	0.112	30.5	7.7	0.5	7.58
Standard deviation	10.21	0.031	8.9	2.34	0.43	0.33

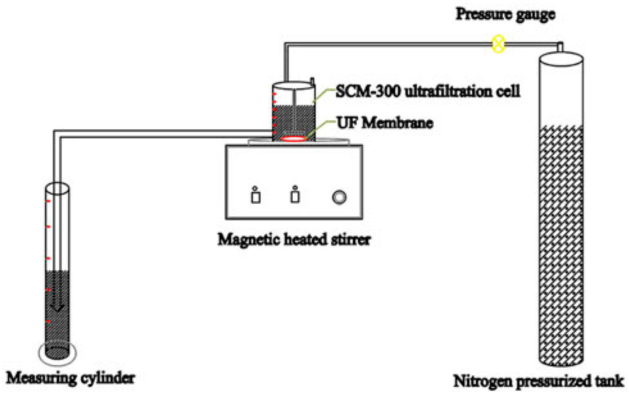

Fig. 1. Schematic diagram of the UF membrane system.

2.3. Operation methods

2.3.1. Optimal dosage

The $Al_2(SO_4)_3$/diatomite composite was prepared by mixing $Al_2(SO_4)_3$ and diatomite at the mass ratio of 1:1.

In order to determine the optimal dosage, the standard jar test was performed. A series of concentrations of $Al_2(SO_4)_3$/diatomite composite, $FeCl_3$, GAC, and O_3 were added to treat the raw water. The solution was rapidly mixed for 1 min at 100 rpm followed by 30 min slow mixing at 30 rpm. Then after 1 h settling, the water sample was collected and filtered through 0.45-μm fiber membrane before DOC analysis [11]. Lastly, the optimal dosages of $Al_2(SO_4)_3$/diatomite composite, $FeCl_3$, GAC, and O_3 were determined with their concentrations of 400, 80, 80, and 6 mg L^{-1}, respectively.

2.3.2. Membrane flux

The pretreated and filtered raw water was used as the feed solution of UF membrane system. Before ultrafiltration, the deionized water of 300 ml was added into the system with pressure to clean the membrane. Then, the feed solution for the filtration process was pumped to the membrane module with different MWCOs of 4,000, 6,000, 10,000, 20,000, and 30,000 Dalton. Permeate was collected in a measuring cylinder and the time for gathering 50 ml permeate was recorded. The membrane flux can be expressed as follows:

$$J_V = \frac{V}{S \cdot T} \tag{1}$$

where J_V is the permeate flux ($m^3\ m^{-2}\ h^{-1}$), V is the volume of permeate (50 ml), S is the effective membrane area ($3.32 \times 10^{-3}\ m^2$), and T is the total time for gathering 50 ml permeate.

2.3.3. Fouling resistance

The fouling resistance was estimated following the Model "Resistance in Series Model" (Eq. (2)) [13]:

$$J_V = \frac{\Delta P}{\mu(R_m + R_p + R_f)} \tag{2}$$

where J_V is the permeate flux ($m^3\ m^{-2}\ h^{-1}$), ΔP is the transmembrane pressure, μ is the dynamic viscosity of permeate, R_m is the intrinsic membrane resistance, R_p is the hydrodynamic resistance of concentration polarization boundary layers, and R_f is the fouling resistance (m^{-1}).

Particularly, μ is equal to 1.14×10^3 Pa S, determined by the water viscosity at 15℃. R_m is equal to $2.43 \times 10^6\ m^{-1}$, as R_p and R_f were zero when filtering deionized water through a clean membrane. R_f is determined after the filtering experiment start to obtain the J_1 and ΔP at a certain flux by the formula as follows (Eq. (3)):

$$R_f = \frac{\Delta P}{\mu \times J_1} - R_m \tag{3}$$

2.4. Analytical methods

The DOC in this study was measured using a TOC analyzer (OI Analytical 1020A, USA). The molecular weight distribution was accounted according to the ratio of DOC of each MWCO to the total DOC of raw water.

The fouled membrane was removed carefully from the filtration cell with the fouled layer retained on its surface. After freeze-drying, the fouled membrane samples were then gold coated by a sputter and observed under SEM (Hitachi S-4800, Japan).

The EEM measurements were performed using a Spectrofluorometer (F-4500, Hitachi, Japan) equipped with a 150-W xenon lamp at ambient temperature of 24℃. The sample was added into a 1-cm quartz cuvette with four optical windows for the analyses. The emission wavelengths were conducted from 220 to 550 nm with excitation wavelengths from 220 to 450 nm. Both of the steps and slit widths of emission and excitation were 5 nm. The scanning speed was maintained at 1,200 nm min^{-1} with the response time of 0.004 ns. The fluorescence spectrum of Milli-Q water, obtained under the same conditions, was subtracted from all the spectra to eliminate water Raman scattering and to reduce other background noise.

3. Results and discussion

3.1. Effects of multi-pretreatments on membrane flux

To estimate the effects of multi-pretreatments, including $Al_2(SO4)_3$/diatomite composite, $FeCl_3$, GAC, and O_3, on membrane fouling of the UF system, a series of filtration tests were conducted with the raw water. Their flux decline curves were shown in Fig. 2 (measure at 13–20℃). The permeate flux sharply decreased until the permeate volume reached 100 ml, followed by the gradually sluggish decline. It is probably related to the foulants adsorbed onto the inner pore fibers at the initial stage, and then formed and maintained the cake layer of a constant thickness on the membrane surface [12,14]. Among multi-pretreatments, the raw water caused the faster flux decline with the final normalized flux (J/J_0) approximately 63.2%, while other pretreatments could alleviate the flux decline to some extent. In the result, the coagulations, including $Al_2(SO4)_3$/diatomite composite and $FeCl_3$, displayed better effects than adsorption and pre-oxidation with the increased membrane flux of 18.1 and 8.1%, respectively. Especially, the change in normalized flux after adding $Al_2(SO4)_3$/diatomite composite appeared to be minimal, with a slightly decline to 82.7% at 300 ml of permeate volume. It is probably related to the dual benefits after compounding diatomite and $Al_2(SO_4)_3$. That is, diatomite is characterized by the strong absorption capacity due to the highly developed capillary structure and large specific surface area. After compounding with $Al_2(SO_4)_3$, the composite overcomes the shortcomings of aluminum coagulant with much and loose alum floc and not easy settlement [15]. Consequentially, the $Al_2(SO4)_3$/diatomite composite, the first time used for the pretreatment of DOM, exhibited excellent treatment performances. $FeCl_3$ pretreated flux higher than activated carbon adsorption. The pre-oxidation of O_3 showed a very limited change of in flux decline (only 0.1% alleviation) that occurred in comparison with the controlled trial, indicating that O_3 played a minor role in the flux amelioration. The result seemed to be inconsistent with the previous report that ozonation effectively controlled the UF membrane fouling, because the ozone could oxide and destroy the organic fouling and the crossflow flushed away any loose fragments on the filtration cake [12]. However, the relatively strong crossflow cannot shade the possibility that the new formed microfoulants may be adsorbed onto the inner pore fibers and cause the second pollution of UF membrane [16].

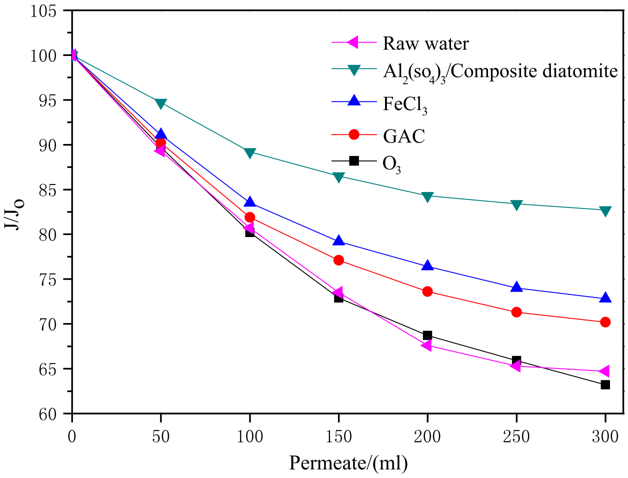

Fig. 2. Effects of multi-pretreatments on UF membrane flux.

3.2. Effects of multi-pretreatments on fouling resistance

The effects of multi-pretreatments on DOM fouling of UF membrane were shown in Fig. 3 (measure at 13–20℃). All of the membrane fouling resistance increased rapidly at the beginning of each pretreatment process, and the growth rate got slower and became stable after the volume of permeates up to 200 ml. Corresponding with the membrane flux, it may be caused by the gradual clogging of the membrane inner pores and the new forming cake layer on the membrane surface [17]. When filtering raw water, the fouling resistance gradually increased with the initial value of $2.90 \times 10^5\ \mathrm{m}^{-1}$ and up to $1.32 \times 10^6\ \mathrm{m}^{-1}$ at 300 ml of permeate volume. Other multi-pretreatments reduced the fouling resistance to some degree and their impacts were as follows: $Al_2(SO4)_3$/diatomite composite > $FeCl_3$ > GAC > O_3. Compared to the raw water, the membrane fouling resistance pretreated by $Al_2(SO4)_3$/diatomite composite greatly reduced by 60.2%, while the pretreatments of $FeCl_3$, GAC, and O_3 only decreased by 30.1, 21.5, and 1.45%, respectively. The reason may lie in the fact that the $Al_2(SO4)_3$/diatomite composite can effectively reduce the concentration of DOC of the raw water from 78.26 to 35.29 ppm, that is, the DOC removal rate was 54.59%, while other pretreatments of $FeCl_3$, GAC, and O_3 were only 28.82, 31.31, and 1.37%, respectively. The pretreatments of $Al_2(SO4)_3$/diatomite composite and GAC for TOC removal were probably much higher than the extent of their alleviations of membrane fouling, due to the additional resistance from diatomite and activated carbon particles [18]. These particles, (<0.45 μm), could cause the increase in resistance to some extent. Even though the coagulations, especially $Al_2(SO4)_3$/diatomite composite, showed the best performance than other pretreatments for the alleviation of UF membrane fouling.

3.3. Effects of multi-pretreatments on MW distribution of DOM

The molecular size distribution of all the water sample was presented in Fig. 4 (measure at 13–20°C). The DOM of raw water was mainly the portion of <4,000 Dalton MW, accounted for 50.6%, and the portion of 10,000–20,000 Dalton MW, accounted for 24.4%, while other components were relatively few. After the pretreatment of $Al_2(SO4)_3$/diatomite composite, the percentage of large MW of 10,000–20,000 Dalton significantly reduced from 24.4 to 4.3%, and the percentage of small MW < 4,000 Dalton reduced from 50.6 to 38.0%. Therefore, the addition of $Al_2(SO4)_3$/diatomite composite could effectively remove the DOM of the two main MW portions in the raw water, as it overcomes the shortcomings of aluminum coagulant with much and loose alum floc and not easy settlement [15]. The pretreatment of $FeCl_3$ mainly removed the large MW of 10,000–30,000 Dalton, due to the hydrolysis of $FeCl_3$ into $Fe(OH)_3$ colloid in the water, and the consequent adsorption of large MW substances via adsorption bridging action [19]. GAC also obviously removed the large MW of 10,000–30,000 Dalton. The surface of GAC contains much carboxyl, which easily adsorbs the protein-like substances in the distribution interval of 10,000–30,000 Dalton [19,20]. Furthermore, in the structure of GAC, the number of medium mesopores were more than micro mesopores, which benefited the adsorption of the organic molecules in the interval of 10,000–30,000 Dalton [21]. After O_3 pretreatment, the DOM of <4,000 Dalton in the water rose from 50.6 to 80.1%, because O_3 destructed the carbon–carbon bond and carbon–hydrogen bonds of organic matter and caused DOM split into smaller molecules [12]. Hence, the pretreatment of the $Al_2(SO4)_3$/diatomite composite could targeted remove the two main MW intervals, <4,000 Dalton and 10,000–30,000 Dalton, of the DOM in the raw water.

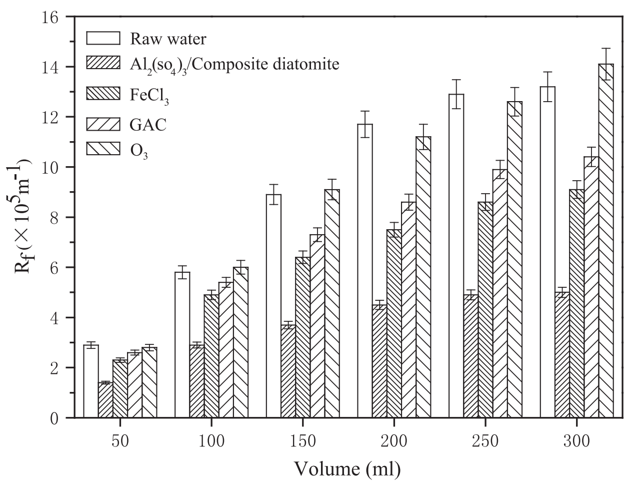

Fig. 3. Effects of multi-pretreatments on fouling resistance of UF membrane.

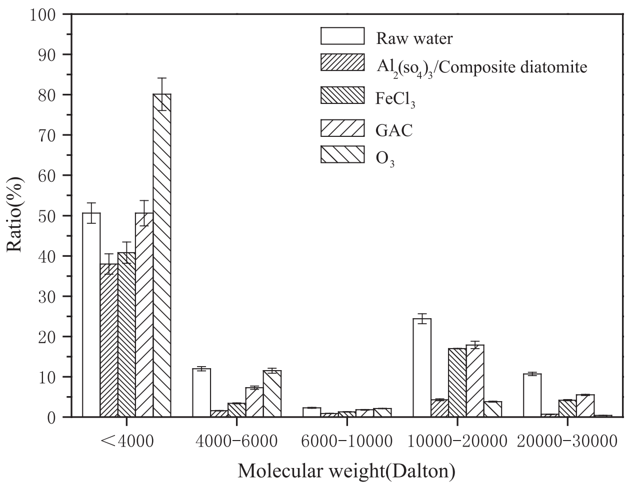

Fig. 4. The distribution of molecular weight of DOM with different pretreatments.

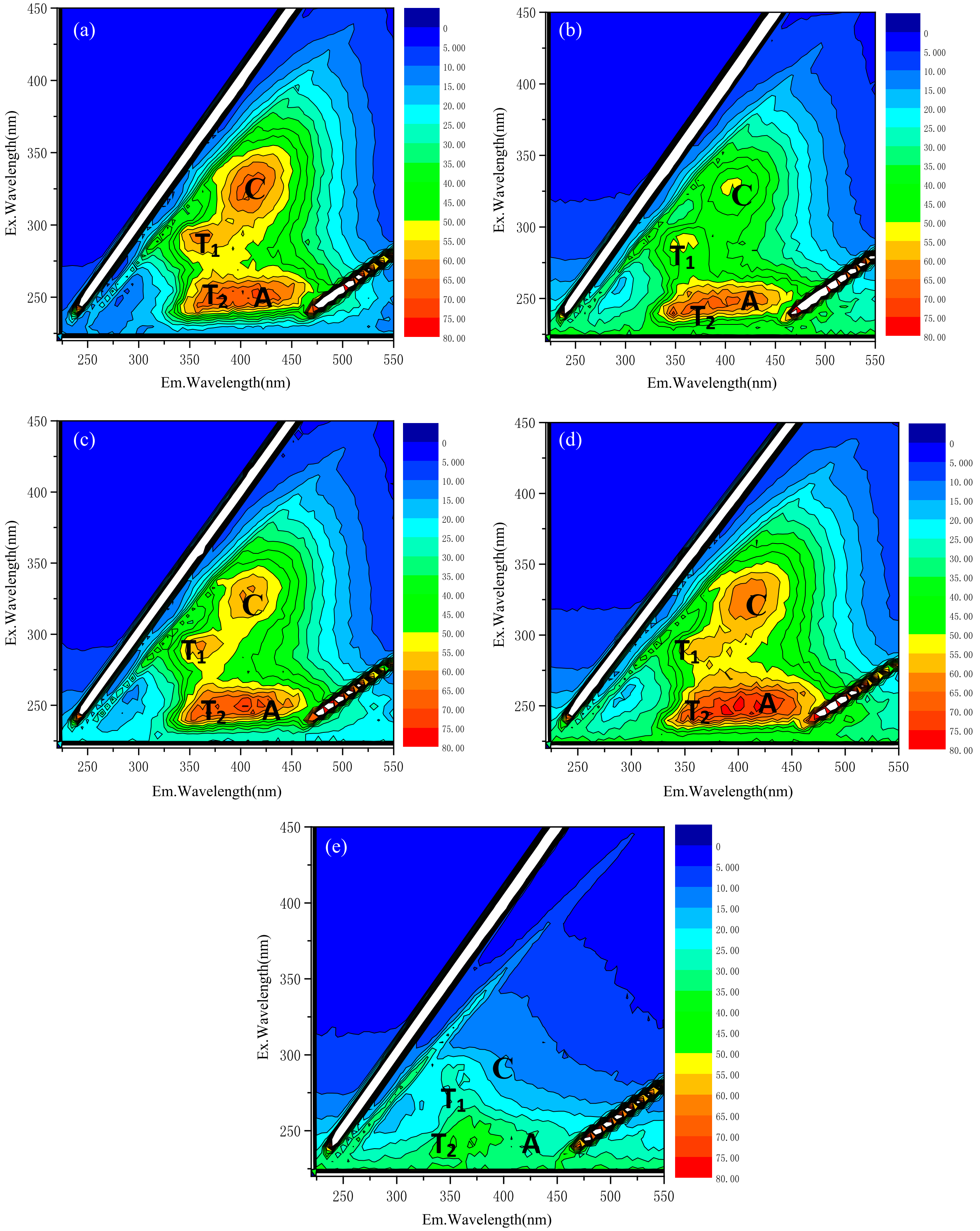

Fig. 5. EEM fluorescence spectra of DOM in (a) raw water (filtered through 0.45-μm fiber membrane), (b) the effluent pretreated by $Al_2(SO4)_3$/diatomite composite, (c) the effluent pretreated by $FeCl_3$, (d) the effluent pretreated by GAC, and (e) the effluent pretreated by O_3.

Table 2

Fluorescence spectral identifications of DOM samples in different pretreatments: (a) raw water (filtered through 0.45-μm fiber membrane), (b) the effluent pretreated by $Al_2(SO4)_3$/diatomite composite, (c) the effluent pretreated by $FeCl_3$, (d) the effluent pretreated by GAC, and (e) the effluent pretreated by O_3

	Peak A		Peak C		Peak T_1		Peak T_2	
Samples	Ex/Em	Int.	Ex/Em	Int.	Ex/Em	Int.	Ex/Em	Int.
A	250/400	73.99	330/410	75.32	290/355	68.75	235/345	150.4
B	240/405	57.74	330/405	51.94	285/350	53.83	240/350	64.68
C	250/400	68.87	325/400	56.19	290/355	63.57	240/345	71.92
D	240/400	76.01	320/410	66.37	290/360	59.88	240/355	70.70
E	240/395	33.75	335/395	19.59	285/345	27.69	235/345	41.23

Note: Int.: intensity.

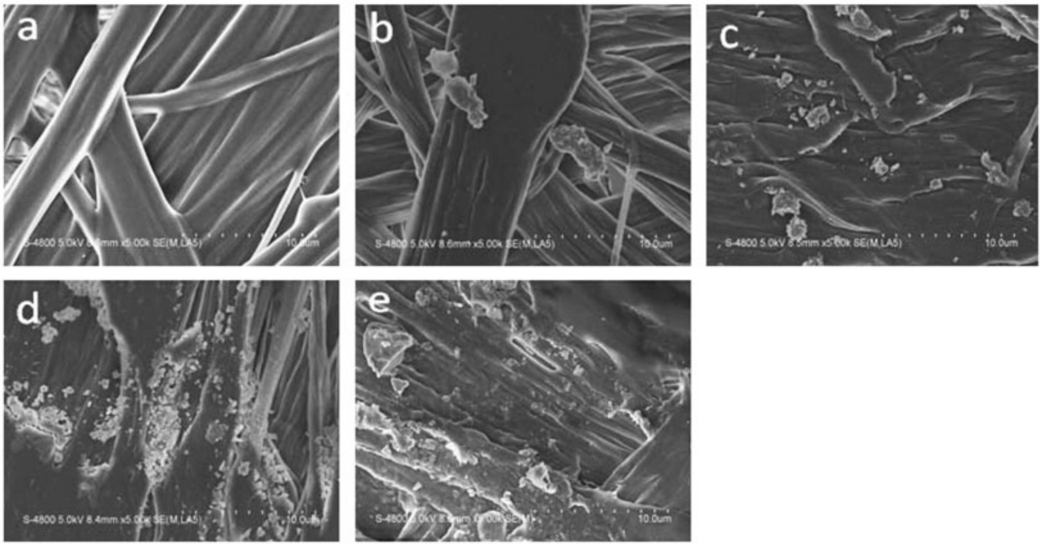

Fig. 6. The SEM profile (magnified 5,000×) of the UF filtered by the raw water pretreated by (a) blank (the new ultrafiltration membrane), (b) $Al_2(SO4)_3$/diatomite composite, (c) $FeCl_3$, (d) GAC, and (e) O_3.

3.4. Effects of multi-pretreatments on EEM fluorescence spectra of DOM

In order to identify the chemical composition of DOM and their variations influenced by the multi-pretreatments, 3DEEM fluorescence spectroscopy was applied in current study because of its ability to distinguish among certain classes of organic matter in natural waters [22,23]. The EEM fluorescence spectrum of the DOM in UF system effluents (Fig. 5 (measure at 23℃)) contained four fluorescence peaks: peak C, peak A, peak T_1 and peak T_2. Peak A [$\lambda_{Ex/Em}$ = (230–260)/(350–450) nm] and Peak C [$\lambda_{Ex/Em}$ = (300–370)/(350–450) nm] represented fulvic-like and humic-like substances, and peak T_1 [$\lambda_{Ex/Em}$ = (270–300)/(350–450) nm] and peak T_2 [$\lambda_{Ex/Em}$ = (220–260)/(350–450) nm] represented tryptophan-like and tyrosine-like substances [24,25]. The fluorescence parameters including peak locations, fluorescence intensity, and different peak intensity ratios were extracted from Fig. 5 and summarized in Table 2, which could be employed for quantitative analysis. In the raw water, the protein-like (peak T_2) substances were found to be dominant. The intensity reduction in the fluorescence peak between raw water and pretreated water might serve as an indicator of DOM content reduction. When raw water was pretreated by $Al_2(SO4)_3$/diatomite composite, $FeCl_3$ and GAC, the intensity of peak C and peak T_2 dramatically decreased, the peak A and peak T_1 intensity did not decrease in the same way. Therein, the pretreatment of $Al_2(SO4)_3$/diatomite composite exhibited stronger removal of humic-like and protein-like substances than $FeCl_3$ and GAC, indicating the broad effects of $Al_2(SO4)_3$/diatomite composite for removing DOM of multi-properties. Much more humic-like substances were removed by the pretreatment of $FeCl_3$ than GAC, in turn, more protein-like substances were removed by the pretreatment of GAC than $FeCl_3$. As presented in Figs. 2 and 3, the membrane flux pretreated by $FeCl_3$ was higher than that of GAC, and the opposite for membrane fouling resistance, which suggested that humic-like substances more easily triggered the blogging of UF membrane. After ozone pretreatment, all of the contents of humic-like, fulvic-like, tryptophan-like, and tyrosine-like substances significantly reduced. Because fluorescent molecules in the WWTP secondary effluents are mainly composed of benzene rings, and ozone oxidation may alter their chemical structure. That is, the C–H bond of benzene rings of protein-like and humic-like substances is damaged and the linear paraffin is formed [12]. Therefore, ozone oxidation could dramatically reduce the fluorescence intensity. It confirms the phenomenon of MW distribution variations that the DOM fraction of <4,000 Dalton MW rose from 50.6 to 80.1% after the pretreatment of ozone oxidation (Fig. 4). Although ozone oxidation could effectively remove DOM, it caused the oxidation the large MWs of DOM into small ones, and consequently limited the improvement of membrane flux or alleviation of membrane resistance.

3.5. SEM morphology of fouling membrane surface

SEM micrographs can exhibit a virtual structure of the foulant layer on the fouled membrane surface. In current study, the morphological changes of UF surface after multi-pretreatments were shown in Fig. 6 (measure at 23˚C). It can be seen that the retentive contaminants on the membrane surface gradually increased and the membrane blocking became more and more serious in the order of blank, $Al_2(SO4)_3$/diatomite composite, $FeCl_3$, GAC, and O_3. These observations were consistent with the variations of membrane flux and resistance (Figs. 2 and 3). For instance, after pretreated by $Al_2(SO4)_3$/diatomite composite, the least retentive foulants were found on the UF surface corresponding to the highest membrane flux and the smallest membrane fouling resistance. Moreover, if combined the aforementioned results: (1) the membrane clogging after the pretreatments of GAC and O_3 appeared to be more serious than that of $Al_2(SO4)_3$/diatomite composite and $FeCl_3$ (Fig. 2); (2) the percentage of the DOM fraction of <6,000 Dalton after the pretreatments of GAC (91.6%) and O_3 (57.9%) were significantly higher than that of $Al_2(SO4)_3$/diatomite composite (39.6%) and $FeCl_3$ (44.2%, Figs. 3 and 4), Therefore, it can be concluded that the DOM fraction of <6,000 Dalton in WWTP secondary effluents easily arouse the UF blocking.

4. Conclusions

In this study, the influence of multi-pretreatments, including coagulation, adsorption and pre-oxidation, of a WWTP secondary effluent via adding $Al_2(SO_4)_3$/diatomite composite, $FeCl_3$, GAC and O_3 on DOM removal and membrane fouling alleviation was evaluated. Compared with other three pretreatments, the overall benefit of $Al_2(SO4)_3$/diatomite is significant. Diatomite is abundant, cheap, and easily available. In addition, it can increase the membrane fluxes of 10.0, 12.8, and 18% comparing to the pretreatments of $FeCl_3$, GAC, and O_3. Correspondingly, the membrane resistances decreased by 20.0, 41.1, and 56.7%, which effectively alleviated the membrane fouling and improved the lifespan of the ultrafiltration membrane. As evidenced by the combined technologies of the MW distribution, SEM and 3DEEM, the pretreatment of $Al_2(SO_4)_3$/diatomite can remove more DOM. Results can be summarized as follows:

(1) The membrane fluxes increased by 18.1, 8.1, 5.3, and 0.1% and membrane resistances decreased by 58.9, 28.9, 17.8 and 2.2%, when the optimal adding dosages of $Al_2(SO4)_3$/diatomite composite, $FeCl_3$, GAC, and O_3 were 400, 80, 80, and 6 mg L^{-1}, respectively.

(2) The DOM of 10,000–30,000 Dalton MW, mainly protein-like substances, in the secondary effluent was dramatically reduced by adding $Al_2(SO4)_3$/diatomite composite, $FeCl_3$, and GAC, while adding $Al_2(SO4)_3$/diatomite composite was available for removing humic acid-like substance simultaneously.

(3) The O_3 addition not removed, but only oxidized protein-like and humic acid-like substances of DOM into the fraction of <4,000 Dalton MW.

(4) The DOM fraction of <6,000 Dalton in WWTP secondary effluents easily arouse UF blocking, which was humic-like substances.

In conclusion, these novel findings should be a valuable reference encouraging the recovery of tertiary effluent by the UF process.

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Abbreviations

WWTP — wastewater treatment plant
DOM — dissolved organic matter
UF — ultrafiltration
$Al_2(SO4)_3$ — aluminum sulfate
GAC — granular activated carbon
$FeCl_3$ — ferric chloride
O_3 — ozone
MW — molecular weight
3DEEM — three-dimensional excitation-emission matrix
PVDF — polyvinylidene fluoride
PFC — polymeric ferric chloride
MWCO — molecular weight cut-off
SEM — scanning electron microscopy

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