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Comparison of flocculant aids as pretreatment reagent for membrane filtration process by fingerprint analysis of organic matters in secondary effluent

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ABSTRACT

Coagulation/flocculation is becoming a conventional and beneficial pretreatment for membrane filtration of wastewater, but how to choose coagulant/flocculant aid and optimal dosage is still a key issue in practice. Two cationic flocculant aids, polyacrylamide (PAM) and Kuriverter EP-301 (EP), were compared for the removal of organic matters from secondary effluents of municipal wastewater plant using $FeCl_3$ as coagulant. EP achieved a better performance than PAM in terms of membrane filtration factor (MFF) and removal of suspended solids, turbidity and dissolved organic carbon. Optimal dosage for PAM was 30 mg Fe/L $FeCl_3$ and 1 mg/L PAM, at which MFF was 2.13, while when 30 mg Fe/L $FeCl_3$ and 1 mg/L EP was injected, MFF was 1.47. Optimal dosage for EP was 50 mg Fe/L $FeCl_3$ and 2 mg/L EP, at which MFF was as low as 1.04. Fingerprint analysis method was first used to analyze the removal characteristics of dissolved organic matters fraction by PAM and EP flocculation. It was found that EP could remove more hydrophobic fractions (HO) than PAM. Moreover, EP could remove part of hydrophilic fractions (HI), while PAM had no effect on HI fractions. Hydrophobic acids (HOA) with MW > 5,000 Da were the major subfraction removed largely by coagulation/flocculation and EP could remove more of it than PAM. Larger MW ($>10^7$ Da) and three-dimensional molecular structure made EP more effective based on polymer bridging mechanism and charge neutralization.

Keywords: Wastewater reclamation; Coagulation; Flocculation aid; Membrane filtration; Dissolved organic matter; Resin fraction; Hydrophobic acid

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1. Introduction

As a viable and attractive approach to dealing with the global water scarcity, wastewater reclamation and reuse is becoming an emerging issue throughout the world [1]. Therefore, various membrane processes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membrane have recently gained recognition as viable technologies for the wastewater reclamation due to their high removal efficiency of pollutants, stable water quality, and easy operation [2–5]. However, membrane fouling is still a major concern in the application of membrane technology as it deteriorates the performance of membranes (e.g. causing serious flux decline, increasing the energy cost, and affecting the produced water quality), especially for RO membrane [6,7].

The possible foulants for RO membrane in the feed water can be governed to particles and colloids (cake layer formation), dissolved inorganic matters (concentration polarization), dissolved organic matters (DOM, electrostatic repulsion and/or hydrophobic interactions), and microbial attachment and growth (biofouling) [6].

A sufficient pretreatment to supply high quality feed water is necessary for ensuring stable and long-term performance of membranes for wastewater reclamation. During the past decades, coagulation/flocculation became a conventional and beneficial pretreatment for membrane process, since it removes particles, colloids, and part of DOM from the feed water. Hence, the substances easily adsorbed on membrane surface are turned to flocs, which are separated from feed water subsequently [8,9].

Potential coagulants widely used for wastewater reclamation are polyaluminum chlorides (PAC) and ferric salts, which can destabilize the colloids to form flocs. Flocculant aids are added after coagulation to enlarge and strengthen flocs by either polymer bridging or charge neutralization or a combination of these mechanisms [10,11]. Also, the addition of polymers as flocculant aids can reduce the dosage of metal coagulant used and sludge production [12].

However, the efficiency of coagulation/flocculation depends on the optimal combination of metal coagulant and polymer as flocculant aid, the best type of polymer, the optimum concentration ratios, and the optimum process conditions [10,11]. Furthermore, before the application in practice, the performance of metal coagulants and polymers as flocculant aids should be examined due to the different raw water quality, and the optimum dosages should be determined. Less dosing of chemicals leads to poor quality of feed for membrane system and consequently causes membrane fouling, while overdosing of flocculant aids results in excess cationic polymers absorbed strongly on the membranes causing the fouling of membranes finally [8,13], and also might increase the chances of chemical toxicity of discharged water [14]. Multiple varieties of polymers are available in the market and the prices of polymers are relatively high, so polymers should be carefully selected to achieve a better water quality with a lower cost.

Moreover, some organic cationic polymers can react with some fractions of DOM [8], which are present in high levels in secondary wastewater effluents and are too complex to remove effectively [15]. Also, specific types of fractions of DOM have important relationship with membrane fouling. Kim et al. reported that the flux decline of NF membranes was positively affected by the hydrophilic fractions of feed water [6,16]. Chon et al. reported that major fractions of DOM deposited on RO membranes were hydrophilic fractions mainly comprised of polysaccharide-like and protein-like functional groups [17]. Zhao et al. reported that hydrophilic neutral fraction (HIN), mainly composed of small size carbohydrates, resulted in the highest flux decline and exhibited highest affinity towards the membranes [18]. Tang et al. also reported that HIN fraction was the largest fraction and occupied 34.2% of the total dissolved organic carbon (DOC) in the deposit on a fouled RO membrane for wastewater reclamation [19]. Also, hydrophobic acids (HOA), especially HOA with high molecular weight (MW), like humic substances, tend to deposit on membranes and become a cake layer [19,20]. Hence, in order to have a better understanding of flocculant aids performance, it is important to figure out the characterization of DOM in feed water before and after coagulation/flocculation.

However, the capacity of RO influent after pretreatment of foul RO membranes is often described using silt density index (SDI), modified fouling index, membrane filtration factor (MFF), and other indexes [21]. Total organic carbon (TOC), color, and turbidity are also used as parameters for determining the removal efficiency of organic polymers used as flocculant aids. However, these indexes or parameters can’t present the change of DOM, which is closely related to organic fouling and bio-fouling of RO membrane [21–23]. Hence, in this paper, size exclusion chromatography (SEC) and fingerprint analysis method (resin fractionation followed by SEC analysis of each resin fraction) of DOM, as well as suspended solids (SS), DOC and ultraviolet absorption at 254 nm (UV_{254}), were applied, trying to identify a logical method to evaluate the water quality of RO influent and predict the capacity of RO influent after pretreatment to foul RO membranes, and finally to select apposite flocculant aids for pretreatment of membrane process.

2. Materials and methods

2.1. Water samples

Wastewater samples used for the experiments were collected from the influent of a microfiltration-reverse osmosis membrane (MF-RO) process in a wastewater reclamation plant located in Beijing. The influent of MF-RO process is the effluent of a wastewater treatment plant, which is using sequencing batch bio-reactors (SBR) system to treat the mixture of industrial and domestic wastewater. The samples were kept in ice and taken back to laboratory immediately and then stored at 4℃ to minimize the changes of constituents in the water. The coagulation experiments took place within 24 h.

2.2. Chemicals preparation

Analytical class reagent $FeCl_3$ and polyacrylamide (PAM) were used as coagulant and flocculant aid in this experiment, respectively, for $FeCl_3$ and PAM are most commonly used in wastewater treatment plants due to their stable performance and cheap cost. In addition, Kuriverter EP-301 (EP) was used as a new kind of flocculant aid to be compared with PAM. EP was invented and supplied by Kurita Company (Japan) in liquid form and the major constituent is methacrylic acid polymer.

EP and PAM were prepared at a concentration of 1 g/L in pure water, stirring the solution at 200 rpm for 1 h. Concentration of $FeCl_3$ solution was 38%. The chemicals were prepared one day before the coagulation/flocculation experiments took place.

2.3. Coagulation/flocculation experiments

Coagulation/flocculation experiments were performed using a coagulation instrument with six 1,200 mL beakers in the laboratory. Before starting the experiments, the secondary effluent sample was brought to room temperature (approximately 25℃). The secondary effluent sample was shaken for re-suspension of settled solids and 1.1 L of secondary effluent sample was transferred to each beaker for coagulation. To determine an effective coagulant dose for coagulation treatment, $FeCl_3$ doses in the ranges of 10–50 mg Fe/L and flocculants (PAM or EP) doses in the ranges of 0.2–2 mg/L were used, respectively. After $FeCl_3$, samples were rapidly mixed for 20 min at 150 r/min, it was followed by gentle stirring for 5 min at 100 r/min. Then flocculants were added to the samples and stirring was continued for 5 min at 100 r/min, after which the flocs generated during mixing were allowed to settle for about 30 min. Hence, 5-μm membrane was used to remove the sediments during the coagulation/flocculation experiment. No pH adjustment was made during coagulation, but pH monitoring revealed that it was about 7.8 before coagulation and no significant change happened thereafter.

2.4. MFF determination

Membrane filtration (MF) is defined as the filtration time of 1 L of the sample through a 0.45 μm membrane at a constant pressure (30 psi) [24]. MFF (MF factor) is the modified MF, which is calculated according to the following calculation:

$$\mathrm{MFF} = T_2/T_1 \quad (1)$$

where T_1 = initial time required to collect the first 500 mL of sample, s, and T_2 = time required to collect the second 500 mL of sample just after test time T_1, s.

If $T_1 < 60$ s, and also MFF < 1.2, the quality of sample is acceptable and can be used as an influent of RO system. Actually, MFF is something like SDI_0. MFF determination can save much time and check out the good water quickly, especially when many samples are waiting.

2.5. Analytical methods of water quality

PH was measured with a Mettler Toledo Fe20 analyzer. Turbidity was measured by portable turbidimeter (2100Q, HACH, USA). DOC concentration of the samples was monitored with a TOC-5000A analyzer (SHIMADZU Corporation, Japan). SEC was used for the molecular weight (MW) analysis of the fractions on a Shimadzu LC-20 high-performance liquid chromatography system combined with a Shimadzu SPD-M20A UV detector and two connected columns (a TSK-GEL G3000PWXL column followed by a TSK-GEL G2500PWXL column). The MW standards used were polyethylene glycol (330, 700, 1,050, 5,250, 10 225, and 30 000 Da) and acetone [25].

2.6. Fingerprint analysis method

Fingerprint analysis method was introduced by Tang et al. [26]. DOM in a water sample was first divided into six resin fractions: hydrophobic acids

(HOA), hydrophobic bases (HOB), hydrophobic neutrals (HON), hydrophilic acids (HIA), hydrophilic bases (HIB), and hydrophilic neutrals (HIN). Resin fractionation was based on the original protocol of Leenheer and a modified one introduced by Zhang et al. [27,28]. Then SEC was performed to separate each resin fraction into several (*n*) subfractions with different molecular weights (MW). In this paper, three MW intervals (MW < 3,000; 3,000 < MW < 5,000; and MW > 5,000) were selected, indicating three SEC fractions of each resin fractions. Thus, the total DOM of water sample was fractionated into 18 subfractions, according to which the fingerprint graph of the water sample was constructed to express the distribution of DOM.

3. Results and discussion

3.1. Selection of experimental condition for comparison of PAM and EP

MFF value of water samples treated by coagulation/flocculation with $FeCl_3$ in ranges of 10–50 mg Fe/L and 0.5–2 mg/L of flocculants (PAM or EP) is shown in Fig. 1. MFF of the water samples treated by flocculant aid EP was significantly lower than that of PAM. As the $FeCl_3$ dosage increased, the MFF of EP decreased constantly. When the dosage of $FeCl_3$ was higher than 20 mg Fe/L, MFF of EP stabilized below two. The lowest MFF was 1.04 ± 0.04, which appeared at the dosage of 50 mg Fe/L $FeCl_3$ and 2 mg/L EP. When PAM was used as the flocculant aid, the lowest MFF appeared at the dosage of 20–30 mg Fe/L $FeCl_3$ and 0.5–1 mg/L PAM, which was considered as the optimal dosage.

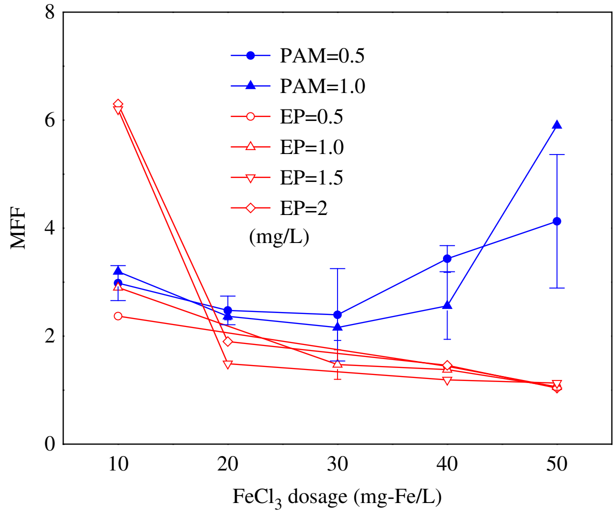

Fig. 1. MFF of samples after coagulation/flocculation with a variety of $FeCl_3$ dosages and flocculant aids (PAM or EP) dosages.

Three typical dosages of chemicals conditions were chosen for the comparison experiments of PAM and EP.

(1) Optimal dosage for PAM: 30 mg Fe/L $FeCl_3$ and 1 mg/L PAM, at which the water samples treated was referred as S_{PAM1}.
(2) Optimal dosage for EP: 50 mg Fe/L $FeCl_3$ and 2 mg/L EP, at which the water samples treated was referred as S_{EP2}.
(3) Same dosage for EP as optimal dosage for PAM: 30 mg Fe/L $FeCl_3$ and 1 mg/L EP, at which the water samples treated was referred as S_{EP1}.

The typical dosages (1) and (2) were used to compare performance of PAM and EP under their optimal dosages, while (1) and (3) were used to compare performance of PAM and EP under the same dosages.

Table 1 presents the MFF of the secondary effluent before and after coagulation/flocculation at the three typical dosages. Because there were large amount of particles, colloids and high molecular weight organic matters in the secondary effluent before pretreatment, the membrane used for MFF determination was fouled quickly and the MFF of the secondary effluent could not be measured accurately. MFF of S_{PAM1}, S_{EP1} and S_{EP2} was 2.13 ± 0.18, 1.47 ± 0.27, and 1.04 ± 0.04, respectively. EP achieved a better performance than PAM when MFF was used as the coagulation/flocculation criterion.

3.2. Removal of particles, colloids, and DOM

The presence of particles and colloids is normally measured as SS and turbidity, and also a pretreatment criterion for seawater desalination is a turbidity of 0.1–0.5 NTU [29]. In this paper, the particles left on the 0.45 μm microfiltration membrane were measured as SS, while turbidity of the filtrate presented the pollutants that passed through the 0.45 μm membrane and retained in the filtrate.

The SS and turbidity of secondary effluent were 1.4 mg/L and 0.90 NTU, which were fairly low, as shown in Table 1. After the coagulation/flocculation treatment, the SS of S_{PAM1}, S_{EP1}, and S_{EP2} decreased to 1.0, 0.9, and 0.7 mg/L, while the turbidity of S_{PAM1}, S_{EP1}, and S_{EP2} decreased to 0.42, 0.26, and 0.17 NTU, respectively. Coagulation/flocculation treatment was effective to remove particles and EP was more effective than PAM.

Table 1
MFF and water quality of the secondary effluent before (S_{SE}) and after coagulation/flocculation (S_{PAM1}, S_{EP1} and S_{EP2})

Water samples	S_{SE}	S_{PAM1}	S_{EP1}	S_{EP2}
MFF	–	2.13 ± 0.18	1.47 ± 0.27	1.04 ± 0.04
SS (mg/L)	1.40	1.00	0.90	0.71
Turbidity (NTU)[a]	0.90	0.42 ± 0.04	0.26 ± 0.05	0.17 ± 0.03
DOC (mg/L)	6.28	5.44 ± 0.12	4.93 ± 0.36	4.21 ± 0.36

Note: "–" indicates that the filtration time for secondary effluent was too long to be measured accurately.

[a] turbidity measured here is for water samples after the 0.45 μm membrane filtration. Errors indicate SD of three replicates of each water sample.

DOC is a collective parameter to characterize the concentration of DOM and is typically 2–5 mg/L in RO influent for seawater desalination [8]. As shown in Table 1, coagulation/flocculation removed a little part of DOC in the secondary effluent. Meanwhile, the DOC of S_{EP1} was lower than that of S_{PAM1}, indicating that 1 mg/L EP added with coagulant $FeCl_3$ could remove more DOC than 1 mg/L PAM.

3.3. SEC chromatography

Fig. 2 shows the UV_{254} absorbance of DOM with different molecular weights (MW) in the secondary effluent before and after pretreatment. Notable UV_{254} peaks were observed in the retention time of 30–35 min, covering the apparent MW range of 2,000–10,000 Da. Specific absorbance bands P1 (around 2,600 Da), P2 (around 3,900 Da), P3 (5,700 Da), and P4 (around 7,200 Da) were picked. Peak P1 presented DOM with MW lower than 3,000 Da, which was changed little by coagulation/flocculation. The peaks (P2–P4) corresponding to the humic substances and extracellular substances were decreased significantly by coagulation/flocculation.

The curve of S_{PAM1} was almost the same as S_{EP1}, indicating that PAM and EP gave no rise to UV_{254} removal efficiency. Moreover, the UV_{254} absorbance intensity of S_{EP2} was lower than those of S_{PAM1} and S_{EP1}. When more $FeCl_3$ was added, more DOM with UV_{254} absorbance was removed. DOM with UV_{254} absorbance always presents DOM with aromatic structures, which usually has fairly high molecular weight. Meanwhile, when those DOM are hydrophobic, they usually carry negative charges, which can easily react with the positively charged $FeCl_3$ and be removed effectively in pretreatment [8].

3.4. Fingerprint analysis of DOM

The SEC chromatography of six resin fractions of S_{SE} is given in Fig. 3. Notable UV_{254} peaks were observed in the retention time of 30–35 min, covering

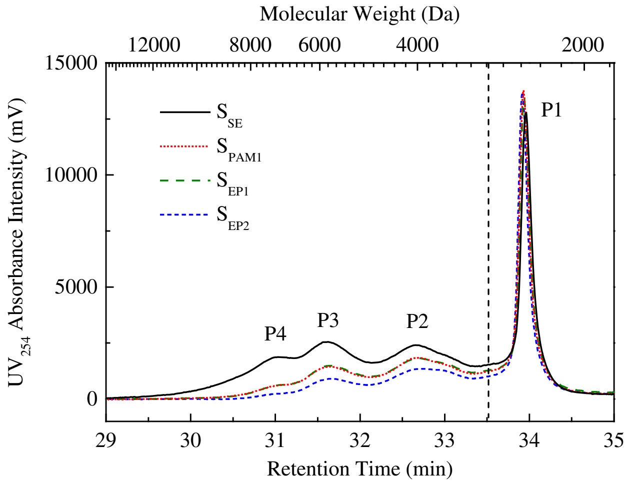

Fig. 2. SEC chromatography of the secondary effluent before (S_{SE}) and after coagulation/flocculation (S_{PAM1}, S_{EP1} and S_{EP2}).

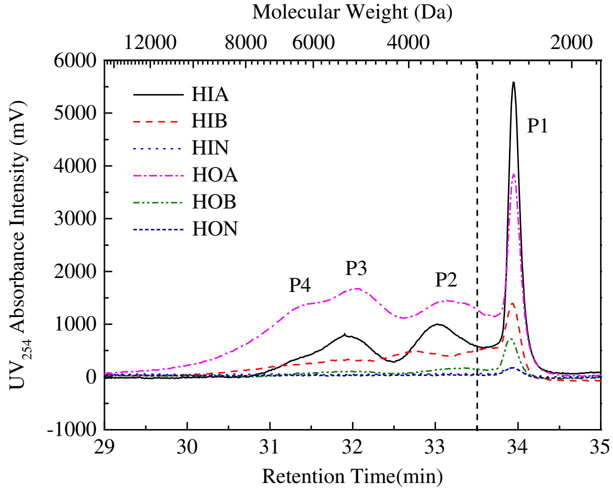

Fig. 3. SEC chromatography of six resin fractions of secondary effluent (S_{SE}).

the apparent MW range of 2,000–10,000 Da. Specific absorbance bands P1 (around 2,600 Da), P2 (around 3,900 Da), P3 (5,700 Da), and P4 (around 7,200 Da) were picked. The peaks (P2–P4) were observed mainly in acid fractions (HOA and HIA), which was inferred that HOA and HIA fractions were the two largest fractions in the DOM of secondary effluent. Furthermore, presenting the DOM with MW < 3,000 Da, the narrow high intensity peak P1 was detected in all of the six fractions and P1 of HIA was higher than that of HOA. However, this phenomenon was just opposite with peaks P2–P4 presenting DOM with high MW, since P2–P4 of HOA was the highest among the six fractions. This result could meet the objective fact that majority of the DOM with high MW belongs to the hydrophobic fraction and majority of the DOM with low MW belongs to the hydrophilic fraction.

According to the SEC chromatography of six resin fractions of the secondary effluent before (S_{SE}) and after coagulation/flocculation (S_{PAM1}, S_{EP1}, and S_{EP2}), the fingerprint graphs are shown in Fig. 4. The fingerprint graph provided a visual description of DOM composition by comprehensively presenting the MW distribution, acidity, and hydrophobicity information.

The whole pie represented the total DOM in water samples. The ratios of S_{PAM1}, S_{EP1}, and S_{EP2} were shorter than those of S_{SE}, indicating that after $FeCl_3$ coagulation and PAM or EP flocculation, the DOM concentration decreased significantly. Especially for EP flocculation, the removal efficiency of DOM was higher than that of PAM.

From the colored sector distribution of the fingerprint graph for S_{SE}, it was easy to recognize that hydrophobic fraction occupied the majority of DOM. The percentages of hydrophobic fraction and hydrophilic fraction were 61.42 and 38.58%, respectively. Among the six resin fractions, HOA was the largest one and accounted for 54.77%. HOA always accounts for the largest fraction (30–80%) in DOM and contains the highest amount of humic substances [30]. DOM with MW > 5,000 Da, 3,000–5,000 Da, and <3,000 Da accounted for 49.77, 32.11, and 18.12%, respectively. As shown in the fingerprint graph of S_{SE}, HOA with high MW (>5,000 Da) was the major subfraction in the total DOM of S_{SE}.

After $FeCl_3$ coagulation and PAM or EP flocculation, the DOM fractions changed a lot. The concentration of hydrophobic fraction decreased significantly and the percentages of hydrophobic fractions for S_{PAM1}, S_{EP1}, and S_{EP2} were 49.01, 58.73, and 57.88%. The removals of hydrophobic fractions for S_{PAM1}, S_{EP1}, and S_{EP2} were 37.4, 39.4, and 46.5%, respectively. The major reason for hydrophobic fraction decreasing was that HOA fraction was removed largely. The

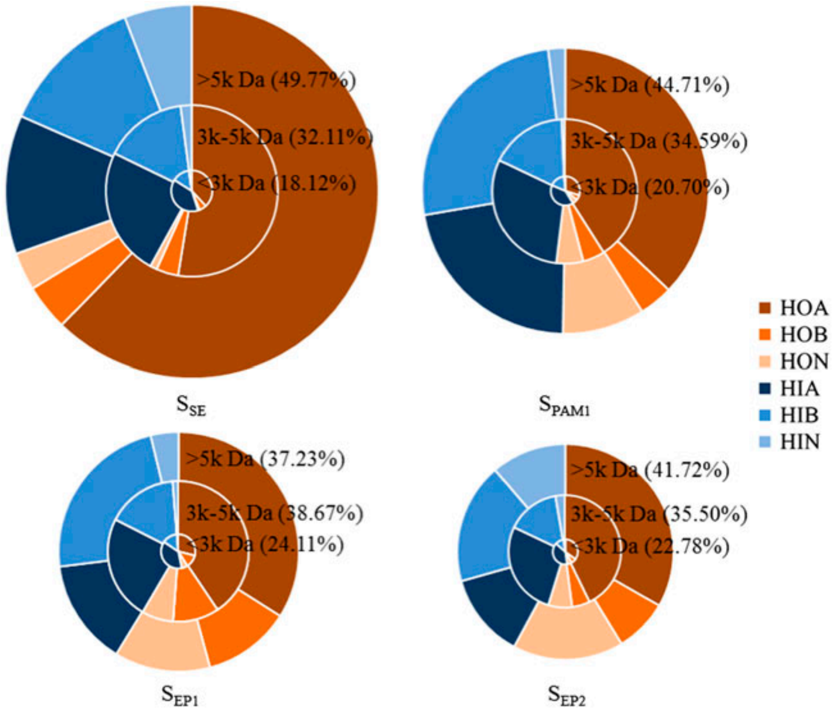

Fig. 4. Fingerprint graphs for secondary effluents before (S_{SE}) and after coagulation/flocculation (S_{PAM1}, S_{EP1}, and S_{EP2}) (On the base of UV_{254}, the diameter of the pie represent total UV_{254} absorbance intensity of the sample).

removals of HOA fractions for S_{PAM1}, S_{EP1}, and S_{EP2} were 46.6, 56.8, and 59.1%, respectively. HOA fraction was a key fraction that could deposit on the membrane easily and fouled the membrane [19]. EP could remove more HOA fraction than PAM did, which indicated that EP could help to decrease the fouling of the membrane in a long-term operation to some extent.

Coagulation/flocculation could remove less hydrophilic organic matters than hydrophobic organic matters. Coagulation/flocculation by $FeCl_3$ and PAM showed no effect on the removal of hydrophilic fractions in the secondary effluent, while flocculation by EP could decrease the concentrations of hydrophilic fractions a little. The removals of hydrophilic fractions for S_{EP1} and S_{EP2} were 22.6 and 27.4%, respectively. Hence, the percentages of hydrophilic fractions of S_{EP1} and S_{EP2} were lower than those of S_{PAM1}. That is why the percentages of hydrophobic fractions of S_{EP1} and S_{EP2} become higher than those of S_{PAM1}, while the concentration of hydrophobic fractions of S_{EP1} and S_{EP2} were lower than those of S_{PAM1}.

Coagulation/flocculation could remove DOM with larger MW, which was reflected clearly by the change of each annular width in the fingerprint graphs. The percentages of DOM with larger MW (>5,000 Da) were decreased largely to 44.71, 37.23, and 41.72% for S_{PAM1}, S_{EP1}, and S_{EP2} from the 49.77% of S_{SE}. Thus, HOA with high MW (>5,000 Da) was the major subfraction removed by coagulation/flocculation in the total DOM of S_{SE} and EP flocculation achieved a better performance. The removals of HOA with high MW (>5,000 Da) were 57.9, 72.6, and 72.7% for S_{PAM1}, S_{EP1}, and S_{EP2}, respectively.

3.5. Analysis of DOM removal mechanisms for PAM and EP

The performance of PAM and EP for DOM removal in the secondary effluent is concluded in Table 2. EP could achieve a better performance than PAM in terms of MFF, SS, turbidity, DOC, hydrophobic fractions (HO), hydrophilic fractions (HI), HOA fraction, and HOA with MW > 5,000 Da, which means the use of EP could help decrease the membrane fouling.

Most important characteristics of polymeric flocculants are MW and charge density (CD). High MWs are essential when the reactions are via a bridging mechanism, while flocculant aids with high CD are effective because of the neutralization reaction with DOM, which is sometimes known as an enhancer of "coagulation" [10,31]. However, charge neutralization is most probably the predominant removal mechanism of DOM molecules, because most organic matter in secondary effluent is in the form of humic substances, which are essentially anionic flocculant aids [31].

PAM and EP used in this paper are both cationic flocculant aids, which are the kind of flocculant aids most commonly used in water treatment. PAM has medium MW (105–106 Da) and CD (30%), while EP has relatively larger MW (>10^7 Da) and similar CD (30%). Because of larger MW, EP was more effective than PAM to remove DOM in terms of polymer bridging mechanism, especially for HOA with MW > 5,000 Da, which mainly comprised of humic substances with large MW. Moreover, as shown in Fig. 5, the molecular structures of PAM and EP are quite different. The structure of EP is three dimensional. This kind of structure can make the integration more tight and enhance the charge neutralization between EP molecular and the flocs or DOM in water. Therefore, the removal of DOM, including HO and HI fractions, by EP flocculation was higher than that of PAM flocculation, even though DOM and EP had similar CD values.

Hence, when choosing the coagulant and flocculant aid for pretreatment, polymer structure, MW, CD, dosage, and DOM fractions of secondary effluent should be considered since they are important factors determining the water quality of secondary effluent treated by coagulant and flocculant aid, which will influence the membrane fouling characteristics. The water quality of secondary effluent after pretreatment should be analyzed comprehensively and the final decision made seriously to achieve better performance of the membrane filtration process.

Table 2
Performance of PAM and EP for DOM removal in secondary effluent in this study[a]

Flocculant	MFF	SS	Turbidity	DOC	HO	HI	HOA	HOA with MW > 5,000 Da
PAM	+	+	++	+	++	–	++	++
EP	++	++	+++	++	+++	+	+++	+++

Notes: "–" indicates that the specific flocculant did no effect on the specific item; "+" "++" and "+++" indicate that the performance of the specific flocculant is good, better and much better in terms of the specific items.

[a] Using $FeCl_3$ as coagulant.

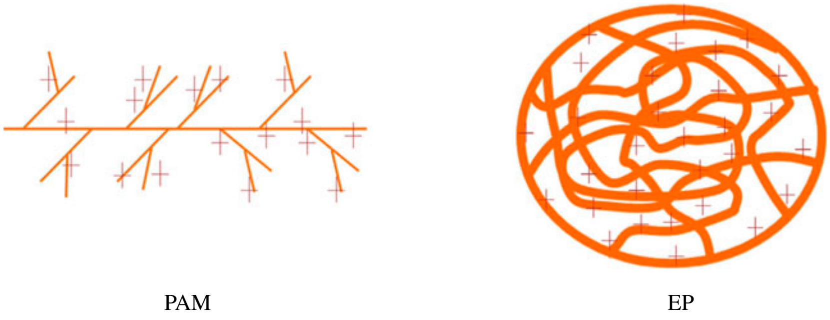

Fig. 5. Schematic diagrams for molecular structures of PAM and EP.

4. Conclusions

In this study, two kinds of flocculant aids (PAM and EP) for removal of organic matters as pretreatment of membrane filtration process were compared using $FeCl_3$ as coagulants. The following conclusions were made:

(1) EP could remove particular, colloidal material and DOM more effectively than PAM in terms of MFF, SS, turbidity, and DOC.
(2) According to the result of fingerprint analysis, EP could remove more hydrophobic fractions (HO) than PAM. Moreover, EP could remove part of hydrophilic fractions (HI), while PAM did not effect HI fractions.
(3) HOA with MW > 5,000 Da was the major subfraction removed by coagulation/flocculation and EP could remove more of it than PAM.
(4) EP was a cationic flocculant aid with larger MW and three-dimensional molecular structure, which achieved better performance in DOM removal in terms of polymer bridging mechanism and charge neutralization mechanism, respectively.

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References

[1] J. Chu, J. Chen, C. Wang, P. Fu, Wastewater reuse potential analysis: Implications for China's water resources management, Water Res. 38 (2004) 2746–2756.
[2] R. Singh, Analysis of energy usage at membrane water treatment plants, Desalin. Water Treat. 29 (2011) 63–72.
[3] M.P. del Pino, B. Durham, Wastewater reuse through dual-membrane processes: Opportunities for sustainable water resources, Desalination 124 (1999) 271–277.
[4] C. Bellona, J. Drewes, Viability of a low-pressure nanofilter in treating recycled water for water reuse applications: A pilot-scale study, Water Res. 41 (2007) 3948–3958.
[5] P.C. Kamp, J.C. Kruithof, H.C. Folmer, UF/RO treatment plant Heemskerk: From challenge to full scale application, Desalination 131 (2000) 27–35.
[6] K. Chon, S.J. Kim, J. Moon, J. Cho, Combined coagulation-disk filtration process as a pretreatment of ultrafiltration and reverse osmosis membrane for wastewater reclamation: An autopsy study of a pilot plant, Water Res. 46 (2012) 1803–1816.
[7] A.H. Johir, C. Khorshed, S. Vigneswaran, H.K. Shon, In-line flocculation–filtration as pre-treatment to reverse osmosis desalination, Desalination 247 (2009) 85–93.
[8] J.K. Edzwald, J. Haarhoff, Seawater pretreatment for reverse osmosis: Chemistry, contaminants, and coagulation, Water Res. 45 (2011) 5428–5440.
[9] H.J. Yang, H.S. Kim, Effect of coagulation on MF/UF for removal of particles as a pretreatment in seawater desalination, Desalination 247 (2009) 45–52.
[10] B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, Water Res. 41 (2007) 2301–2324.
[11] A.Y. Zahrim, C. Tizaoui, N. Hilal, Coagulation with polymers for nanofiltration pre-treatment of highly concentrated dyes: A review, Desalination 266 (2011) 1–16.
[12] S. Haydar, J.A. Aziz, Coagulation–flocculation studies of tannery wastewater using combination of alum with cationic and anionic polymers, J. Hazard. Mater. 168 (2009) 1035–1040.
[13] S.P. Chesters, E.G. Darton, S. Gallego, F.D. Vigo, The safe use of cationic flocculants with reverse osmosis membranes, Desalin. Water Treat. 6 (2009) 144–151.
[14] J. Bratby, Coagulation and Flocculation in Water and Wastewater Treatment, IWA Publishing, London, 2006.
[15] J. Kim, F.A. DiGiano, R.D. Reardon, Autopsy of high-pressure membranes to compare effectiveness of MF and UF pretreatment in water reclamation, Water Res. 42 (2008) 697–706.

[16] H. Kim, J. Choi, S. Takizawa, Comparison of initial filtration resistance by pretreatment processes in the nanofiltration for drinking water treatment, Sep. Purif. Technol. 56 (2007) 354–362.

[17] K. Chon, J. Cho, H.K. Shon, K. Chon, Advanced characterization of organic foulants of ultrafiltration and reverse osmosis from water reclamation, Desalination 301 (2012) 59–66.

[18] Y. Zhao, L. Song, S.L. Ong, Fouling of RO membranes by effluent organic matter (EfOM): Relating major components of EfOM to their characteristic fouling behaviors, J. Membr. Sci. 349 (2010) 75–82.

[19] F. Tang, H.Y. Hu, L.J. Sun, Q.Y. Wu, Y.M. Jiang, Y.T. Guan, J.J. Huang, Fouling of reverse osmosis membrane for municipal wastewater reclamation: Autopsy results from a full-scale plant, Desalination 349 (2014) 73–79.

[20] A.S. Al-Amoudi, R.W. Lovitt, Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency, J. Membr. Sci. 303 (2007) 4–28.

[21] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: Water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348.

[22] A. Matin, Z. Khan, S.M.J. Zaidi, M.C. Boyce, Biofouling in reverse osmosis membranes for seawater desalination: Phenomena and prevention, Desalination 281 (2011) 1–16.

[23] T. Nguyen, F. Roddick, L. Fan, Biofouling of water treatment membranes: A review of the underlying causes, Monit. Tech. Control Meas., Membr. 2 (2012) 804–840.

[24] Y. Taniguchi, Long-term experiences of 3.5 mgd Roga-spiral RO installation, Desalination 20 (1977) 353–364.

[25] X. Tang, Q.Y. Wu, H. Huang, H.Y. Hu, Q. Li, Removal potential of anti-estrogenic activity in secondary effluents by coagulation, Chemosphere 93 (2013) 2562–2567.

[26] X. Tang, Q.Y. Wu, X. Zhao, H. Huang, X.J. Shi, H.Y. Hu, A fingerprint analysis method for characterization of dissolved organic matter in secondary effluents of municipal wastewater treatment plant, Environ. Sci. Pollut. Res. 21 (2014) 14211–14218.

[27] J.A. Leenheer, Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters, Environ. Sci. Technol. 15 (1981) 578–587.

[28] H. Zhang, J. Qu, H. Liu, X. Zhao, Characterization of isolated fractions of dissolved organic matter from sewage treatment plant and the related disinfection by-products formation potential, J. Hazard. Mater. 164 (2009) 1433–1438.

[29] N. Voutchkov, Considerations for selection of seawater filtration pretreatment system, Desalination 261 (2010) 354–364.

[30] H.P. Chu, J.H.C. Wong, X.Y. Li, Trihalomethane formation potentials of organic pollutants in wastewater discharge, Water Sci. Technol. 46 (2002) 401–406.

[31] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: A review, Adv. Colloid Interface Sci. 159 (2010) 189–197.