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Reversible and irreversible membrane fouling in hollow-fiber UF membranes filtering surface water: effects of ozone/powdered activated carbon treatment†

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This study investigated the reversible and irreversible membrane fouling behavior of micro polluted water by ozone/powdered activated carbon (PAC)/ultrafiltration treatment. The results indicated that PAC mainly adsorbed low-molecular weight organics and reduced the irreversible fouling resistance in ultrafiltration, while there existed a threshold PAC dosage for total and reversible fouling resistance alleviation. Ozone at low doses exerted little effect on membrane fouling alleviation, while higher doses controlled total and reversible fouling by reducing macromolecular biopolymers and humic-like substances. Combined ozone and PAC pretreatment had greater effects on both reversible and irreversible fouling reduction than individual PAC and ozone treatment, demonstrating synergistic effects in the reduction of organic content in the feed water, including macromolecular biopolymers, humic-like, low-molecular weight neutral and building blocks. Backwashing and chemical cleaning analysis revealed that biopolymers and humic-like substances were the main organics that caused hydraulic reversible fouling, whereas low-molecular organics of building blocks and neutral, as well as humic-like substances were the main components that caused hydraulic irreversible fouling. Combined ozone and PAC treatment not only improved the backwashing efficiency but also reduced the membrane fouling during backwashing, as well as reversible and irreversible fouling. The cake layer formation and standard pore blocking were the major mechanisms for ultrafiltration membrane fouling, of which standard pore blocking exerted more important effects in the membrane fouling formation and alleviation by individual and combined PAC and ozone treatment.

1. Introduction

Membrane filtration has grown in prevalence in drinking water and wastewater treatment due to its advantageous water quality and relatively low energy consumption compared with traditional water treatment.[1] Nevertheless, two limitations to its wider application are membrane fouling and inefficiency regarding the removal of low-molecular weight of organic matter. As such, fouling may markedly reduce the filtration flux and increase the operation cost, as well as the membrane life.[2]

Natural organic matter (NOM) is one of the main critical elements leading to membrane fouling. Because NOM exists ubiquitously in natural water and consists of multiple components, such as microbial cells, proteins, polysaccharides, and humic acids,[3] the membrane fouling might become more complicated and difficult to resolve.

To overcome fouling issues during ultrafiltration (UF), many pretreatment methods, such as coagulation, pre-adsorption, pre-oxidation, and pre-filtration have been proposed.[4,5] Powdered activated carbon (PAC) adsorption prior to membrane filtration is a promising technology for removing organic matter, which has been widely employed in water treatment. PAC can efficiently remove low-molecular weight (MW) organics.[6] While the effects of PAC on membrane fouling are inconsistent. Some researchers have found that PAC adsorption of membrane foulants helps to alleviate membrane fouling; while the fraction of NOM not adsorbed by PAC may result in higher membrane fouling.[7] Ozone is also one of the potential alternative pretreatments that can be used to enhance macromolecular organic rejections. Because O₃ can break down

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macromolecular organics into small molecular organics, aromatic rings can be efficiently removed, and the hydrophobic organics are reduced.[8] Previous research indicated that ozone, when applied solely as a pretreatment, is in some cases able to reduce membrane fouling;[9] however, the polymeric membrane fouling might be intensified at high ozone doses.[10]

Combined ozone and PAC technology might better enhance the removals of contaminants and alleviate UF fouling.[11,12] Researchers used combined ozone and PAC treatment to remove biocides, antimycotics, and antibiotics in a sewage treatment plant and found that conventional treatment with added full-scale ozonation was able to remove most of the studied micropollutants, except for benzotriazoles and fluconazole (<50%).[13] Nevertheless, as the membrane fouling induced by NOM in natural waters was not composed of a certain specific membrane foulant or single membrane fouling mechanism but instead of multiple membrane foulants that work together, while during the operation process, the changes of organic substances might lead to dynamic changes of membrane fouling, whereas both ozone and PAC treatment might influence the membrane fouling separately and simultaneously, which might result in more complicated membrane fouling behavior, despite some efforts have been made to investigate the membrane fouling mechanism by ozone and PAC treatment,[11] the dynamic changes of reversible and irreversible resistance remain need to be clearly elucidated, which might provide more accurate information for large-scale UF application as well as membrane fouling control in actual engineering.

This study therefore systematically investigated the dynamic changes in reversible and irreversible membrane fouling of raw water by ozone and PAC treatments. High-performance size-exclusion chromatography (HPSEC) combined with peak-fitting prediction[14] was utilized to analysis the NOM removal, the effectiveness of organic removal was determined which was suspected to provide the further information of specific organics on reversible and irreversible membrane fouling.

2. Materials and methods

2.1 Raw water

The water used was collected from Sanhaowu Lake, on the campus of Tongji University, Shanghai, China, which was collected to represent surface water polluted by allochthonous NOM. The pH of the water sample was 8.2, the turbidity level was 43 NTU, and the dissolved organic carbon (DOC), UV_{254} values were approximately 2.697–3.7 mg L^{-1} and 0.067–0.124 cm^{-1}, respectively.

2.2 Membrane modules

A hollow-fiber UF membrane (Inge, Germany) made of modified polyethersulfone was utilized in this study. The membrane was consisted of seven capillaries with a unique porous membrane structure. The diameter of each capillary was 0.9 mm, and the pore size of the membrane was 0.02 μm. Seven tubes of modified polyethersulfone (Inge, Germany) with a length of 50 cm

each were assembled into a module with a total surface area of 0.064 m^2. The filtration mode was dead-end inside-out filtration. A cross-sectional diagram of the porous membrane can be found in Fig. 1.

2.3 Pretreatments and UF experiment

Ozone gas was generated by passing high-purity oxygen gas through an ozone generator (COM-AD-01, ANSEROS, Germany). The ozone experiment was consistent with that in our previous research.[8] Low doses of ozone (0.5 mg L^{-1} and 1 mg L^{-1}) were used in this study because low ozone concentrations might have less adverse effects on the membrane than ozone of high doses.[15]

PAC adsorption tests were performed at doses of 10 mg L^{-1}, 20 mg L^{-1}, and 100 mg L^{-1}. Adsorption treatment was performed with rapid mixing for 30 min at 90 rpm, slow mixing for 20 min at 50 rpm, and supernatant filtration with a 10 μm filter. Then, the water sample was pumped into a water tank for UF treatment. The characteristics of PAC and the isothermal adsorption curve are in Fig. S1 and Table S1,† as can be seen, the DOC in water decreased with increasing of PAC dosage, whereas the declining trend of DOC decreased when PAC >30 mg L^{-1}, which indicated that PAC 30 mg L^{-1} might have great effects on the concentration of equilibrium solutions.

UF experiments were carried out in a low-pressure membrane cycle-based automatic operating system with a programmable logic controller (PLC); the system was consisted of a raw water tank, a backwash tank, two centrifugal pumps (MGP-M256B220, IWAKI, Japan), two flow meters, an inlet pressure gauge (XP2i, Crystal), an outlet pressure gauge, and a hollow fiber module. A schematic illustration of the experimental setup can be found in Fig. 1. When conducting the filtration experiment, the filtration flux was set at 80 L $(m^2 h)^{-1}$. Each UF experiment included 3 continuous filtration cycles. Every filtration cycle included 4 steps: (1) filling with water for 80 s at 200 ml min^{-1} during the first operation cycle (20 s in the remaining filtration cycles), (2) filtration for 90 min at 80 ml min^{-1}, (3) positive flushing using raw water for 60 s at 200 ml min^{-1}, and (4) backwashing using filtered water for 80 s at 240 ml min^{-1}. Before filtration, the membrane filtration flux of Milli-Q water under different operation pressures was determined, and the feed water was prefiltered with a 10 μm filter.

After all the filtration cycles ended, the UF membrane was subjected to chemical cleaning. The following specific cleaning processes were used: the fouled membranes were first alkaline-cleaned with 0.6 wt% NaOH for 2 h at 60 ml min^{-1}, then acid-washed with 0.1 wt% HCl for 2 h at 60 ml min^{-1}. Thereafter, the organic matter from the feed water, permeate, backwashing effluent, and chemical cleaning effluent was analyzed. Notably, despite the chemical cleaning were conducted after each filtration, there were slight differences among the initial transmembrane pressure (TMP_0) levels; therefore, TMP/TMP_0 was adopted for the convenience of comparison among various pretreatment methods. And the characteristics of water samples are consistent during every batch of UF experiment.
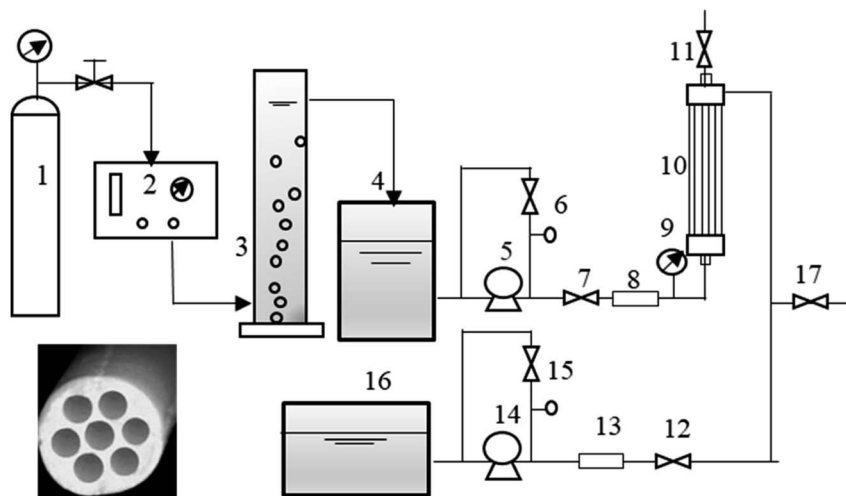
Fig. 1 Schematic of the membrane filtration setup and a cross-sectional diagram of the porous membrane. (1) Oxygen tank (2) ozone generator (3) ozone contact column (4) PAC and feed water tank (5) centrifugal pump (6) flow control (7) valve 1 (8) flow meter (9) pressure gauge (10) hollow fiber membrane (11) valve 3 (12) valve 2 (13) flow meter (14) centrifugal pump (15) flow control (16) backwashing tank (17) valve 4.

2.4 Membrane fouling analysis

The membrane filtration resistance (R_m), reversible fouling resistance (R_{re}), and irreversible fouling resistance (R_{ir}) at the end of filtration were calculated by Darcy's law:

$$R = \frac{\Delta P}{\mu J} = R_m + R_{re} + R_{ir} \tag{1}$$

where R is the total fouling resistance; R_m, R_{re}, and R_{ir} are the membrane resistance, the hydraulic reversible resistance (external fouling resistance, m^{-1}), and the hydraulic irreversible resistance (internal fouling resistance, m^{-1}), respectively; ΔP is the TMP; μ is the dynamic viscosity. A viscosity coefficient of 0.8737×10^{-3} Pa s was used considering that the water temperature was 26 °C.

R_m was first obtained by measuring the module flux of the virgin membrane (J_0) and TPM of P_0 under deionized (DI) water, which can be calculated according to eqn (2).

$$R_m = \frac{\Delta P_0}{\mu J_0} \tag{2}$$

Then, the total fouling resistance (R) in each experiment was acquired by measuring the fouling membrane flux (J) and TPM of ΔP at the end of filtration of raw water.

$$R = \frac{\Delta P}{\mu J} \tag{3}$$

Thereafter, the fouled membrane surface was flushed and backwashed with DI water to remove the external foulants, the clean water flux (J_1) and TPM of ΔP_e were measured again with the flushed membrane to obtain R_1,

$$R_1 = \frac{\Delta P_e}{\mu J_1} \tag{4}$$

R_{re} and R_{ir} were calculated by eqn (5) and (6), respectively.

$$R_{ir} = R_1 - R_m \tag{5}$$

$$R_{re} = R - R_{ir} \tag{6}$$

2.5 Analytical methods

DOC was determined by a TOC analyzer (TOC-VCSH, Shimadzu, Japan). Ultraviolet (UV) absorbance at 254 nm (UV$_{254}$) was measured by a UV spectrophotometer (Hach-5000). Aqueous ozone was measured using a spectrophotometer *via* the indigo method.[16]

Protein was determined by the modified Lowry method.[17] Ammonia nitrogen was determined by the salicylic acid method. A Hach ammonia nitrogen detection reagent package and cyanuric acid ammonia reagent were used for the determination.

HPSEC (Waters e2695, USA) coupled with a UV/visible detector (Waters 2489, USA)-TOC analyzer (Sievers 900 Turbo, USA) was adopted to measure the MW distribution of organic matter. The chromatogram analyses were performed using the peak-fitting technique with the PeakFit software package, Version 4.12 (Systat Software Inc., CA, USA), with 54 samples (9 treatments × 2 samples (raw water, permeate) ×3 parallel = 54 samples) analyzed.[18,19]

To ensure the accuracy of the experimental results, all UF experiments repeated three times, and the errors between the data and TMPs of duplicated tests were calculated and <0.05.

2.6 Modeling for membrane fouling process

Four constant flow individual fouling models including complete blocking, standard blocking, intermediate blocking, and cake filtration were developed to interpret the TMP increases of low-pressure membrane filtration in dead-end mode with constant flowrate.[20] However, considering that individual fouling model might not be sufficient to elucidate the membrane fouling mechanism, five combined fouling

models including cake-complete, cake-intermediate, complete-standard, intermediate-standard, and cake-standard were therefore utilized to better interpret the membrane fouling mechanisms, which were as follow[21]

Cake-complete:

$$\frac{P}{P_0} = \frac{1}{1-K_b t}\left(1 - \frac{K_c J_0^2}{K_b}\ln(1-K_b t)\right)$$

(5)

Cake-intermediate:

$$\frac{P}{P_0} = \exp(K_i J_0 t)\left(1 + \frac{K_c J_0}{K_i}(\exp(K_i J_0 t)-1)\right)$$

(6)

Complete-standard:

$$\frac{P}{P_0} = \frac{1}{(1-K_b t)(1+(K_s J_0/2K_b)\ln(1-K_b t))^2}$$

(7)

Intermediate-standard:

$$\frac{P}{P_0} = \frac{\exp(K_i J_0 t)}{(1-K_s/2K_i)(\exp(K_i J_0 t)-1)^2}$$

(8)

Cake-standard:

$$\frac{P}{P_0} = \left(1 - \frac{K_s J_0 t}{2}\right)^{-2} + K_c J_0^2 t$$

(9)

where the fitting parameters were K_c (s m^{-2}) and K_b (s^{-1}) for cake-complete model, K_c (s m^{-2}) and K_i (s^{-1}) for cake-intermediate model, K_b (s^{-1}) and K_s (m^{-1}) for complete-standard model, K_i (m^{-1}) and K_s (m^{-1}) for intermediate-standard model, K_c (s m^{-2}) and K_s (m^{-1}) for cake-standard model, respectively. P is the TMP data at a given time (kPa); P_0 represents the initial TMP$_0$ (kPa); J_0 represents the constant filtration flux (80 L m^{-2} h^{-1}); and t is the filtration time (s).

The modeling process was conducted using Origin 9.0. Moreover, the experimental data were fitted according to these equations with the sum of squares (R^2) between the experimental data and fitted values, which indicated the goodness of model fit.

3. Results and discussion

3.1 Variations in TMP and fouling resistance with PAC and ozone treatment

Fig. 2 shows the normalized TMP/TMP$_0$ during the filtration of natural waters with individual PAC and ozone treatment and combined PAC and ozone treatment. For the control sample of natural water without any treatment, TMP/TMP$_0$ was 2.15 after the first filtration cycle and increased to 3.21 at the end of filtration. However, when the water was treated with individual PAC pretreatment, PAC had little effects on membrane fouling alleviation at low doses, and TMP/TMP$_0$ increased at 10 mg L^{-1} and 20 mg L^{-1} PAC but decreased at 100 mg L^{-1} PAC, indicating that there might exist a threshold PAC dosage for membrane fouling control when UF is conducted in constant-flux mode.
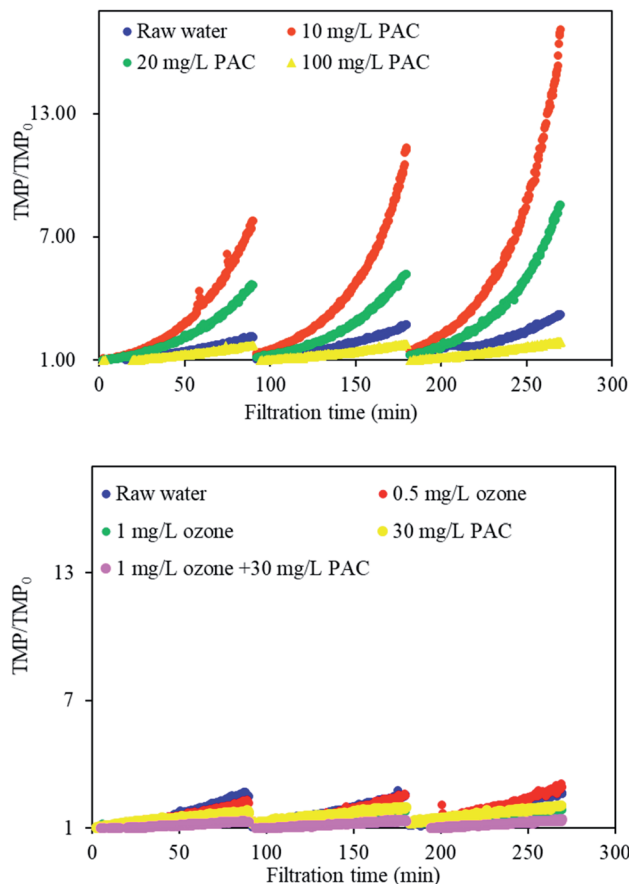

Fig. 2 Variation in normalized TMP/TMP$_0$ during ozone/PAC/UF processes as a function of time.

This phenomenon might be explained that although PAC could absorb some organic matter as previous research suggested,[22] as the organics absorbed by PAC at low doses might not the organics of membrane foulants, while those organics not adsorbed might remain cause severe membrane fouling,[7,23] leading to the aggravated TMP at PAC low doses.

The TMP/TMP$_0$ results with ozone were slightly different from those obtained with the PAC procedure. Preozonation effectively decreased the TMP in the first filtration cycle, while at the end of filtration, TMP/TMP$_0$ increased at a low dosage of 0.5 mg L^{-1} but decreased at 1 mg L^{-1} ozone, suggesting that low doses of ozone exerted little effects on membrane fouling alleviation, while higher doses of ozone greatly decreased the TMP. Combined with the isothermal adsorption curve and the TMP changes that PAC 30 mg L^{-1} might have great effects on the concentration of equilibrium solution, 30 mg L^{-1} PAC and 1 mg L^{-1} ozone were therefore used in the following combined treatment to improve the effects of PAC and ozone treatment on membrane fouling alleviation.

A comparison with the corresponding results from individual PAC or ozone treatment revealed that TMP/TMP$_0$ was further decreased under combined ozone and PAC treatment. TMP/TMP$_0$ was 1.33 under combined treatment, in contrast to values of 1.74 for 1 mg L^{-1} ozone and 2.00 for 30 mg L^{-1} PAC at the end of filtration. This result suggested that combined PAC

and ozone treatment could better control the increases in TMP. This effect may be attributed to the fact that ozone oxidation can decrease membrane fouling, as found in many studies;[21] when ozone is present, macromolecular organics can be oxidized, the small-MW organics can also be adsorbed by PAC, which might further alleviate membrane fouling.[24]

Fig. 3 compares the extent of membrane fouling in terms of R, R_{ir}, and R_{re} under individual PAC and ozone treatment and combined treatment. R_m was relatively consistent for all the natural water; however, under individual PAC treatment, R was 1.7×10^{13} (m^{-1}) for 10 mg L^{-1} PAC but decreased to 1.16×10^{13} (m^{-1}) and 2.88×10^{12} (m^{-1}) for 20 mg L^{-1} and 100 mg L^{-1} PAC, respectively; R was 4.7×10^{12} (m^{-1}) with direct UF. The R_{re} changes were consistent with the R results, following the order of 10 mg L^{-1} PAC > 20 mg L^{-1} PAC > raw water > 100 mg L^{-1} PAC, which suggested that low doses of PAC could lead to increases in R and R_{re}, whereas high doses (100 mg L^{-1}) of PAC reduced R_{re}. This result might because PAC at low doses might have limited effects on adsorbing macromolecular organics, while macromolecular organic-bound PAC particles might strongly attach to the membrane surface, form a close-packed PAC cake layer and block the membrane pores, causing an increase in fouling resistance.[7] In contrast, more macromolecular organics might be adsorbed by PAC at increased doses as

well as by the porous membrane formed by PAC,[25] thus alleviating R_{re}. The overall R_{ir} decreased with increasing PAC dose, suggesting that although R_{ir} accounted for only a small proportion of R, PAC pretreatment prior to UF significantly enhanced the control of R_{ir}. Liu *et al.* reported that PAC primarily adsorbed the low-MW (<1 kDa) fraction and was effective in mitigating irreversible fouling.[26] This result further suggested that there might exist a threshold PAC dosage to alleviate UF fouling during constant-flux mode; when the PAC dosage is below the threshold, R_{re} is greater than that in direct UF, while when the PAC dosage is higher than the threshold, both R and R_{re} are alleviated.

For the samples subjected to individual ozone treatment, both R and R_{re} increased after 0.5 mg L^{-1} ozone treatment, while the values decreased after 1 mg L^{-1} ozone treatment, consistent with the TMP changes (Fig. 2). In addition, R_{ir} increased with increasing ozone doses. This phenomenon might occur because ozone oxidation can degrade molecular chains and macromolecules into smaller fragments (see Fig. 5); these smaller fragments would improve organic adsorption in the membrane pores and decrease the affinity of macromolecular organics on the membrane surface and the formation of cake layer.[27] Nevertheless, at low doses, not all the macromolecular organics could be oxidized, and R_{re} increased with increasing filtration cycle.

Comparison among the treatments revealed that R was reduced more by combined ozone and PAC treatment than by individual PAC or ozone treatment. R was 7.16×10^{11} (m^{-1}) under combined treatment, in contrast to 9.2×10^{11} and 1.89×10^{12} for individual treatments with 1 mg L^{-1} ozone and 30 mg L^{-1} PAC, respectively. In addition, R_{re} and R_{ir} were 2.01×10^{11} and 2.24×10^{11}, in contrast to 2.57×10^{11} and 3.38×10^{11} for 1 mg L^{-1} ozone and 6.66×10^{11} and 9.43×10^{11} for 30 mg L^{-1} PAC, respectively. This result suggested that combined ozone and PAC treatment had synergistic effects on both reversible and irreversible membrane fouling reduction, yet the effects were not simply summed or subtracted. To better analyze the dynamic membrane fouling behavior, the organic removals, water characteristics and fouled membrane were subsequently investigated.

3.2 Performance of individual and combined PAC/ozone processes on organic removal

3.2.1 TOC and SUVA removal. Fig. 4 presents the effectiveness of TOC and SUVA removal during UF. UF resulted in low TOC removal when the water was filtered directly. When PAC was added, the TOC removal increased with increasing PAC doses (Fig. 4a). The removal efficiency of UF after PAC treatment was greater than that obtained with direct UF, suggesting that UF enhanced organic removal during PAC treatment and that a synergistic effect between PAC and UF might exist for the removal of organics, especially of UV-absorbent organics (Fig. S2†). Notably, although the TOC removal was increased by UF after 20 mg L^{-1} PAC, the removal decreased after 100 mg L^{-1} PAC, which may be because 100 mg L^{-1} PAC had higher TOC removal; thus, more organics would not be adsorbed in the subsequent UF.

When the water was pretreated with ozone, the UV removal also increased with increasing ozone doses (Fig. S2†), whereas
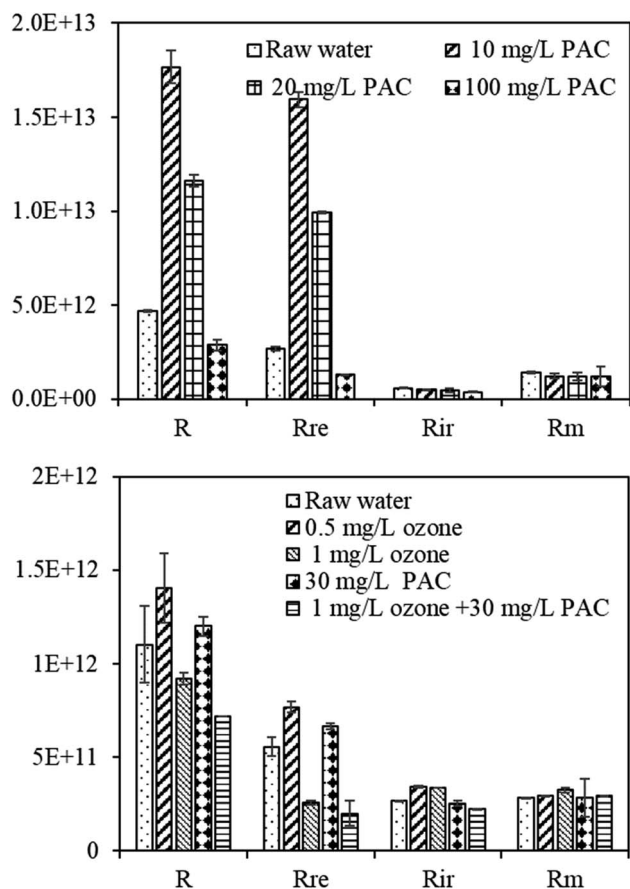

Fig. 3 Variation in membrane fouling resistance during ozone/PAC/UF processes.
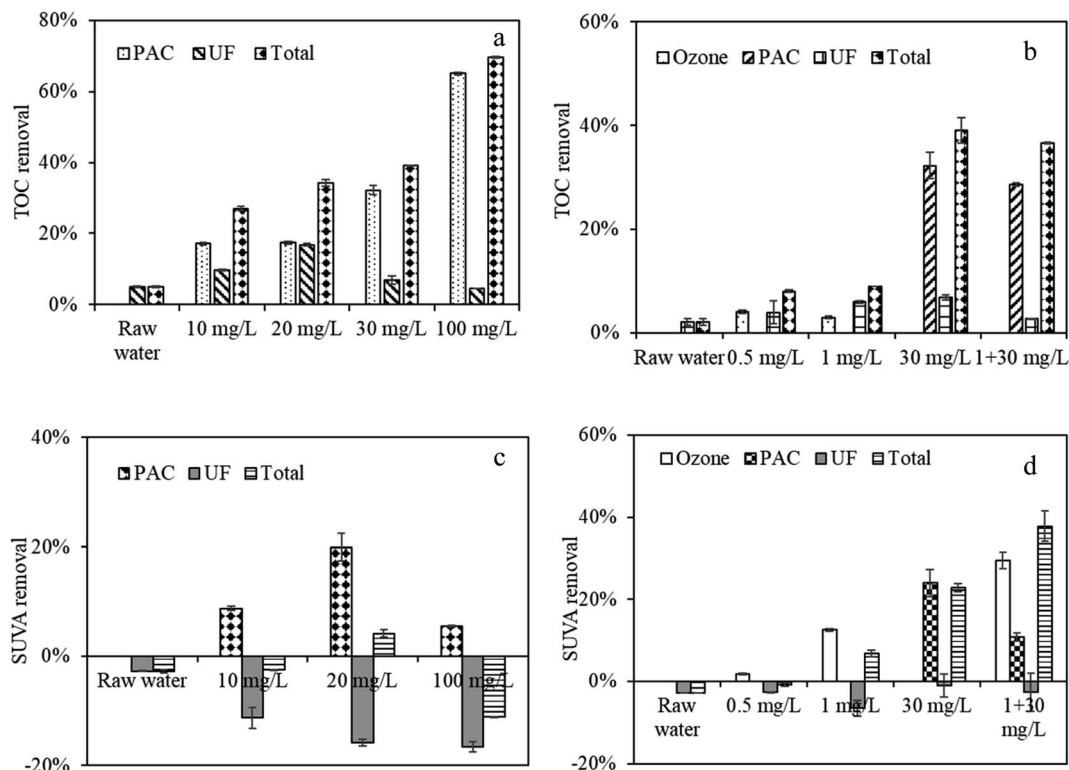
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Fig. 4 TOC and SUVA removal during UF treatment and PAC and ozone treatment, (a and b) TOC removal during PAC and/or ozone treatment, (c and d) SUVA removal during PAC and/or ozone treatment.

the TOC removal was slightly increased when ozone increased from 0.5 mg L^{-1} (8.02%) to 1 mg L^{-1} (8.8%). This phenomenon likely occurred because ozone oxidation had a certain selectivity for organic removal, and those organics with a benzene ring and C=C might be preferentially removed.[28] Combined ozone and PAC treatment had higher TOC removal relative to that with individual ozone treatment (Fig. 4b). The overall TOC removal was 36.65%, in contrast to 8.88% for 1 mg L^{-1} ozone and 39% for 30 mg L^{-1} PAC, which differed slightly from the TMP/TMP$_0$ trend. This phenomenon might be explained that despite ozone could oxidize some macromolecular organics into small molecule substances, R_{ir} might be induced due to the increases of small MW organics, whereas the R_{ir} can be greatly alleviated by the absorption of small MW organics of PAC treatment, which further suggested that the removal of total organic matter might not have a direct relation with TMP increases but with specific organic removals.

The SUVA removal by individual and combined PAC and/or ozone treatment is also detected (Fig. 4c and d). The SUVA value reflects the degree of aromaticity of organic matter in water. Cho *et al.* suggested that the SUVA value of NOM is consistent with a material with a very hydrophilic nature.[29] Raw water had a high SUVA of 2.91 L (mg m)$^{-1}$, which suggested an aromatic structure of organic matter. After PAC treatment, the SUVA value was reduced; however, the value increased after subsequent UF, indicating that hydrophobic organics with strong UV absorbance can be preferably removed by PAC, whereas UF membrane might mainly reject organics of weak UV absorbance.

When the water was treated with individual ozone treatment, the percent reduction in SUVA was markedly lower at 0.5 mg L^{-1} but increased at 1 mg L^{-1}. Van *et al.* suggested that ozone oxidation could cause substantial structural changes in the NOM present in feed water, including the removal of aromatic rings,[28] moreover, the amount of carboxylic groups increased, leading to an increased repulsion by the negative membrane surface and the prevention of cake/gel layer formation.[27] The above results suggested that ozone at higher doses could effectively reduce hydrophobic organics in the water, which might prevent the formation of membrane cake/gel layer, whereas low ozone doses exerted little effects on aromatic structure changes. When PAC was further added to the combined ozone–UF system, the total SUVA was further decreased, which indicated that more hydrophobic organics can be removed by combined ozone and PAC treatment, thus alleviating membrane fouling. However, from the SUVA values by UF, it was found that the SUVA removals were all negative no matter during individual ozone treatment or combined ozone and PAC treatment, which again indicated the substance removed of weak UV absorbance by UF. And UF had a lower SUVA removal after combined ozone and PAC treatment than that after individual ozone treatment, which might suggest the organic load reduction of UF.

3.2.2 MW distribution. Fig. 5 displays the MW distribution of feed water before and after PAC and ozone treatment. Four peaks were calculated from the DOM profile and assigned to various MWs (Fig. S4†): peak A (1000 kDa), peak B (6500 Da),

peak C (1200 Da), and peak D (440 Da); these fractions are associated with biopolymers (BP, such as polysaccharides and amino sugars), humic-like substances (HS), building blocks (BB) of low-MW acids and HS, and low-MW neutral substances (LMWN), respectively, according to previous studies.[14,18] Raw water had lower peak A areas, suggesting that the water used in this study was mainly consisted of medium and small MW organics of HS, BB, and LMWN.

After UF, macromolecular BP and medium-MW HS were highly rejected, whereas the BB of low-MW acids and humics and LMWN (Table S2†) were lower rejected, suggesting that although the content of macromolecular organic matter in the raw water was not very high, after three periods of accumulation during UF, macromolecular BP and medium-MW HS remain the major organics that were responsible for the UF membrane fouling.

After PAC treatment, macromolecular BP was progressively decreased with increasing PAC doses (Fig. 5a). The percentage reduction in peak A area between the feed water and water after PAC treatment increased from 25% to 75% for 20 mg L^{-1} PAC to 100 mg L^{-1} PAC, suggesting that PAC was effective in removing some macromolecular organics. In addition to the high removal of macromolecular organics, peak B, which represents HS, was also greatly decreased with increasing PAC doses, which was

consistent with Liu et al.,[26] who found that PAC was much effective in the reduction of organic components of HS but not LMWN. However, the treatment effectiveness of peaks C and D were limited. This phenomenon can be explained by the fact that the carbon used in this study was mainly composed of pores 5–15 nm in width. According to an empirical equation, organics with MWs of 100 kDa and 1 kDa are approximately 10 nm and 1 nm in size; thus, HS, with size of approximately 3.5 nm, can be preferably adsorbed. However, LMWN and BB were less adsorbed, which might be ascribed to the decreased adsorption strength with declining adsorbate size.[30] Bourgeous et al. indicated that macromolecular organics mainly led to reversible fouling by the formation of cake and/or gel layer,[31] whereas irreversible fouling was mainly related to direct interactions between the foulants and membrane. The above results thus indicated that PAC could prevent membrane R_{re} and R_{ir} to some extent by reducing macromolecular organics and HS, which was consistent with the results in Fig. 3.

When natural water was treated by individual ozone treatment (Fig. 5b), ozone oxidation also led to high degradation of BP constituents. The peak area reduction between the feed water and water after ozone treatment was 20% and 45% for 0.5 mg L^{-1} and 1 mg L^{-1} ozone, respectively. However, HPSEC analysis presented remarkable increases in the low-MW components of BB and LMWN. Prior research suggested that lower-MW components can be generated from higher-MW constituents after ozonation.[32] The small-MW organics produced by oxidation might both reduce the fouling layer's hydraulic resistance and mitigate organic adsorption to the membrane,[33] which might be considered as one of the explanations of the R_{re} changes with ozone treatment (Fig. 3).

The reduced peak area of various molecular organic fractions following combined ozone and PAC treatment indicated that not only macromolecular BP but also HS, LMWN, and BB were further removed compared with the results of individual PAC and/or ozone treatment. The reduction in peak A area (organic BP removal) between the feed water and water after combined treatment was 100%, in contrast to 45% for 1 mg L^{-1} ozone and 25% for 30 mg L^{-1} PAC, while for HS, BB, and LMWN, the removal efficiency was 38%, 5%, and 18%, in contrast to 28%, 5%, and 1% for 30 mg L^{-1} PAC and 20%, −2%, and −18% for 1 mg L^{-1} ozone, respectively. The elevated reductions in organic BP, HS, LMWN, and BB might both reduce the membrane fouling layer and mitigate organic adsorption in the membrane pores. Therefore, the altered molecular structures of organic matter, as well as PAC adsorption, are likely the dominant factors by which combined ozone and PAC treatment alleviated reversible and irreversible membrane fouling, which suggested that combined ozone and PAC treatment had complementary effects on the reduction of organic content and thus alleviated membrane R_{re} and R_{ir}.

Although considerable amounts of organic matter in natural water can be eliminated by the pretreatment employed in this study, the residual contaminants remain can be rejected by UF, which results in serious membrane fouling. Single UF resulted in high rejection of macromolecular BP whether individual PAC treatment or ozone treatment was applied; however, the
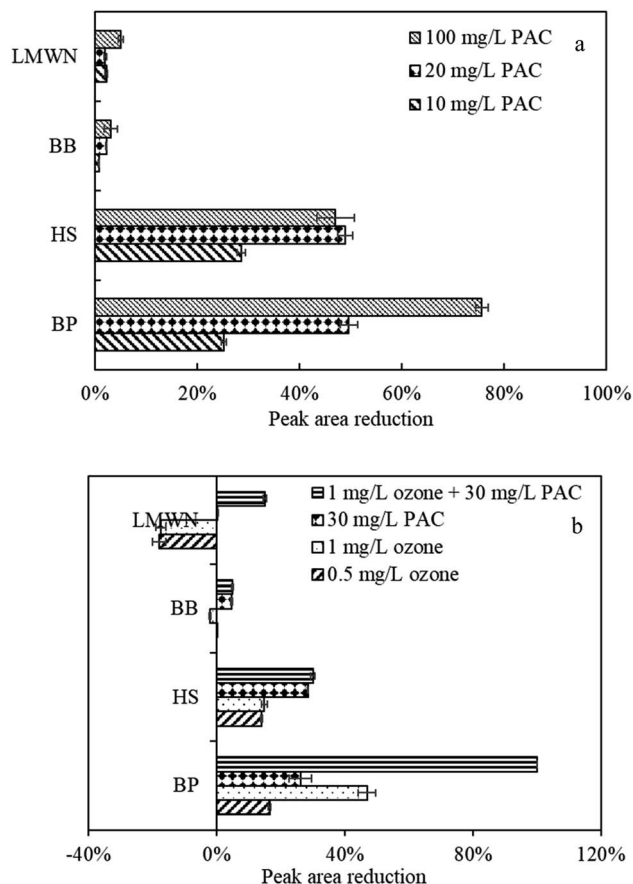
Fig. 5 Peak area reduction of various MW components by PAC and ozone treatment via HPSEC peak-fitting, (a) by PAC treatment, (b) by ozone and PAC treatment.

rejection rate was greatly reduced under combined treatment compared with those obtained under individual PAC and ozone treatment (Table S2 in the ESI†). In fact, the rejection rate was 0 after combined ozone and PAC treatment. Moreover, HS and LMWN were less rejected by UF after combined ozone and PAC treatment than after individual treatment, which again demonstrated the alleviation of both R_{re} and R_{ir}.

3.2.3 Protein and ammonia nitrogen removal. Previous research suggested that protein, a dominant constituent of NOM, has important effects on membrane fouling.[34] Fig. 6 displays the protein removal efficiencies obtained with individual and combined PAC and ozone treatment. When water was treated by UF without any pretreatment, the protein removal was 11% (Fig. 6a). When PAC pretreatment was used, the protein content in the influent water was effectively reduced. The protein removals were 45%, 43%, and 71% for PAC doses of 10 mg L^{-1}, 20 mg L^{-1}, and 100 mg L^{-1}, respectively. Combined PAC and UF resulted in 45.29%, 58.33%, and 77.31% protein removals with 10 mg L^{-1}, 20 mg L^{-1}, and 100 mg L^{-1} PAC, respectively.

Ozone oxidation had minimal effects on protein removal at a low dose of 0.5 mg L^{-1} (1.2%); however, the removal efficiency increased (14.2%) at 1 mg L^{-1} (Fig. 6b). When PAC was added to the combined ozone–UF system, the protein removal efficiency

was 28.94%, higher than that of 21.64% for 1 mg L^{-1} ozone, but lower than that of 40.32% for 30 mg L^{-1} PAC. This phenomenon likely occurred because when the protein was oxidized, the organics after oxidation might be easily adsorbed by PAC, weakening the adsorption effects of protein. When the water was further filtered by UF, the protein removal efficiency was lower (0.75%) than that under separated ozone (7.1%) and PAC treatment (4.76%). The decreased protein removals might also suggest an organic load reduction on the membrane surface, thus alleviated membrane fouling.

In addition to protein, ammonia nitrogen was determined. Ammonia nitrogen of high concentration was reported to have harmful effects on human health and aquatic life.[35] Fig. S4† displays the ammonia nitrogen removal under separated PAC and ozone treatment and combined treatment. UF alone could not remove ammonia nitrite effectively, while PAC pretreatment presented high adsorption effects on ammonia nitrogen removal, and approximately 10% of ammonia nitrogen was removed. However, for ozone, the ammonia nitrogen removal was limited. In fact, the ammonia nitrogen content in the effluent increased after ozone treatment, and the percentage increased from 12% to 25% for 0.5 mg L^{-1} and 1 mg L^{-1} ozone, respectively. This phenomenon can be explained by the fact that when ozone was applied, some nitrogenous substances in the water might be oxidized into ammonia nitrogen, increasing the ammonia nitrogen content. After combined ozone and PAC treatment, the ammonia nitrogen removal increased to −9%, suggesting that combined PAC and ozone treatment also had synergistic effects on ammonia nitrogen removal in the feed water.

3.3 Analysis of MW distribution by physical–chemical cleaning

To better analyze the membrane fouling behavior of NOM, the efficiency of backwashing and chemical cleaning under individual and combined PAC and ozone treatment during the UF cycle was also investigated.

Fig. 7 displays the variations in peak area of various MW organics after backwashing and chemical cleaning. BP had the highest peak area increases after backwashing (Fig. 7a), which suggested that although BP accounted for a small proportion of the feed water, backwashing can remove most of the macro-molecular BP accumulated on the membrane surface. The BP peak area decreased with increasing PAC doses, which was consistent with the MW distribution in Fig. 5 and the TMP results in Fig. 2 that PAC could adsorb macromolecular organics with increasing PAC doses, thus alleviated R_{re}. In addition to the highest removal of BP, the TOC peak areas were all negative for HS, BB, and LMWN when the water was filtered directly by UF. This phenomenon might be because the back-washing velocity was 2.8 times the filtration permeate flux, thus, new membrane fouling might be caused when the water was filtered directly after UF. However, this phenomenon was greatly alleviated when the water was pretreated with PAC. From the changes of HS and LMWN, it can be seen that when PAC > 20 mg L^{-1}, the peak areas of HS and LMWN were all positive,
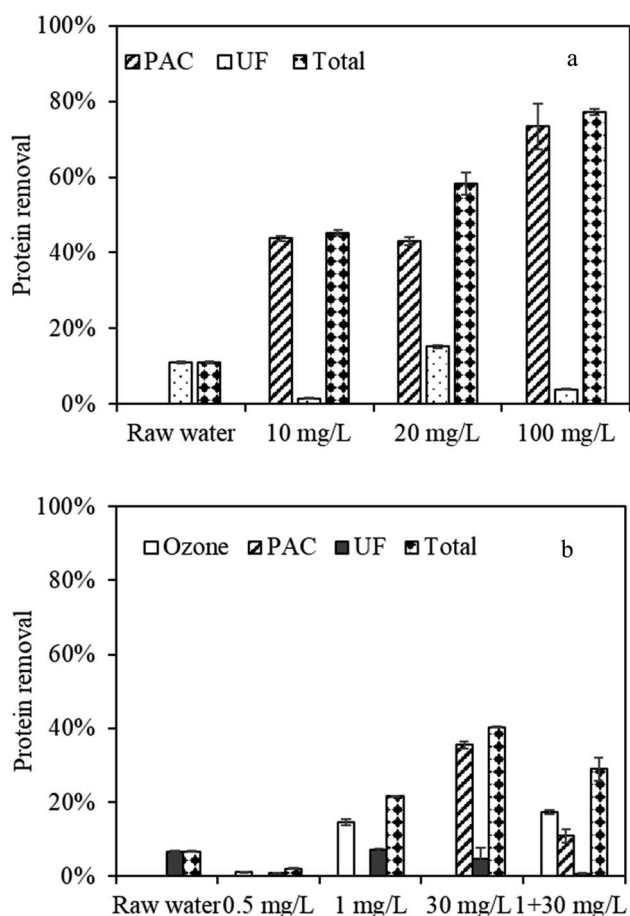
Fig. 6 Protein removal by PAC and ozone treatment during UF, (a) by PAC treatment, (b) by PAC and ozone treatment.

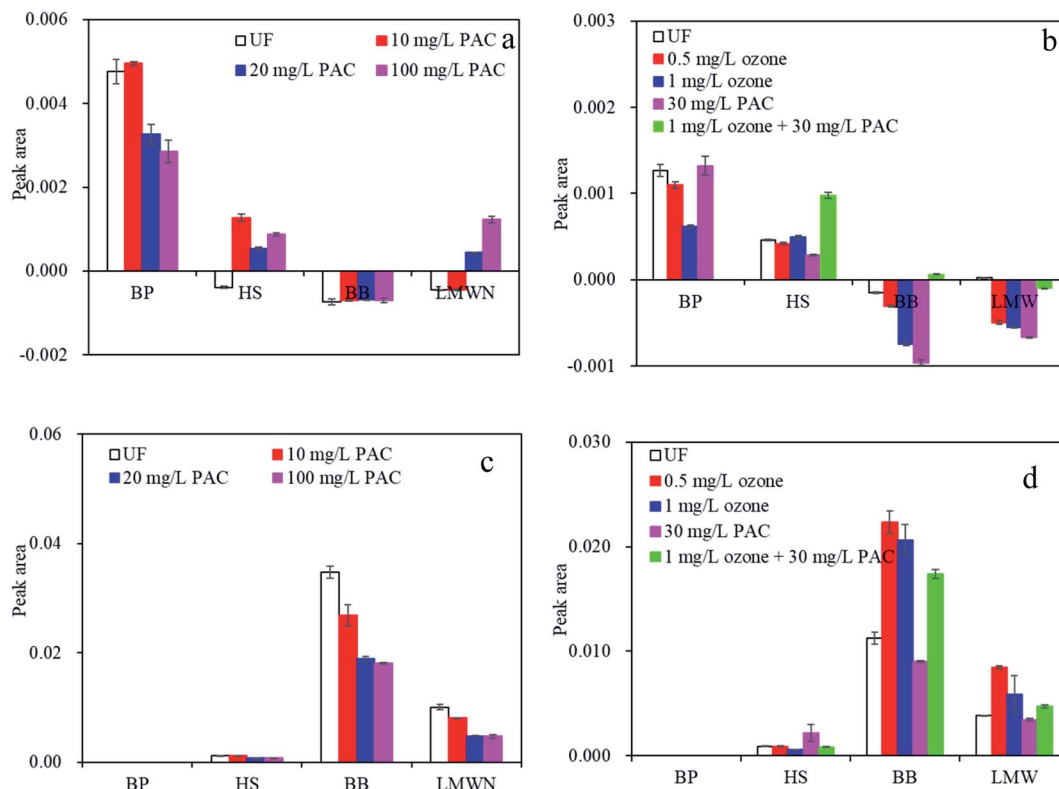© 2021 The Author(s). Published by the Royal Society of Chemistry

Fig. 7 Variation in peak area of various MW components with PAC/ozone treatment after backwashing and chemical cleaning, (a and b) backwashing, (c and d) chemical cleaning.

which again indicated that PAC treatment improved not only the organic removals in the feed water but also the backwashing efficiency of macromolecular organics as well as a certain content of low-MW organics.

Similar to PAC pretreatment, in ozone treatment (Fig. 7b), the BP fraction had the highest peak area increases, followed by HS, while the TOC peak areas were all negative for BB and LMWN after backwashing, which suggested that whether PAC treatment or ozone treatment was used, BP organics were the main components that caused hydraulic R_{re}. However, the BP peak areas were reduced with increasing ozone doses and completely disappeared after combined PAC and ozone treatment, consistent with the results in Fig. 5 and Table S2:† with increasing ozone doses, more macromolecular organics could be oxidized; thus, the amount of BP organics entering the UF system was reduced. In addition, when PAC was further added in the combined ozone–PAC–UF system, the residual macromolecular content might also be adsorbed by PAC, decreasing the BP organics entering the UF system, thus alleviated R_{re}. Notably, the HS peak areas had the second highest increases, followed by BB and LMWN, under combined ozone and PAC treatment. Combined with the organic removal in Fig. 4b, HS can be more effectively removed by combined treatment than by individual PAC and ozone treatment; the above result thus indicated that combined PAC and ozone treatment not only could enhance the removal of HS in the feed water but also improve the backwashing efficiency. HS have long been believed to be one of the major fouling components affecting UF

performance.[36] Wang et al. suggested that the adsorption of HS in membrane inner pores could lead to the constriction and blocking of membrane pores.[37] The adsorption of HS to the membrane could also result in membrane pore narrowing and the increased retention of larger-MW organics.[38] The above results thus indicated that combined ozone and PAC treatment could control membrane R_{re} and R_{ir} by removing organics in the feed water and by improving the organic removal efficiency during backwashing.

Further analysis of the MW organic fractions after ozone treatment revealed that the higher the ozone dose was, the greater the negative BB and LMWN values were, which suggested that new irreversible membrane fouling would happen whether by direct UF or ozone treatment; and the higher the ozone dose was, the more serious new membrane fouling would be brought during backwashing. However, combined PAC and ozone treatment could greatly alleviate this situation, based on the changes in the peak areas of BB and LMWN, which further suggested that combined PAC and ozone treatment could improve the removal of organics in the feed water as well as the backwashing efficiency and reduce the membrane fouling brought by backwashing.

Analysis of the MW distribution in the chemical cleaning effluent (Fig. 7c and d) demonstrated that regardless of the PAC treatment or ozone treatment, BB had the highest peak areas, followed by LMWN and HS, while the BP peak areas were 0, suggesting that low-MW organics of BB and LMWN, as well as HS, were the main components that caused irreversible

Table 1 R^2 for the five combined fouling models fit at various treatments

R^2		Cake-complete	Cake-intermediate	Complete-standard	Intermediate-standard	Cake-standard
Raw water	1st cycle	0.98283	0.97225	0.98308	0.98255	0.98375
	2nd cycle	0.85305	0.69443	0.9266	0.93612	0.96996
	3rd cycle	0.65636	0.48529	0.92549	0.93903	0.98848
Ozone 0.5 (mg L^{-1})	1st cycle	0.97118	−0.00763	−0.00763	−19.035	−0.00763
	2nd cycle	0.84302	0.67986	0.95211	0.96055	0.98499
	3rd cycle	0.71076	0.51289	0.93449	0.94537	0.9732
Ozone 1 (mg L^{-1})	1st cycle	0.94603	−0.00763	−0.00763	−55.5542	−0.00761
	2nd cycle	0.75117	0.65779	0.95341	0.95726	0.97963
	3rd cycle	0.58772	0.49168	0.96475	0.96722	0.98282
PAC 30 (mg L^{-1})	1st cycle	0.9405	−0.90124	0.9432	0.94567	0.96572
	2nd cycle	0.9371	0.8687	0.9388	0.94007	0.94694
	3rd cycle	0.80482	0.66697	0.9179	0.92322	0.94226
Combined 1 + 30 (mg L^{-1})	1st cycle	0.80482	0.66697	0.9179	0.92322	0.94226
	2nd cycle	0.52551	0.48739	0.90785	0.88974	0.94917
	3rd cycle	0.3015	0.27755	0.92479	0.84651	0.96899

membrane fouling. In addition, the TOC peak areas of BB and LMWN decreased with increasing PAC and ozone doses, while combined PAC and ozone treatment had the lowest TOC content of BB and LMWN (Fig. 7d), suggesting that combined PAC and ozone treatment was effective in removing BB and LMWN. When the water was pretreated by combined ozone and PAC treatment, the irreversible membrane fouling was the least, which further verified that combined ozone and PAC treatment prior to feed water could greatly alleviate R_{ir}.

3.4 Modeling of filtration process

In order to obtain a profound understanding of fouling alleviation mechanism by combined PAC and ozone treatment, five combined fouling models were adopted to fit the experimental data. Table 1 shows the sum of squares (R^2) between the experimental data and fitted values, the TMP (P/P_0) *vs.* time with the combined cake-standard fouling model at the last filtration cycle was also depicted (Fig. 8), it can be seen from Table 1 and Fig. 8 that combined cake-standard model fitted the experimental data excellently no matter for the raw water or by the individual and/or
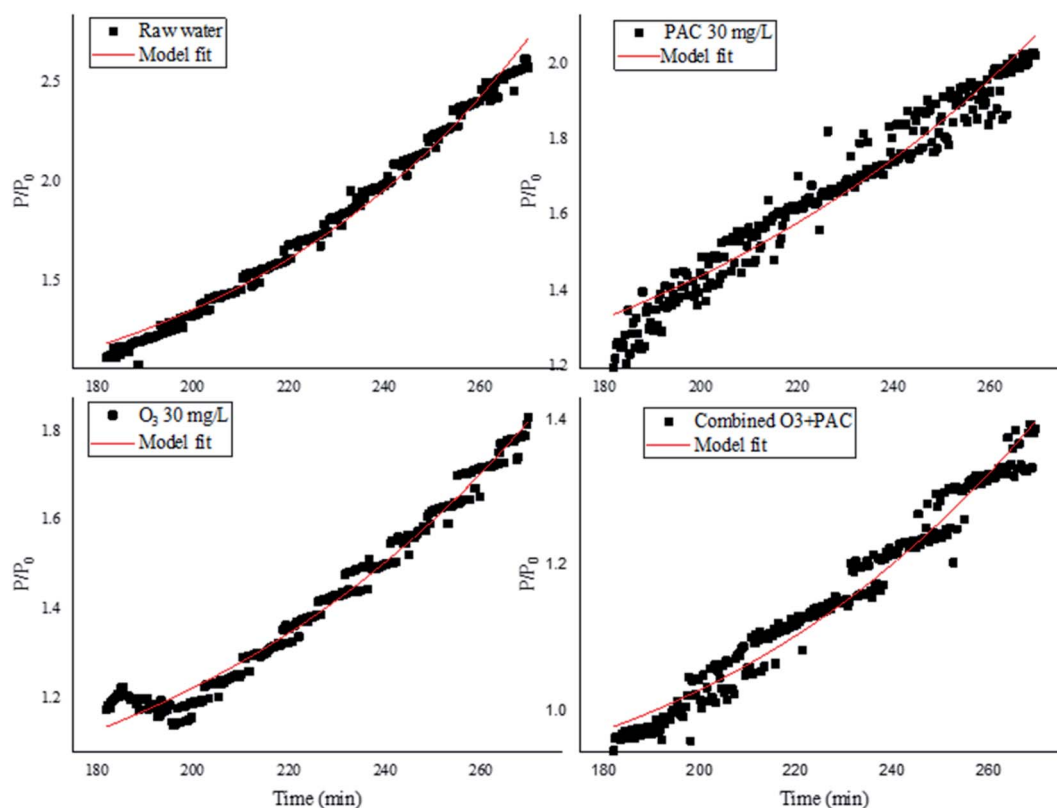

Fig. 8 TMP (P/P_0) *vs.* time with the combined cake-standard fouling model at the third filtration cycle, symbols represent the experimental data and solid lines represent the model fit using the combined cake-standard fouling model.

combined PAC and ozone treatment, suggesting that the NOM-related membrane fouling of raw water was more likely attributed to the formation of cake layer and standard pore blocking. From Fig. 8, it can be seen the individual and/or combined PAC and ozone treatment might alleviate UF membrane fouling which may ascribe to the alleviation of cake layer and standard pore blocking. Moreover, it was found that with increasing with the filtration time, the R^2 varied. The R^2 were 0.98283, 0.97225, 0.98308, 0.98255, and 0.98375 for combined cake-completed, cake-intermediate, complete-standard, intermediate-standard, and cake-standard model, respectively, at the first filtration cycle of raw water, while they were 0.85305, 0.69443, 0.9266, 0.93612, and 0.96996 for the second filtration cycle, and 0.65636, 0.48529, 0.92549, 0.93903, and 0.988848, for the third filtration cycle, respectively, suggesting that with increasing with filtration time, the membrane fouling caused by the formation of cake layer and standard pore blocking increased, however, the membrane fouling induced by the other four combined models might decline. Similar phenomenon was also observed for the R^2 changes during individual/combined PAC and ozone treatment (except for that of ozone 1 m L^{-1}), suggesting that the mitigation of NOM-related membrane fouling due to cake layer and standard pore blocking was also increased with increasing with filtration time under individual/combined PAC and ozone treatment, however, combined complete-standard pore blocking and intermediate-standard pore blocking might exert some effects in the alleviation of membrane fouling during ozone 1 mg L^{-1} treatment by the increased R^2 at the end of filtration cycle (Table 1).

When comparing the magnitude of R^2 of combined cake-standard model, it was found that the R^2 was 0.9732 for ozone 0.5 mg L^{-1}, comparing with 0.98282, 0.94226, and 0.96899 for ozone 1 mg L^{-1}, PAC 30 mg L^{-1}, and combined ozone 1 mg L^{-1} + PAC 30 mg L^{-1}, respectively, at the third filtration cycle. The respective contribution of cake model and standard model to the combined cake-standard model was also evaluated,[39] and from the calculated fitted parameters of cake model and standard model to the combined cake-standard model, it was found that the ratio K_cJ_0/K_s were −1.712 for raw water comparing with −1.4623, −1.082, and −1.6356 of ozone 1 mg L^{-1}, PAC 30 mg L^{-1}, and combined ozone 1 mg L^{-1} + PAC 30 mg L^{-1}, respectively, at the last filtration cycle, suggesting that standard pore blocking might exert more important effects on the NOM-related membrane fouling as well as the membrane fouling control.

The fitting parameters K_c and K_s for the combined cake-standard model under various ozone and PAC pretreatment can also be found in Fig. S5.† The K_c increased under various individual and/or combined treatment, while the K_s decreased, which further implied that the NOM-related membrane fouling mitigation by individual and/or combined ozone and PAC treatment might mainly be ascribed to the alleviation of standard pore blocking.

3.5 Discussion of membrane fouling mitigation by combined ozone and PAC treatment

Prior research has suggested that there are two membrane fouling mitigation mechanisms associated with the

preozonation of feed water: reduced organic loading and structural changes in organic matter.[28] In this study, macromolecular organics (such as polysaccharides, protein-like organics) were the major organics that were rejected by UF, while HS were meanwhile rejected, which suggested that macromolecular organic BP and HS were the main organics that caused membrane fouling during constant-flux UF. Combined with the modeling results and the R_{re}, R_{ir} changes in Fig. 2, 8, and Table 1, it could be speculated that macro molecular organics might quickly accumulated and dominated in membrane pores after attaching and/or plugging the membrane pores,[40] followed by the formation of cake/gel layer on the membrane surface during a long-time accumulation, thereafter, more macro and medium molecular substances might be rejected on the membrane surfaces and/or in the membrane pores by the already formed fouling layers with increasing with filtration cycle. When the physical cleaning was conducting, as the interaction between the membrane and foulants was insignificant,[40] macro molecular organics deposited within the membrane pores and/or on the membrane surface might be significantly rinsed (Fig. 7), as such, the total resistance was greatly recovered (Fig. 2).

When ozone was applied, macromolecular organics were progressively reduced, while small-MW organics were increased. These macro molecular organics might significantly contribute to the standard pore blocking with these organics easily attaching and/or plugging membrane pores and then formed the cake/gel layer. By ozonation, these macro molecular organics were break down into small molecular organics, which led to the reversible fouling resistance reduced at higher ozone doses, meanwhile, the small MW organics generated might be easily permeate through the membrane pores and/or attaching to the membrane pores,[21] leading to the R_{ir} increased.

When PAC was further added, not only macromolecular BP but also medium-MW HS organics, as well as LMWN and BB, were further reduced by combined ozone and PAC treatment than by individual PAC or ozone treatment. This reduction in organics alleviated both the reversible and irreversible resistance of the membrane. In addition, more hydrophobic organics were removed, according to the analysis of SUVA values (Fig. 4c and d). Hydrophobic organics have been reported to have a greater tendency to adhere to the membranes and have a strong influence on the cake layer.[8,21] The reduction in hydrophobic organics in the feed water after combined ozone and PAC treatment might further mitigate the standard pore blocking and cake layer formation (Table 1). Moreover, when physical cleaning was performed, new membrane fouling was caused under both direct UF and ozone treatment; however, combined ozone and PAC treatment could greatly alleviate this situation, first by the enhanced removal of organic matter during backwashing and second by the reduction of organic matter during chemical cleaning.

Based on the results, the behavior of combined PAC and ozone treatment on membrane fouling mitigation during UF of micro polluted water can be illustrated as follows in Fig. 9:
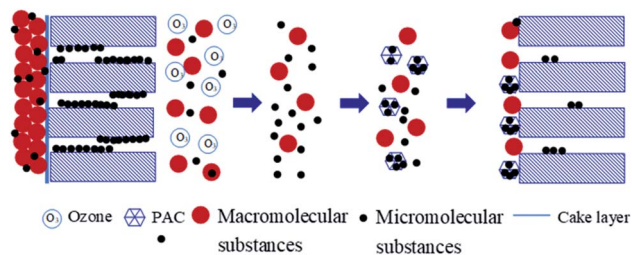
Fig. 9 Mechanism of membrane fouling by combined ozone–PAC pretreatment.

R_{re}	Reversible fouling resistance
BP	Biopolymers
HS	Humic-like substances
LMWN	Low-molecular-weight neutral substances
BB	Building blocks
HPSEC	High-performance size-exclusion chromatography

4. Conclusion

This paper investigated the reversible and irreversible membrane fouling changes of raw water by ozone/PAC treatment, and the following conclusions can be drawn:

(1) Macromolecular BP and medium-MW HS were the major organics that caused membrane fouling during UF. PAC–UF could improve the removal efficiency of organic compounds, especially HS. Suitable amounts of PAC during UF not only enhanced the irreversible resistance in UF but also the reversible resistance, and there existed a threshold PAC dosage for membrane fouling alleviation in terms of both R and R_{re}. PAC reduced R_{ir} mainly because PAC not only reduced the organic matter in the influent water but also improved the backwashing efficiency.

(2) Ozone mainly removed macromolecular BP and HS in water, while the content of BB and LMWN increased. Ozone at low doses exerted little effects on membrane fouling alleviation in this study, while higher doses decreased R and R_{re}.

(3) Combined ozone and PAC pretreatment had enhanced effects on both R_{re} and R_{ir} reduction, which demonstrated synergistic effects in the reduction of organic content in the feed water, including macromolecular BP, LMWN, and BB.

(4) BP was the mainly organics that caused R_{re}, whereas low-MW organics of BB and LMWN, as well as HS, were the main components that caused irreversible membrane fouling. New irreversible membrane fouling caused by BB and LMWN was induced by backwashing under both direct UF and individual ozone treatment, and the higher the ozone dose was, the more serious new membrane fouling occurred. Combined ozone and PAC treatment not only improved the backwashing efficiency but also reduced the new membrane fouling and R_{ir}.

(5) Cake layer formation and standard pore blocking were the major mechanism for NOM-UF fouling and alleviation by individual and/or combined PAC and ozone treatment, of which standard pore blocking exerted more important effects in the formation and alleviation of membrane fouling.

Abbreviations

NOM	Natural organic matter
UF	Ultrafiltration
PAC	Powdered activated carbon
R_{ir}	Irreversible fouling resistance

Author contributions

Weiwei Huang, Bingzhi Dong done all the experiments and wrote the main manuscript text, Yuanhong Zhu, Lin Wang contributed to analytic tools, Weiguang Lv, Wenzong Zhou reviewed the whole manuscript.

Conflicts of interest

All authors declare that the research was not involved human participants and/or animals, there is no conflict of interest exits in the submission and publication of this manuscript, all of us consent for publication, and all data and materials are available, besides, all funding, authors' contributions, acknowledgements were included in the manuscript.

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