The change of NOM in a submerged UF membrane with three different pretreatment processes compared to an individual UF membrane

Yue Zhang a, Xinhua Zhao a,b, Xinbo Zhang c, Sen Peng a,⁎

a School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China
b State Key Laboratory of Hydraulic Engineering Simulation and Safety, Tianjin University, Tianjin 300072, China
c School of Environmental and Municipal Engineering, Tianjin Chengjian University, Tianjin 300384, China

HIGHLIGHTS
• All three pretreatments could reduce the accumulation of NOM in the membrane pores.
• The PAC/UF had a distinct advantage for removing NOM in effluent.
• The Al pretreatment increased all the chemical fractions in external foulants.
• The O3/UF process was more appropriate for controlling UF membrane fouling compared with other three processes.
• The HiM chemical fraction removal rate of O3/UF was lower than in the other three processes.

ABSTRACT
Three identical submerged ultrafiltration (UF) membranes with different pretreatment processes (coagulation, adsorption and ozonation) were compared with an individual UF membrane to investigate the performance of the process and characterize organic membrane foulants by natural organic matter (NOM) molecular weight distribution (MWD) and chemical fraction techniques. The results indicated that the preferred amount of organic matter removal was achieved in three integrated processes (coagulation/UF, adsorption/UF, ozonation/UF), and the trans-membrane pressure (TMP) increased at a rate much lower than that in an individual UF membrane. The ozonation pretreatment, with O3 as an oxidant, improved the NOM fraction removal and hindered the b3 kDa NOM fraction removal for raw water, while the adsorption pretreatment, with powdered activated carbon (PAC) as an adsorbent, improved the b10 kDa NOM fraction removal. The total NOM content of internal foulants extracted from the three integrated processes was lower than UF, indicating that all three pretreatments could reduce the accumulation of NOM in the membrane pores. The PAC/UF had a distinct advantage for removing NOM in effluent. It is observed that the hydrophilic matter (HiM) chemical fraction removal rate of O3/UF was lower than in the other three processes.

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1. Introduction

Low-pressure microfiltration/ultrafiltration (MF/UF) membrane filtration, as an independent process or as a method to replace or enhance conventional water treatment, is widely used for drinking water purification [1,2]. MF/UF is able to remove almost all particulates larger than their pore size but has a distinct disadvantage on controlling particulates smaller than their pore size [3]. A number of studies have reported that both MF and UF are ineffective for the removal of dissolved organic substances, such as natural organic matter (NOM), which plays an important role in membrane fouling, as well deterioration in performance because of membrane fouling [4–7]. Therefore, it is important to integrate MF or UF with an appropriate pretreatment process to improve the NOM removal efficiency and lighten membrane fouling and clogging. Currently, in the application of low pressure membrane filtration technology, feasible and practical pretreatment methods mainly involve coagulation, adsorption and oxidation [8–10].

Coagulation as a membrane pretreatment is an effective method for reducing membrane fouling. It is also the most successful technology for improving the flux of low-pressure membrane [11,12]. The most ideal coagulants for charging neutralization and sweeping flocculation are aluminium-based and iron-based coagulants that can remove the charged, hydrophobic and larger substances [13–16]. The hydrophilic NOM fraction cannot be removed by coagulation effectively, and neutral hydrophilic compounds with a lower molecular weight (MW) seem to induce membrane fouling soon after the coagulation process.
The hybrid adsorption-membrane process has been used in drinking water treatment. The adsorbents are used to wipe out organic compounds that aggravate membrane fouling and are difficult to remove by low pressure membranes. To improve the performance of the adsorption-membrane process, not only are high concentration adsorbents needed but a long contact time is also needed [17–19]. Powdered activated carbon (PAC) is widely used as an adsorbent for adsorption-low pressure membranes. With PAC as an addition, DOC (dissolved organic carbon) removal has been observed to increase from 35% to 46% with a UF membrane, and NOM removal from molecular sizes to 20 kDa enhanced the PAC-UF process utilization program [19–21].

To improve membrane performance, the ozonation process is also used in combination with the use of a membrane for treating raw water [22]. The ozonation of drinking water can form a number of low MW organic by-products resulting from the oxidative breakdown of complex NOM, containing organic compounds such as organic acids, aldehydes and ketones [23,24]. Ozone oxidation, which is used as a pretreatment for membrane filtration, offers a higher percentage of UV absorbance removal than DOC removal, and changes in the organic matter composition tend to improve the membrane flux. Ozone oxidation results in the degradation of macromolecular organic material, which is responsible for membrane fouling, for small-molecule organic substances [25,26]. Although pre-ozonation has many advantages for the treatment of drinking water, the main disadvantage is pre-ozonation is an insufficient assimilable compound formation. Compounds can block membrane pores and aggravate biofouling membrane processes and water distribution systems [27].

However, due to the differences in raw water quality, operation conditions and low-pressure membrane performance, as well as the diversity of each pretreatment method, the decision to apply this pretreatment technology for practical use is wrought with complexity and uncertainty [28–30]. It is necessary to identify the major membrane foulants to choose suitable pretreatment process to improve UF performance. NOM in surface water is considered to be the most relevant membrane foulant in UF processes. Although the contaminants can be removed partly by pretreatment methods, including coagulation, adsorption and oxidation, a better understanding of the influence of different pretreatments on membrane fouling is still needed. Furthermore, common water quality parameters, such as DOC, chemical oxygen demand (COD), UV254, pH, turbidity and color, cannot give information about NOM characteristics, such as molar mass or hydrophobicity. In some research, the characterization of NOM can be performed using the ultrafiltration method, where the molecular weight distribution (MWD) of NOM can be determined, or by fractionation techniques, where the NOM compounds are divided into hydrophilic and hydrophobic fractions with resins [29,31,32]. Thus, to understand the role of NOM in hybrid processes, the MWD and fractionation of NOM in the effluent water should be conducted. Furthermore, according to a review by Metsamuuronen et al. [33], membrane fouling mainly results from the accumulation of retained substances on the membrane surface (i.e., external fouling) and the deposition of substances in membrane pores (i.e., internal fouling). Some studies have found that external fouling external fouling or foulant layer formation is the major cause of membrane fouling in membrane reactors; however, other researchers have found that internal fouling or pore-blocking can result in irreversible fouling, which is harmful to the long-term operation of membrane reactors [34–36]. Therefore, if external and internal foulants are taken into analyzed through MWD and chemical fractionation, it will be of great significance to give an insight into the fouling behavior in membrane-based water treatment processes. Meanwhile, this analytical method provided an insight into selecting an appropriate pretreatment method for mitigating membrane fouling because of complex particle composition in raw water and quality characteristics variation of different water sources.

The goal of this paper is to investigate the different performances of four processes (coagulation–UF, adsorption–UF, ozonation–UF and UF) by researching the influence of pretreatments on raw water characteristics, the characteristics of membrane foulants, and the effluent characteristics of integrated processes. Through research on external and internal foulants, the influence of diverse integrated processes on the membrane fouling mechanism were investigated and the comparison of contaminant removals’ efficiency between them was conducted to achieve a better understanding of membrane fouling and removal efficiency in different integrated processes. The research on the NOM removal behaviors of different treatment processes provided a new method to select an appropriate water treatment process among many different treatment processes by analyzing molecular weight distribution and chemical fractionation of NOM in raw water.

2. Materials and methods

2.1. The combined processes

A coagulation–UF process, an adsorption–UF process, an ozonation–UF process and a UF process were operated in parallel. Aluminium sulfate hydrate (Al2(SO4)3·18H2O; analytical reagent ‘alum’ was used as a coagulant. The PAC (Norit Activated Carbon, China) was used as adsorbent in the adsorption–UF process during the experimental period. The chosen PAC has a BET surface area of 580.4 m2/g with a median diameter d50 of 10 μm. The iodine number and the methylene blue adsorption are 995.8 mg/g and 238 mg/g. Ozone (O3) was used in the ozonation–UF process and the O3 gas was generated from an O3 generator (DHX-1, Jiujiu, China) that was continuously bubbled into the water through a porous glass plate in an O3 contact column. The four processes were denoted as Al/UF, PAC/UF, O3/UF and UF, respectively. Prior to use, each membrane was washed, flushed and compacted with deionized water under the same condition as that used in the subsequent experiments. A schematic illustration of Al/UF is shown in Fig. 1. Raw water was fed into a constant-level tank to maintain the water head for the membrane reactor. Certain doses of alum were continuously added into the mix tank and a mix speed of 150 rpm was maintained in the mix tank with hydraulic retention time (HRT) of 15 min. The coagulated water was then directly fed into the UF membrane reactor with an effective volume of 1 L. The hollow fiber modules of a polyvinylidene fluoride (PVDF) UF membrane (Litree, China) with a 0.1 m2 membrane area (20 cm length and 100 fibers) and a nominal pore size of 0.01 μm was used. The porosity of PVDF membrane was 88%–95%. The permeation through the submerged membrane module was continuously withdrawn using a peristaltic pump at a constant flux of 20 L/(m2·h), corresponding to a HRT of 0.5 h. The trans-membrane pressure (TMP) was continuously monitored with a pressure sensor.

The schematic illustration of PAC/UF is shown in Fig. 2. Certain doses of PAC solution were continuously added into the mix tank, and the adsorbed water was then fed into the UF membrane reactor. The UF membrane reactor and the experimental conditions were the same as Al/UF. To supply oxygen for PAC mixing and turbulence for membrane surface cleaning continuous aeration was provided at the bottom of the reactor. Every day 5% of the mixed liquid was removed from the discharge outlet, which was at the bottom of the membrane reactor.

The schematic illustration of O3/UF is shown in Fig. 3. Each UF process was the same as the O3/UF process without pre-ozonation. Pre-ozonized feedwater was then supplied to the UF membrane reactor from a retention column for further reaction of residual O3 to prevent its impact on membrane in the reactor. The HRT of the O3 contact column and the retention column was 15 min and 20 min respectively. Continuous aeration was performed at the bottom of the reactor to create strong turbulence for membrane cleaning. The experimental set-up of O3/UF was the same as that of Al/UF except for the absence of an ozonation unit.

To determine the optimum doses of Al in the reactor, the influence of Al doses (0, 0.02, 0.04, 0.06, 0.08, 0.10 mM) on the DOC and the UV254 removal rate of raw water was pre-examined through jar tests. The jar
tests result of different Al doses was summarized in Table 1. It was found that when the dose of Al was 0.06 mM, the DOC and UV254 removal were the highest in the tested doses. Similar analysis methods were adopted to determine the optimum doses of PAC and O₃ for PAC/UF and O₃/UF, respectively. The optimum dosage of PAC and O₃ was identified as 6 mg/L and 1.5 mg/L for long-term trials.

2.2. Raw water

Water was sampled from water source of a drinking water treatment plant in northern China during the period of study. During the experiment, the raw water was kept at a temperature in the range of 16.2 to 18.5 °C and the pH was kept in the range of 7.1–7.3; other water quality characteristics, for example, turbidity, conductivity, DOC, CODMn, UV254, SUVA (specific UV absorbance), and zeta potential were in the range of 2.52 ± 0.92 NTU, 82 ± 5 μS/cm, 3.52 ± 1.51 mg/L, 2.98 ± 1.09 mg/L, 0.187 ± 0.009 cm⁻¹, 1.152 ± 0.005 L/mg·m, and −15.6 ± 0.5 mV, respectively.

2.3. Extraction of foulants

At the end of the operation, the fouled membrane modules were removed from the reactors when the TMP exceeded 30 kPa. The foulants were extracted from the fouled membranes and were analyzed. In this study, fouling was divided into two categories: reversible fouling and irreversible fouling [37]. The former fouling can be controlled efficiently by physical membrane cleaning; however, irreversible fouling can be eliminated only by chemical membrane cleaning. Controlling membrane fouling is important; thus, external foulants and internal foulants on the membrane surface were analyzed in this study. The external foulants were carefully scraped off with a plastic sheet and concurrently flushed with deionized water. The samples were fully mixed by a magnetic stirrer at 200 rpm for 1 h and then filtered through a 0.45 μm acetate fiber membrane for the MWD and fractions of NOM analysis. After wiping with a sponge, the membrane was submerged in a 0.01 mol/L NaOH solution for 24 h at 20 °C to extract internal foulants.

2.4. Analytical methods

2.4.1. Water quality analysis

The water quality analysis was conducted using standard methods as previously published [38]. Turbidity was monitored using a turbidity meter (WGZ-500B, HACH, and America). DOC was measured using a total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu, Japan). CODMn was analyzed by the potassium permanganate oxidation methods. The UV absorbance at 254 nm, UV254, of 0.45 μm filtered
solutions was determined using an ultraviolet/visible spectrophotometer (U-3010, Hitachi High Technologies Co., Japan). Zeta potential of suspended solution was analyzed by a Zetasizer Nano2000 (Malvern Instruments, UK). SUVA was determined as the UV absorbance at 254 nm divided by the DOC concentration.

2.4.2. MWD of NOM

MWD fractionation was performed with an Amicon stirred cell (300 mL capacity; Millipore Corp., Bedford, MA) in conjunction with the following membranes: Millipore YM 1, Millipore YM 3, Millipore YM 10, and Millipore YM 30. These membranes were flat, circular membranes 90 cm in diameter with MW cut-offs of 1, 3, 10, 30 kDa. The membranes made of regenerated cellulose (Millipore YM) offer a low proteic adsorption rate and are considered non-ionic [39]. Before use, the membranes were soaked and washed repeatedly with Milli-Q water to remove all traces of the glycerine protective coating. Nitrogen was applied to pressurize the UF cell at 0.1 MPa for the membranes. The test procedure of MWD fractionation by UF was the same as the method described in the literature [40]. The DOC of the samples was measured, filtered with 0.45 μm pore size of the microfiltration membranes and different molecular mass ultrafiltration membrane intercepts, and, finally, the organic matter distribution was obtained at a range of different molecular weights. The DOC concentration of each NOM MWD fraction was calculated by subtraction method.

2.4.3. NOM chemical fractionation

This study used Amberlite XAD-8 (40–60 mesh, Supelco Co., America) and XAD-4 (60–80 mesh, Supelco Co., America) resins, which were stable and not influenced by the ionic strength of water for the NOM fractionation. The experimental parameters of fractionation were as follows: the ratio of water volume and resins' volume (wet volume) was 35:1; the velocity of the passing column was 15 times of bed volume per hour (the bed volume of resin was calculated according to the wet volume).

This experiment utilized methods of other researchers and improved some details: to reduce the influence of the back flush solution for the TOC analyzer hydrochloric acid was substituted for phosphoric acid as the back flush solution [41,42]. In order to minimize system error and eliminate the recovery problem, the DOC of each part was calculated employing different value methods. The resin purification steps were carried out according to the method described in the literature [43]. The NOM fractionation steps were as follows: first, the samples passing through the 0.45 μm pore size of the microfiltration membranes went directly through the XAD-8 resins. A fivefold bed volume dilute acid (0.1 mol/L H3PO4) was then used to back wash the XAD-8 resins. The NOM sections that could be recycled through the back wash were hydrophobic bases (HoB), and the NOM section that could not be eluted (which was the hydrophobic neutral fraction (HoN)). Second, the samples that passed through the XAD-8 resins were acidified and then passed through the XAD-8 again. The NOM section adsorbed by the XAD-8 resins included hydrophobic acids (HoA) containing humic acid and some fulvic acid. Third, samples remaining after the first and second steps were then immediately passed through the XAD-4 resins. The NOM section adsorbed by the XAD-4 resins was weakly hydrophobic acid (WHoA), while the NOM section which was not adsorbed by any resins was hydrophilic matter (HiM). Thus, according to continuous distribution, the NOM was divided into five parts: HoB, HoN, HoA, WHoA, and HiM.

3. Results and discussion

3.1. Process performance

The pollutants’ (turbidity, COD, DOC, UV254) removal efficiencies of the four drinking water processes are summarized in Table 2. As seen in Table 2, the turbidity removal efficiency was approximately 96.5% for the four processes indicating the excellent performance of particle removal. The results also showed that the performance of organic matter removal improved dramatically in Al/UF, PAC/UF and O3/UF processes compared with that in the UF process without pretreatment. Particularly, the DOC decreasing rate was almost 20% higher in PAC/UF (44.8 ± 3.5) compared with that in UF because PAC could absorb part

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**Table 1**

<table>
<thead>
<tr>
<th>Water quality indexes</th>
<th>Al (mmol/L)</th>
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<tbody>
<tr>
<td>DOC (mg/L)</td>
<td></td>
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<tr>
<td>0</td>
<td>3.521 ± 1.423</td>
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<tr>
<td>0.02</td>
<td>3.158 ± 0.418</td>
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<tr>
<td>0.04</td>
<td>3.028 ± 0.407</td>
</tr>
<tr>
<td>0.06</td>
<td>2.722 ± 0.311</td>
</tr>
<tr>
<td>0.08</td>
<td>2.727 ± 0.349</td>
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<tr>
<td>0.10</td>
<td>2.730 ± 0.337</td>
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</table>

<table>
<thead>
<tr>
<th>UV254 (cm⁻¹)</th>
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<tbody>
<tr>
<td>0.187 ± 0.009</td>
<td></td>
</tr>
<tr>
<td>0.184 ± 0.004</td>
<td></td>
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<tr>
<td>0.180 ± 0.003</td>
<td></td>
</tr>
<tr>
<td>0.165 ± 0.005</td>
<td></td>
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<tr>
<td>0.166 ± 0.004</td>
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<tr>
<td>0.166 ± 0.003</td>
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of the DOC, which was higher than in other pretreatments. Furthermore, an approximately 33% higher UV254 decreasing rate was achieved in O3/UF compared with that in UF because of the synergetic effect of the three functions, including the partial degradation or mineralization effect of O3 oxidation, the retention of the UF membrane and the biodegradation effect of microbes in the reactor [44].

The TMP that was required to maintain the desired flux was utilized as the indicator of membrane fouling. In the experiments, the TMP increased with the operation time, while the flux of the four processes was maintained constant at approximately 20 L/(m²·h) before the TMP exceeded 35 kPa. The developments of TMP for different processes are shown in Fig. 4. As seen from the figure, there was an evident difference of TMP developments during the operation of the four processes. The TMP gradually increased with time from the initial 2.2 kPa for all processes with a similar trend within the beginning phase (0–15 h). However, there was a distinct gap between them at 25 h. As time goes on, the TMP development of the three combined processes exhibited a slower increase than that in the UF process, indicating that all three pretreatments, in different ways, lessened membrane fouling. Furthermore, during the period of 25 h to 110 h, the TMP rate increased in the following order in the four processes: O3/UF < Al/UF < PAC/UF < UF, indicating that the O3 pretreatment was more appropriate for controlling UF membrane fouling compared with the other two pretreatments because O3 can oxidize unsaturated structures such as aromatic rings and double bonds, generating more small molecule organic matters which improves the biodegradability of organic matter, and thus reduces membrane pollution by organic matter. However, after 110 h, the PAC/UF process TMP increased much higher than in the other three processes. This was because more and more small MW PAC particles accumulated on the membrane surface forming a close-grained gel layer and the air bubble applied was not so effective in reducing membrane fouling [45,46].

### 3.2. The influence of pretreatments on water characteristics

Different pretreatment processes have different influences on water quality. The MWD and the fractionation of NOM in water after pretreatment processes completed were investigated. The NOM was reduced from 3.521 mg/L for raw water to 2.726 mg/L, 2.287 mg/L and 3.036 mg/L after the pretreatment of coagulation, adsorption and oxidation, respectively, indicating that the PAC pretreatment process had the highest removal efficiency for NOM in water. The Al, PAC and O3 pretreatment processes led to NOM removal of 22.11%, 34.66% and 13.26%, respectively. However, as seen in Fig. 5, which presented the MWD of NOM for raw water after pretreatments, the O3 pretreatment process led to the highest removal rate of 56.86% and 54.06% for the N<sub>30 kDa</sub> fraction and the 10–30 kDa fraction, respectively, while the PAC pretreatment process was lower than the other two pretreatments for the two fractions. For the 1–3 kDa fraction and the <1 kDa fraction, the O3 pretreatment process, in contrast, had a lower removal rate (5.70% and −5.4%, respectively) than the Al and PAC pretreatment processes, indicating that O3 could not remove the lower MW NOM fraction but might increase the <1 kDa NOM fraction (−5.4% removal rate), because the O3 oxidized the higher MW NOM fraction into the lower MW NOM fraction [47]. It can be concluded from the above analysis that O3 pretreatment had an advantage on the >10 kDa NOM fraction removal and causes a disadvantage on the <3 kDa NOM fraction, while the PAC pretreatment

### Table 2

<table>
<thead>
<tr>
<th>Water quality indexes</th>
<th>Raw water</th>
<th>UF Effluent</th>
<th>Total removal (%)</th>
<th>Al/UF Effluent</th>
<th>Total removal (%)</th>
<th>PAC/UF Effluent</th>
<th>Total removal (%)</th>
<th>O3/UF Effluent</th>
<th>Total removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>2.52 ± 0.92</td>
<td>0.08 ± 0.01</td>
<td>96.2 ± 1.8</td>
<td>0.07 ± 0.02</td>
<td>96.5 ± 2.1</td>
<td>0.06 ± 0.03</td>
<td>96.7 ± 2.4</td>
<td>0.06 ± 0.02</td>
<td>96.9 ± 1.92</td>
</tr>
<tr>
<td>COD&lt;sub&gt;Mn&lt;/sub&gt; (mg/L)</td>
<td>2.98 ± 1.09</td>
<td>1.52 ± 0.28</td>
<td>43.8 ± 3.2</td>
<td>1.21 ± 0.21</td>
<td>59.2 ± 2.9</td>
<td>1.24 ± 0.24</td>
<td>58.7 ± 1.8</td>
<td>1.23 ± 0.25</td>
<td>61.4 ± 3.1</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>3.521 ± 1.423</td>
<td>2.60 ± 0.682</td>
<td>243 ± 1.7</td>
<td>2.181 ± 0.598</td>
<td>35.8 ± 2.4</td>
<td>1.986 ± 0.187</td>
<td>44.8 ± 3.5</td>
<td>2.017 ± 0.318</td>
<td>42.2 ± 2.9</td>
</tr>
<tr>
<td>UV254 (cm&lt;sup&gt;−1&lt;/sup&gt;)</td>
<td>0.187 ± 0.009</td>
<td>0.153 ± 0.003</td>
<td>21.1 ± 2.5</td>
<td>0.122 ± 0.005</td>
<td>35.2 ± 3.4</td>
<td>0.111 ± 0.004</td>
<td>40.8 ± 4.1</td>
<td>0.093 ± 0.003</td>
<td>54.1 ± 2.7</td>
</tr>
</tbody>
</table>

Fig. 4. Comparison of TMP variations in the four processes.
could remove the <10 kDa NOM fraction effectively because the microporous structure of PAC had a greater internal surface area strengthening the adsorption effect between PAC and lower MW NOM fraction [48,49].

Fig. 6 shows that the chemical fractions of NOM for raw water after pretreatment. As seen from the figure, the Al pretreatment process had a higher removal rate (25.20%, 52.01%, 35.19% and 31%) for the hydrophobic NOM fractions (HoB, HoN, WHoA and HoA, respectively), because the hydrophobic NOM consisting of humic substances that could be regarded as natural anionic polyelectrolytes effectively adsorbed onto the surface of the hydrolysis products of aluminium ion [50]. The O₃ pretreatment process had the highest removal rates of 59.55%, 68.84% and 79.21% for HoB, WHoA and HoA, while the HoN and HiM removal rates were the lowest among the three pretreatments. It was noted that the HiM content had increased after the O₃ pretreatment process because O₃ could oxidize organic compounds that were hydrophobic and high MW compounds into hydrophilic, low MW organic materials [51–54]. Furthermore, the PAC pretreatment that easily removed the HON, WHoA and HiM chemical fractions, had the highest removal rate of 53.14% for HiM than the other two pretreatments, indicating that PAC could adsorb aliphatic carbon and nitrogenous compounds, such as carboxylic acids, carbohydrates and proteins composed of a majority of the hydrophilic fractions of NOM.
3.3. The characteristic of membrane foulants

The component and quantity of membrane foulants were connected with the interaction between membranes and organic substances. The UF membrane is made of PVDF, which is a hydrophobic material. The three pretreatment processes are able to increase the hydrophilicity and polarity of the NOM to make the hydrophobic membrane less susceptible to fouling. Although the NOM characteristics have changed after the pretreatments that reduced the membrane fouling, the accumulation of foulants existed on the membrane surface and/or in the membrane pores. Unlike traditional indexes, such as the ratio of carbohydrates to proteins, which is unable to fully characterize membrane foulants, the MWD and the chemical fractions of NOM analysis are able to provide more useful information on the characteristics of membrane foulants [55]. Therefore, at the end of the experiment, both external and internal membrane foulants were extracted from the fouled membranes and analyzed with MWD and resins’ fractionation technology.

3.3.1. External foulants

Fig. 7 shows the NOM MWD measured for external foulants that were extracted from the fouled membranes of the four processes. The total NOM content of foulants extracted from Al/UF and PAC/UF (8.965 mg/L and 8.57 mg/L, respectively) were much higher than the NOM content of foulants extracted from UF and O3/UF (5.9 mg/L and 4.854 mg/L, respectively) because the cake layer on the membrane surface contained the hydrolysate of Al3+ adsorbing the negative NOM in the Al/UF process as well as PAC molecules with a high specific surface area adsorbing NOM during the PAC/UF process. The total NOM content of foulants extracted from O3/UF was the lowest among the four processes because the low molecular weight ozonation products cause a lower accumulation of foulants on the membrane that might be a causative effect on the lowest rate of TMP development shown in Fig. 4. The coagulation and adsorption pretreatment increased the 1–3 kDa fraction and the <1 kDa fraction, while the O3 pretreatment had no obvious effect. Furthermore, the coagulation pretreatment increased the molecular weights of all of the external foulants in the Al/UF process, especially the >30 kDa NOM fraction (4.022 mg/L) compared with the UF process (2.95 mg/L), while the PAC and O3 pretreatments reduced the >30 kDa NOM fraction (1.715 mg/L and 1.221 mg/L) in the external foulants. Based on the above data, the coagulation pretreatment enhanced the entire NOM fractions and NOM fractions (>30 kDa, 10–30 kDa, 3–10 kDa, 1–3 kDa and <1 kDa) 1.072, 0.444, 0.79, 0.434 and 0.325 mg/L more than that in the UF process, indicating that the floc in the external foulants could combine with almost equal molecular weight NOM fractions. The <1 kDa NOM fractions was much higher in PAC/UF than in the other three processes because of the PAC adsorptive action in the foulants. Otherwise, O3 pretreatment can reduce higher MW and lower MW materials in foulants. All of the three pretreatments improved the 10–30 kDa fraction and the 3–10 kDa fraction contents in the external foulants.

Fig. 8 shows the chemical fractions of external foulants extracted from the fouled membranes of the four processes. The three NOM chemical fractions, including WHoA, HoA and HiM, were the basis of external foulants in the four processes. Because of the O3 oxidation, the content of each chemical fraction in the external foulants was reduced, particularly the HiM fraction in the external foulants was much lower than in other processes, indicating less accumulation of external foulants on the membrane surface. The PAC pretreatment increased the contents of HoN, HoA and HiM among which special attention should be paid to HoA and HiM as more were found here than in the other two processes, indicating that the PAC in the gel layer could improve the content of aliphatic carbon and nitrogenous compounds in the external membrane foulants. The coagulation pretreatment increased 0.429, 0.453, 1.05, 0.682 and 0.20 mg/L more than the UF process for HoB, HoN, WHoA, HoA and HiM, respectively, and especially enhanced the HoB and WHoA fractions much more than the other two pretreatments, indicating that the floc in the gel layer could enhance the accumulation of all of the chemical fractions in the external foulants.

3.3.2. Internal foulants

Membrane fibers of the four processes with the same quantity were chemically treated to extract the internal pore foulants for investigation. With the purpose of identifying the NOM characteristic difference of internal foulants caused by different pretreatments, analysis of the NOM MWD and chemical fractions of internal foulants was carried out and the results are shown in Figs. 9 and 10. As seen in Fig. 9, the total
NOM of foulants in the membrane pores of O$_3$/UF was the lowest of all of the processes. The NOM content of foulants extracted from Al/UF, PAC/UF and O$_3$/UF (1.756, 1.828 and 1.501 mg/L, respectively) was lower than that from UF (2.011 mg/L), showing that all three pretreatments could decrease the accumulation of NOM in the membrane pores. For the $<1$ kDa NOM fraction, coagulation and adsorption pretreatments had no obvious effect, but O$_3$ pretreatment improved the accumulation in the membrane pore because ozonation decomposed higher MW substances to lower MW compounds, leading to the size of some NOM molecules to be smaller than the nominal pore size of the PVDF membrane. For the 1–3 kDa NOM fractions, the coagulation and oxidation pretreatments decreased the accumulation of NOM by 0.092 and 0.231 mg/L, respectively, more than in the UF process. The $>30$ kDa and the 10–30 kDa NOM fractions of foulants in the three processes were lower than the UF process, indicating that the three pretreatments could reduce the content of higher MW NOM in membrane pores. However, the pretreatments had a different effect on the lower MW NOM. The coagulation improved the 3–10 kDa NOM fractions 0.157 mg/L more than in the UF process; however, the adsorption and oxidation had no obvious effect. According to the above analysis, all three processes reduced higher MW NOM ($>10$ kDa fractions); however, these processes had different effects on lower MW NOM, especially as the O$_3$ pretreatment could improve the $<1$ kDa NOM fraction in membrane pores because of the oxidation effect. Furthermore, the three pretreatments could reduce the NOM total quantity in membrane pores, especially the O$_3$ pretreatment caused the least accumulation of

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**Fig. 8.** The NOM chemical fractions of external membrane foulants for the four processes.

**Fig. 9.** The NOM MWD of internal membrane foulants for the four processes.
foulants in the membrane pores because the NOM in the ozonized water was too small to be retained by UF membrane. Fig. 10 shows the chemical fractions of internal foulants extracted from the fouled membranes of the four processes. The PAC/UF process increased the content of hydrophobic fractions (HoB, HoN, WHoA and HoA), primarily consisting of humic and fulvic acids, and cut down the hydrophilic fractions in the internal foulants. The HiM contents in the three combined processes were much lower than in the UF process, and these processes decreased HiM fractions by 0.393, 0.604 and 0.575 mg/L, respectively, more than in the UF process. The Al and PAC pretreatment reduced the HoA chemical fractions 0.137 and 0.223 mg/L more than in the UF process, while the O3 pretreatment was decreased by 0.130 mg/L more than in the UF process. For the WHoA chemical fractions, the coagulation and oxidation pretreatments were decreased by 0.045 and 0.178 mg/L, respectively, more than in the UF process, while the adsorption pretreatment was increased by 0.038 mg/L more than in the UF process. For HoN chemical fractions, the coagulation and oxidation pretreatments reduced 0.076 and 0.019 mg/L, respectively, more than in the UF process, while the adsorption pretreatment increased 0.038 mg/L more than in the UF process. Furthermore, the O3/UF process increased all of the chemical fraction content expected for the HoB fraction because of the oxidative effect of O3. The three pretreatment processes increased the HoB by 0.047, 0.04 and 0.121 mg/L, respectively, more than that in the UF process. According to the above analysis, it can be discerned that the Al/UF process could aggravate the accumulation of HoB and HoA fractions in internal foulants. It had the opposite effect on the other three chemical fractions, indicating that the coagulation pretreatment could reduce the aliphatic carbon and nitrogenous compounds in the internal foulants.

3.4. Effluent characteristics

There were differences among the four processes' effluent. The NOM MW and chemical fractionation of the four processes effluent were investigated. The NOM content was reduced from 3.500 mg/L to 2.600, 2.181, 1.986 and 2.017 mg/L for raw water treated by the four processes (UF, Al/UF, PAC/UF and O3/UF). Through the comparison of contaminant removals' efficiency among the four treatment processes in this special condition of water quality, it can be seen that the PAC/UF had a distinct advantage for NOM in effluent. Different combined treatment processes had different NOM removal behaviors. The three combined process removal efficiency for each NOM MW fraction was better than using the UF process alone. As shown in Fig. 11, the sequence of the four processes for the >30 kDa NOM fraction removal rate was O3/UF > Al/UF > PAC/UF > UF (71.19%, 63.15%, 60.28% and 48.96%, respectively), so as for the 10–30 kDa NOM fraction (81.56%, 52.30%, 43.26% and 40.38%, respectively) and the 3–10 kDa NOM fraction (56.23%, 39.28%, 28.17% and 27.53%, respectively). For 1–3 kDa NOM fraction, the removal rate of the three combined processes (Al/UF, PAC/UF and O3/UF) had no obvious differences (36.22%, 36.75% and 37.02%, respectively), but it was much higher than the UF process removal rate (21.46%). However, for the <1 kDa NOM fraction, the PAC/UF removal rate (44.58%) was much higher than the other three processes (18.85%, 29.44% and 26.98%, respectively). This was mainly because the thicker gel layer composed of PAC particulate matters formed on the surface of membrane, which hindered the contaminating material reaching to the membrane pores [56]. Compared with other processes, the O3/UF process had a good advantage on reducing >3 kDa NOM fractions because of the O3 oxidation effect. For the 1–3 kDa NOM fractions, the removal rate of the three combined processes had no obvious difference and was higher than in the UF processes. For lower MW NOM, the PAC/UF process had outstanding merit in its removal rate compared to the other processes. In conclusion, the PAC/UF had the highest removal efficiency for NOM in effluent.

Fig. 12 shows the chemical fractions of NOM for the four processes' effluent. This type of analysis (NOM fractionation based on its hydrophobicity into five fractions) could be applied to the selection of drinking water treatment process because various raw water contains different types of NOM. Through analyzing NOM fractionation based on its hydrophobicity into five fractions for the four processes' effluent, it can achieve a better understanding of the different removal rates of the four processes for NOM, which plays an important role in membrane fouling. In this research, the removal rate of each process for the five chemical fractions varied considerably. From the NOM chemical fractions' removal rate of the four processes, it can be seen that the three integrated processes had an advantage on removing hydrophobic organic compounds (HoB, HoN, WHoA and HoA); however, their removal rate on hydrophilic organic material was not ideal. For the HiM chemical fraction, the sequence of the four processes was Al/UF > UF > PAC/UF > O3/UF. The HiM chemical fraction removal rate of O3/UF
was lower than in the other three processes because O$_3$ could oxidize hydrophobic, high MW compounds into hydrophilic, low MW organic compounds [40]. For the HoA chemical fraction, the three combined processes did not have distinct discrepancy on the removal rate (53.22%, 51.84% and 49.27% for O$_3$/UF, PAC/UF, Al/UF, respectively). Furthermore, the combined processes (O$_3$/UF, PAC/UF and Al/UF) increased the WHoA chemical fraction removal rate (62.16%, 51.28% and 38.73, respectively) compared with the UF process (32.65%). For the HoB chemical fraction, the removal rate of the O$_3$/UF and the PAC/UF processes (49.89% and 25.99%, respectively) was much higher than the UF and the Al/UF processes (5.37% and 5.06%, respectively) and the same as for the HoN chemical fraction (63.22%, 63.78%, 5.36% and 5.25% for O$_3$/UF, PAC/UF, Al/UF and UF processes, respectively).

4. Conclusions

The main conclusions of this study are as follows:

1. During the period of 25 h to 120 h, the TMP increasing rate of the four processes is as follows: O$_3$/UF < Al/UF < PAC/UF < UF, indicating that O$_3$/UF process was more appropriate for controlling UF membrane fouling compared with the other three processes.
2. The Al, PAC and O3 pretreatment processes led to a NOM removal of 22.1%, 34.6% and 13.2%, respectively, in water. The O3 pretreatment process had the lowest removal rate for the HoN and HiM among the three pretreatments.

3. The total NOM content of external foulants extracted from AlUF, PAC/UF and O3/UF were much higher than in UF and O3/UF. The < 1 kDa NOM fractions were much higher in PAC/UF than in the other three processes because of the PAC adsorptive action in the foulants.

4. The total NOM content of the internal foulants extracted from AlUF, PAC/UF and O3/UF was lower than in UF, indicating that all of the three pretreatments could reduce the accumulation of NOM in the membrane pores. Furthermore, the Al/UF process could aggravate the accumulation of HoB and HoA fractions in internal foulants.

5. The sequence of the four processes for the NOM fraction removal rate in effluent was PAC/UF > O3/UF > AlUF > UF. For the < 1 kDa NOM fraction, the PAC/UF removal rate (44.58%) was much higher than the other three processes. The HiM chemical fraction removal rate of O3/UF was lower than in the other three processes.

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References


