Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1159991

57 (2016) 26022–26030
November

Modification of ultrafiltration membrane with iron/aluminum mixed hydrolyzed precipitate layer for humic acid fouling reduction

Yiruiwen Xie[a,b], Baiwen Ma[b], Xuehong Zhang[a,*], Huijuan Liu[b], Jiuhui Qu[b]

[a]*College of Environmental Science and Engineering, Guilin University of Technology, Guilin, Guangxi 541006, China, Tel. +86 773 3693255; emails: mine_901020@163.com (Y. Xie), zhangxuehong@x263.com (X. Zhang)*
[b]*Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China, Tel. +86 10 62918589; emails: bwma@rcees.ac.cn (B. Ma), hjliu@rcees.ac.cn (H. Liu), jhqu@rcees.ac.cn (J. Qu)*

Received 30 September 2015; Accepted 24 February 2016

ABSTRACT

Iron/aluminum mixed flocs were pre-deposited onto an ultrafiltration (UF) membrane surface to test their antifouling properties in the presence of humic acid (HA). Membranes modified with higher aluminum mole ratios in the mixture were more effective in controlling membrane fouling. Relatively strong adhesion was observed between the mixed flocs and the UF membrane used. The differences in the structure of the deposited layer were an important contributing factor for antifouling properties, which was significantly influenced by solution pH. Scanning electron microscopy showed that dense deposition layers were formed by small flocs at pH 6.0, while loose deposition layers were formed by large flocs at pH 8.0. Atomic force microscopy showed that the surface roughness of the deposition layer was much larger at pH 6.0 than that at pH 8.0. The corresponding positive charge of the mixed flocs was also higher at pH 6.0, resulting in stronger adsorption ability to the negatively charged HA molecules. These factors reduced the amount of HA getting to the membrane surface and thus helped increase membrane flux at lower pH values. In addition, HA molecules with various molecular weights were removed much faster at pH 6.0 than at pH 8.0.

Keywords: Ultrafiltration; Humic acid; Fouling reduction; Iron/aluminum mixed flocs; Pre-deposition

1. Introduction

Humic substances (HS) can form during the decomposition of plant/animal biomass in natural systems and are some of the most abundant materials on earth. The typical molecular weight (MW) of HS ranges from a few hundred to tens of thousands of daltons, depending on their different sources [1]. HS exist commonly in natural waters [2] and always cause serious environmental and health problems. The main problems are that HS can cause undesirable color and taste, and also serve as food for bacterial growth [3]. Previous studies have also demonstrated that HS can react with chlorine during water treatment to form disinfection by-products, such as trihalomethanes [4,5]. Additionally, serious microfiltration (MF)/ultrafiltration (UF) membrane fouling can

---

*Corresponding author.

be induced by HS during filtration [1,6]. Consequently, the removal of HS has been widely investigated to minimize their impact on environmental and human health.

UF membranes have been increasingly used in water treatment, due to their superior and stable permeate quality even with varied feedwater [7]. In the past 20 years, the installed capacity of UF systems has grown rapidly [8]. However, membrane fouling is inevitable, and is still the main limitation for broader application of membrane technology [9,10]. In order to reduce membrane fouling, coagulation is often used before a membrane system. Up to now, three technologies have been investigated to combine adsorption and membrane filtration: (1) pre-coagulation, in which there is a sedimentation tank after coagulation and the coagulants are pre-deposited before membrane filtration; (2) direct coagulation, in which feedwater is applied directly to a membrane system after coagulation; (3) pre-deposition, in which an adsorbent layer is pre-deposited onto a membrane surface before filtration of the solution [10,11]. The first two processes have been successfully used in many full-scale treatments, while the last has only been tested at laboratory-scale [12–14]. Compared with the pre-coagulation process, the pre-deposition process has a large advantage in terms of reducing land use because a sedimentation tank is unnecessary. When an adsorbent layer is pre-deposited onto the membrane surface, better performance has been achieved than that of the direct coagulation process to some extent. A potential reason is that pollutants cannot easily get to the membrane surface, owing to the pre-deposited layer. In addition, the pre-deposition process has been shown to have excellent results in comparison to the other two processes, and some researchers have even demonstrated much better organics removal and membrane fouling control [11,15].

So far, many different adsorbents have been pre-deposited onto membrane surfaces to test their antifouling properties, such as carbon nanotubes [13], powdered activated carbon (PAC) [16], heated iron oxide particles [17], heated aluminum oxide particles [18], nanoscale zerovalent iron [19], and so on. Although they have shown better performance in reducing membrane fouling, PAC can cause severe membrane damage, while the other adsorbents mentioned above are expensive. It is well known that iron salts and aluminum salts are widely used as coagulants in water treatment due to their strong abilities in removing pollutants and cheap price [20–23]. Compared with the adsorbents mentioned above, UF membranes pre-layered with iron/aluminum flocs performed even better in removing pollutants [13,19]. In our previous study, it was found that pre-deposited iron flocs or aluminum flocs performed better in organic matter removal and membrane fouling control, especially aluminum flocs alone [14]. However, the settling rate of aluminum flocs was relatively slow, which would cause difficulty for sludge discharge in practical operation. Furthermore, although the overall performance of the pre-deposition process has been explored in some detail as indicated above, the mechanism of its effect on membrane fouling has not been fully investigated or established.

Herein, this research focused on the effect of pre-deposited iron/aluminum mixed flocs on membrane fouling reduction, with the aim of understanding the membrane fouling characteristics induced by HS in the presence of a pre-deposited iron/aluminum mixed hydrolyzed precipitate layer. As part of this study we also identified factors responsible for determining the antifouling properties of iron/aluminum mixed flocs. Moreover, the fouling control mechanisms are also elucidated in detail.

2. Materials and methods

2.1. Materials

All chemicals were analytical reagent grade, and deionized (DI) water (Millipore, Milli-Q) was used to prepare stock solutions. Humic acid sodium salt (HA, Aldrich, USA), a representative of HS, was dissolved in DI water with a concentration of 10 g/L. HA solution was stored in a prewashed glass bottle in the dark at 4°C and was brought to room temperature immediately prior to use. Ferric chloride hydrate (0.02 M) and aluminum chloride hydrate (0.02 M) were freshly prepared before the experiments.

2.2. Ultrafiltration experiments

A polyvinylidene fluoride (PVDF, Ande membrane separation technology & engineering (Beijing) Co., Ltd, China) flat sheet UF membrane (100 kDa) was used in the experiments. All membranes used were placed in DI water for 24 h to remove impurities before use. Fresh membranes were filtered with 300 mL DI water to keep the membrane flux constant. The stirred cell (Millipore, Amicon 8400) was driven by nitrogen gas, maintained at a stable pressure of 0.1 MPa. J/J_0 was monitored in the stirred cell experiments to determine the flux variation, and J_0 was the initial membrane flux.

For the tests, the ferric chloride and/or aluminum chloride stock solutions were diluted in 300 mL DI water, in the UF stirred cell, with 0.1 M $NaHCO_3$

(3 mL) as a buffer. During the test, the final solution pH was maintained by prior addition of a predetermined amount of 0.1 M HCl or NaOH. Rapid mixing (300 rpm) lasted for 1 min while slow mixing (100 rpm) lasted for 14 min to allow floc growth to occur. The stirrer was carefully taken out and the UF cell was kept static for 20 min to allow flocs to deposit on the membrane surface. Afterward, 20 mg/L HA was prepared by adding the corresponding stock solution into the feedwater and the stirred UF cell was kept static for another 30 min to allow the HA to dissolve completely in the feed.

2.3. Jar tests

A 1.2 L beaker with a flocculator device (ZR4-2, Zhongrun, China) was used in the jar test, which enabled the mixing speed and duration to be preset. The jar test was used to provide comparative information regarding the coagulation processes under different pH conditions. During the coagulation and flocculation process, the dynamic floc size and the fractal dimension (D_f) were measured by a laser diffraction instrument (Mastersizer 2000, Malvern, UK). The rapid mixing speed of 300 rpm was maintained for 1 min, and then reduced to 100 rpm for 14 min to allow floc growth to occur. The suspension was analyzed by circulating the solution through the optical unit of the Mastersizer and was sent back into the jar by a peristaltic pump on the return tube. Size measurements were taken every 30 s for the duration of the jar test and recorded by computer. This method has been successfully applied by other researchers [24,25], and previous studies have extensively described the determination of fractal dimension of flocs using small angle-light scattering [26,27].

2.4. Other analytical methods

pH was measured by an Orion benchtop pH meter; membrane flux was recorded by a data logger. Samples after 1 min rapid mixing in the jar tests were immediately taken for zeta potential measurements by a zeta meter (Delsa Nano C, Beckman Coulter Ltd, USA). The HA concentration and corresponding peak value of the MW distribution were analyzed by gel permeation chromatography (GPC, Agilent Technologies, USA; detector: UV_{254}; TSK gel: G3000PWXL; temperature: 25℃). Images of the pre-layered membrane surface were obtained using scanning electron microscopy (SEM), which was carried out with a JSM-7401F Field Emission instrument equipped with a cold Field Emission Gun in SEI mode at 3 kV accelerating voltage (JEOL Ltd, Tokyo, Japan). The roughness of the membrane surface was measured by an atomic force microscopy (AFM, Nanoscope, IIIa, Multimode) [28].

3. Results and discussion

3.1. Effect of flocs on the filtration properties of HA

To investigate the effect of iron and/or aluminum hydrolyzed precipitate layer on antifouling properties, 20 mg/L HA was filtered with the pre-deposited membrane. The concentration curves of HA obtained during each fouling run are compared with the original HA concentration in Fig. 1. The results showed that the iron flocs alone (0.3 mM) performed worse, for which the removal efficiency of HA was only about 28.3%. With increasing aluminum mole ratio in the mixture, the residual HA concentration decreased gradually. The removal efficiency of HA was found to be 44.8, 63.7, and 77.8% for the iron/aluminum mole ratios of 4:1, 1:1 and 1:4, respectively. The maximum removal efficiency for HA was observed to be 86.5% when 0.3 mM aluminum flocs were used alone. It was clearly shown that HA molecules were mainly removed by aluminum flocs during the filtration.

With the removal of HA, the peak value of the MW distribution of HA also varied [19]. The peak value of the MW distribution of HA alone was 11,826 Da, while that was gradually reduced to 7,803 Da in the presence of 0.3 mM aluminum flocs. In comparison to iron flocs alone or iron/aluminum mixed flocs, aluminum flocs alone performed better. However, the iron/aluminum mixed flocs (mole ratio: 1:4, the same below) were chosen as the pre-deposited layer. The main reason was that the HA removal

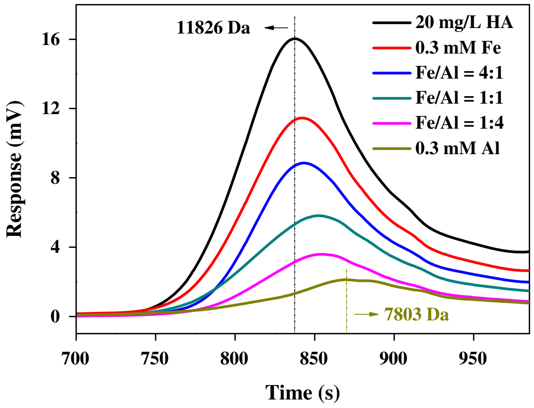

Fig. 1. Concentration and peak value of MW distribution of HA before and after filtration in the presence of flocs at pH 7.0.

efficiency was similar to that of aluminum flocs alone, but the settling rate was faster.

3.2. Iron/aluminum mixed floc adhesion to membrane

Periodic backwashing is a commonly used method for cleaning porous MF/UF membranes. Iron/aluminum mixed flocs must have strong adhesion to the membrane surface to prevent their removal during backwashing. Thus, it is necessary to investigate the ability of the mixed flocs to adhere to the UF membrane used. Here, the iron/aluminum mixed flocs layered membrane that had been fouled by 20 mg/L HA was backwashed by pushing 10 mL of permeate collected during the filtration run, at a roughly constant flowrate through the fouled modified membrane from the PVDF side. Images of the membrane surface were taken before and after backwashing. Fig. 2 shows that relatively strong adhesion was observed between the iron/aluminum mixed flocs and the PVDF UF membrane used. The modified UF membrane looked similar before and after the backwash. However, some flocs still detached from the membrane surface after backwashing. In addition, the efficiency of the flux recovering was 89 ± 5% because of the pre-layered iron/aluminum hydrolyzed precipitate layer. Therefore, further research will be focused on enhancing the adhesion properties of the iron/aluminum mixed flocs to the membrane surface and improving the backwashing efficiency.

3.3. Effect of solution pH on membrane fouling

Solution pH always plays an important role in the particle size and natural characteristics of iron flocs and aluminum flocs [29,30]. To investigate the membrane performance in detail, fouling experiments were performed at pH 6.0, 7.0 and 8.0 in the system. The HA concentration after filtration and the curves of membrane specific flux decline are presented in Fig. 3. The results showed that HA molecules were almost completely removed by iron/aluminum mixed flocs at pH 6.0. The corresponding removal efficiency of HA at pH 6.0 was 98.1%, while it was reduced to 77.8% and 52.3% at pH 7.0 and 8.0, respectively. In addition, the corresponding peak values of HA MW distribution were 6,365 Da (pH 6.0), 9,878 Da (pH 7.0), and 11,257 Da (pH 8.0).

Owing to the smaller MW of HA molecules (a few hundred daltons to tens of thousands of daltons) [1], UF membrane pores could be easily blocked by HA molecules, resulting in serious membrane fouling [1,6]. The final J/J_0 (running time: 600 s, the same below) caused by 20 mg/L HA alone was 0.23 at pH 7.0. Most HA molecules were removed by the iron/aluminum mixed flocs, resulting in less chance of HA getting to the membrane surface. Thus, membrane specific flux was significantly increased by the modification with iron/aluminum mixed flocs. The final J/J_0 was 0.79, 0.73, and 0.67 at pH 6.0, 7.0, and 8.0, respectively. In fact, flocs alone could not cause any serious membrane specific flux decline (data not shown) due to the characteristics of flocs under different pH values [14]. Compared with the membrane specific flux decline at pH 7.0 and 8.0, less decline was observed at pH 6.0 because of the higher removal efficiency of HA. Moreover, the peak value of the MW distribution of HA was reduced to 6,365 Da after filtration (Fig. 3(a)), due to the higher removal efficiency of HA at pH 6.0.

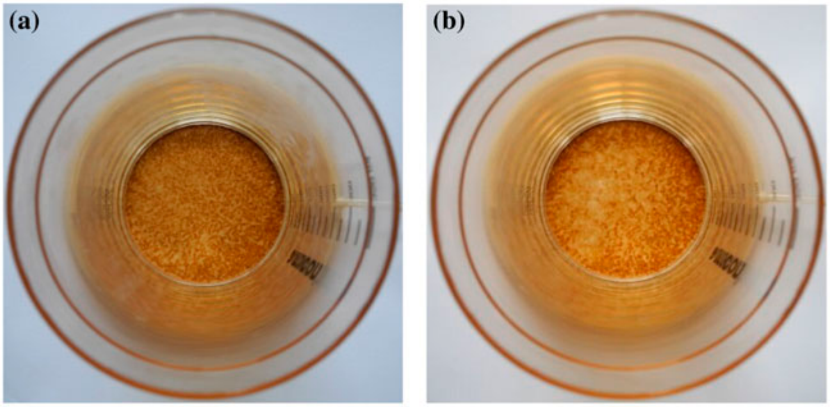

Fig. 2. Images of iron/aluminum mixed flocs layered membrane before (a) and after (b) backwashing with 10 mL permeate at pH 7.0. Other experimental conditions during the fouling runs: $M_{\text{mixed flocs}}$ = 0.3 mM and $M_{\text{iron}}/M_{\text{aluminum}}$ = 1:4.

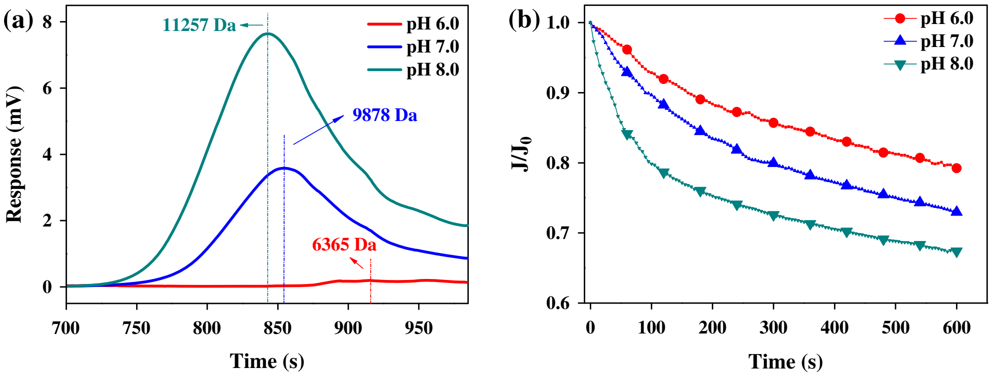

Fig. 3. Effect of solution pH on (a) concentration and peak value of MW distribution of HA and (b) membrane specific flux decline. Other experimental conditions during the fouling runs: initial HA concentration = 20 mg/L, $M_{\text{mixed flocs}}$ = 0.3 mM and $M_{\text{iron}}/M_{\text{aluminum}}$ = 1:4.

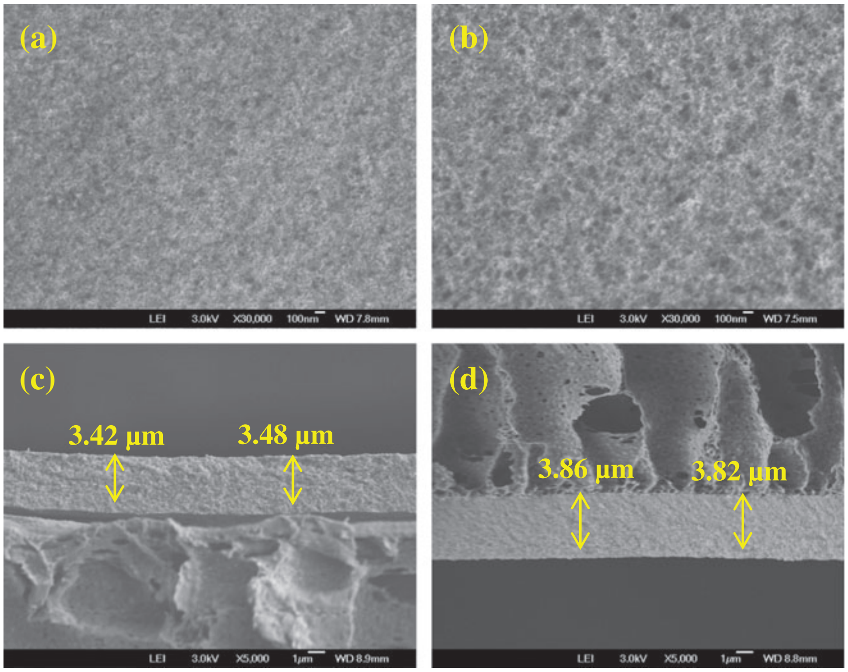

Fig. 4. Morphology of the membrane when iron/alum mixed flocs were pre-deposited under different pH conditions: (a and b) membrane surface at pH 6.0 and 8.0; (c and d) cross section at pH 6.0 and 8.0. Other experimental conditions during the fouling runs: $M_{\text{mixed flocs}}$ = 0.3 mM and $M_{\text{iron}}/M_{\text{aluminum}}$ = 1:4.

3.4. SEM and AFM imaging of mixed flocs layered membrane

To further understand the antifouling properties, SEM images were taken of membranes coated with the 1:4 mol ratio of mixed iron/aluminum flocs at pH 6.0 and 8.0 (Fig. 4). In comparison to the membrane coated with the iron/aluminum mixed flocs at pH 6.0 (Fig. 4(a)), the membrane surface morphology at pH 8.0 was much looser (Fig. 4(b)). Thus, fewer HA molecules could get to the membrane surface and less serious fouling was caused at pH 6.0. In addition, the thickness of the hydrolyzed layer was investigated at different pH values (Fig. 4(c) and (d)). It was shown that the thickness of the hydrolyzed layer was 3.45 ± 0.02 µm at pH 6.0, while it was 3.84 ± 0.02 µm at pH 8.0. Although the thickness of the hydrolyzed layer was lower at pH 6.0, the modified UF membrane performed better in removing HA. It seemed that the thickness of the hydrolyzed layer had little contribution to performance.

Compared with SEM, AFM is able to provide more information on the morphology of membrane surfaces in other aspects [28]. As shown in Fig. 5, the AFM presented a three-dimensional image of the membrane surface pre-layered with the iron/aluminum mixed flocs. A darker color represents a higher depth on the membrane surface, indicating greater roughness. The specific roughness of the modified membrane surface was 317.9 ± 43.2 nm at pH 6.0, while it was only 166.3 ± 27.5 nm at pH 8.0. Previous studies have demonstrated that pollutants were preferentially accumulated in the "valley" of a rough membrane [28,31,32], which is shown as the dark area in Fig. 5. As a result, more HA molecules could be removed by the membranes coated with the dense and rough deposition layer at pH 6.0.

3.5. Particle size of flocs and the corresponding fractal dimension

Characteristics of flocs play an important role on the performance of a cake layer [24,33–35]. To further understand the different membrane surface morphologies formed (Fig. 4), the properties of the iron/aluminum mixed flocs were investigated in detail (Fig. 6). It was found that a rapid rise in the median size (d_{50}) of flocs at pH 6.0, 7.0, and 8.0 occurred during the early flocculation period (<3 min). The d_{50} values of the flocs reached a maximum value after approximately 4 min (Fig. 6(a)). However, the d_{50} value of the iron/aluminum mixed flocs at pH 6.0 was much smaller than those at pH 7.0 and 8.0. The d_{50} values were about 45.4 ± 16.2 μm, 443.5 ± 19.6 μm, and 531.2 ± 31.7 μm for the iron/aluminum mixed flocs formed at pH 6.0, 7.0, and 8.0, respectively. Furthermore, the fractal dimension of flocs formed at pH 6.0 was 1.14 ± 0.05, which was much smaller than those at pH 7.0 (2.54 ± 0.03) and 8.0 (2.61 ± 0.07).

It is well known that flocs with larger fractal dimension will more easily form a compact cake layer after filtration [24,36]. However, Fig. 4 shows that the deposition layer was more compact at pH 6.0, for which the fractal dimension was smaller (1.14 ± 0.05). In comparison to the fractal dimension, it seemed that the particle size of flocs was the main factor dominating the properties of the deposition layer. A possible reason was that the particle size of flocs varied greatly with the forming pH, especially between pH 6.0 and 7.0.

3.6. Variation of zeta potential

Zeta potential was analyzed to show the adsorption ability of the mixed flocs toward HA molecules (Fig. 7). At pH 6.0, the zeta potential of the mixed flocs was 4.65 ± 1.02 mV, while it was reduced to 2.05 ± 0.51 mV and 1.19 ± 0.35 mV at pH 7.0 and 8.0, respectively. It has been shown that HA is negatively charged between pH 6.0 and 8.0 [37], with values of −0.43 ± 0.08 mV, −0.83 ± 0.05 mV, and −1.74 ± 0.16 mV. After coagulating with HA molecules, the corresponding zeta potentials decreased to −7.17 ± 0.56 mV, −1.85 ± 0.33 mV, and −1.23 ± 0.42 mV. The zeta potential indicated that more HA molecules were adsorbed at lower pH values due to the higher positive charge of the mixed flocs.

3.7. Removal efficiency of HA molecules of different MW

To highlight the differences in HA removal, the MW results for permeate samples under different pH conditions are shown in Fig. 8. Owing to the large

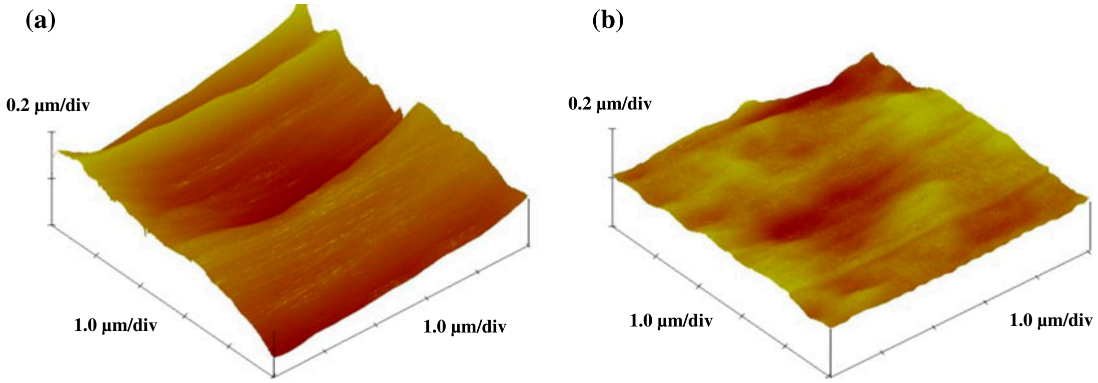

Fig. 5. Surface roughness of membrane coated with the iron/aluminum mixed flocs: (a) pH 6.0 and (b) pH 8.0. Other experimental conditions during the fouling runs: $M_{\text{mixed flocs}} = 0.3$ mM and $M_{\text{iron}}/M_{\text{aluminum}} = 1:4$.

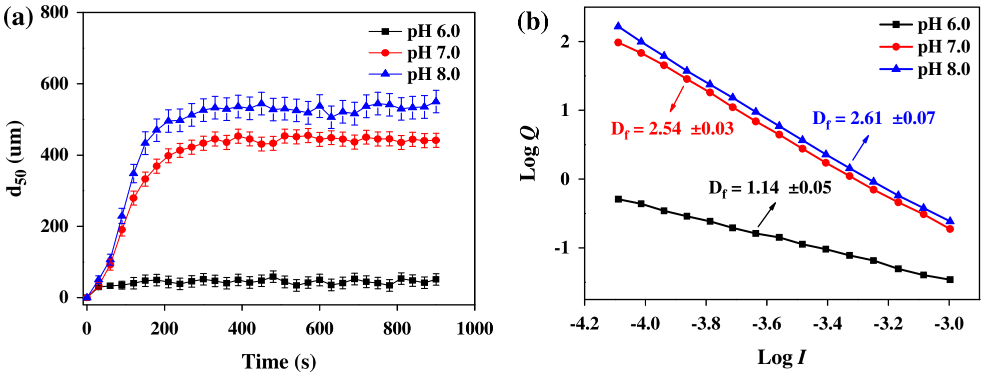

Fig. 6. Comparison of floc characteristics under different pH conditions: (a) formation of flocs and (b) fractal dimension of flocs. Other experimental conditions during the fouling runs: $M_{\text{mixed flocs}}$ = 0.3 mM and $M_{\text{iron}}/M_{\text{aluminum}}$ = 1:4.

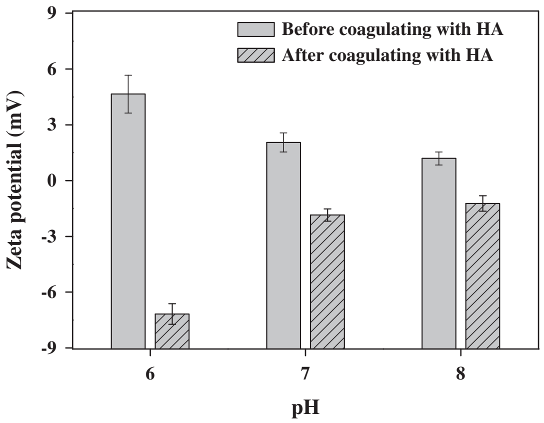

Fig. 7. Zeta potential of the iron/aluminum mixed flocs before and after coagulating with 20 mg/L HA under different pH conditions. Other experimental conditions during the fouling runs: $M_{\text{mixed flocs}}$ = 0.3 mM and $M_{\text{iron}}/M_{\text{aluminum}}$ = 1:4.

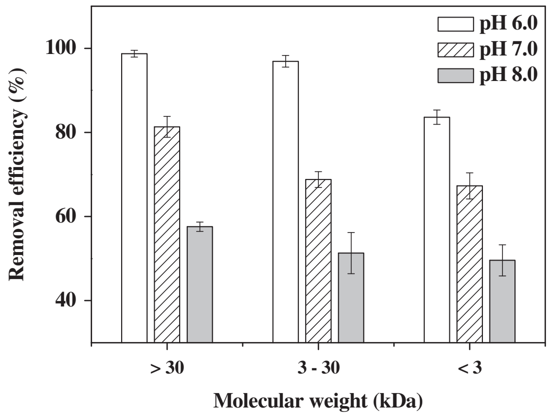

Fig. 8. Removal efficiency of different MW fractions of HA at pH 6.0, 7.0, and 8.0, respectively. Other experimental conditions during the fouling runs: $M_{\text{mixed flocs}}$ = 0.3 mM and $M_{\text{iron}}/M_{\text{aluminum}}$ = 1:4.

removal efficiency of HA at pH 6.0, HA molecules over a range of MW were also removed to a large extent. The results showed that the removal efficiency of large MW HA (>30 kDa) was 98.7 ± 0.8% at pH 6.0, while the removal efficiency of small MW HA (<3 kDa) was as high as 83.6 ± 1.7% at the same pH value. With increasing solution pH, the removal efficiencies of large MW HA (>30 kDa) decreased to 81.3 ± 2.5% and 57.6 ± 1.1% at pH 7.0 and 8.0, while the removal efficiencies of small MW HA (<3 kDa) were reduced to 67.3 ± 3.1% and 49.6 ± 3.7% at pH 7.0 and 8.0, respectively.

It has been shown that a homogeneous layer can more easily remove large MW organic matter, because some regions of the underlying membrane could be exposed in the presence of a heterogeneous layer [13,19]. Therefore, large MW HA (>30 kDa) were removed first during filtration, especially at pH 6.0. However, the removal efficiency of the small MW HA (<3 kDa) was also high at pH 6.0. With rising solution pH, the surface roughness of the deposition layer and the positive charge of flocs decreased, resulting in less HA molecules being removed. Moreover, the larger particle size of flocs, which caused a loose deposition layer, was also responsible for the lower removal efficiency of HA at pH 8.0.

4. Conclusions

Pre-deposition can mitigate membrane fouling by decreasing the chance of pollutants getting to the membrane surface. This study investigated the ability of a pre-layered membrane coated with iron/aluminum mixed flocs to reduce the fouling caused by HA. The overall findings of the study are as follows:

(1) Pre-layered membranes prepared by deposition of iron/aluminum mixed flocs have the ability to resist membrane fouling, especially with higher mole ratios of aluminum flocs in the mixture. Relatively strong adhesion was observed between the mixed flocs and the UF membrane used. HA molecules could be removed to a large extent and the corresponding peak value of the MW distribution of HA was reduced.

(2) Solution pH played an important role for the pre-layered membranes, which performed better under lower pH conditions. In comparison to fractal dimension, the particle size of the mixed flocs significantly influenced the membrane fouling properties. Additionally, the surface roughness of the deposition layer was greater and the positive charge of the mixed flocs was higher at lower pH values, resulting in more HA molecules being removed.

(3) Large MW HA molecules (>30 kDa) were relatively easily removed compared to the small MW HA molecules (<3 kDa) due to the dense and uniform deposition layer. Furthermore, small MW HA molecules could also be substantially removed at pH 6.0.

Acknowledgments

This work was supported by the State Key Program of the National Natural Science Foundation of China (51138008). Also, some of this work was supported by the Natural Science Foundation of China (41273142), and the Scientific Research and Technological Development Project of Guangxi (GuikeZhong 14124001-4).

References

[1] W. Yuan, A.L. Zydney, Humic acid fouling during microfiltration, J. Membr. Sci. 157 (1999) 1–12.

[2] Y.C. Woo, J.K. Lee, H.S. Kim, Fouling characteristics of microfiltration membranes by organic and inorganic matter and evaluation of flux recovery by chemical cleaning, Desalin. Water Treat. 52 (2014) 6920–6929.

[3] R. Bai, X. Zhang, Polypyrrole-coated granules for humic acid removal, J. Colloid Interface Sci. 243 (2001) 52–60.

[4] C. Tian, R.P. Liu, H.J. Liu, J.H. Qu, Disinfection by-products formation and precursors transformation during chlorination and chloramination of highly-polluted source water: Significance of ammonia, Water Res. 47 (2013) 5901–5910.

[5] H.C. Kim, M.J. Yu, Characterization of aquatic humic substances to DBPs formation in advanced treatment processes for conventionally treated water, J. Hazard. Mater. 143 (2007) 486–493.

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

[7] D. Jermann, W. Pronk, S. Meylan, M. Boller, Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production, Water Res. 41 (2007) 1713–1722.

[8] W.L. Ang, A.W. Mohammad, N. Hilal, C.P. Leo, A review on the applicability of integrated/hybrid membrane processes in water treatment and desalination plants, Desalination 363 (2015) 2–18.

[9] M.J.C. Báguena, S.Á. Blanco, M.C.V. Vela, Fouling mechanisms of ultrafiltration membranes fouled with whey model solutions, Desalination 360 (2015) 87–96.

[10] S.A. Gaurav, G. David, M. Kristofer, D.H. Fairbrother, J.S. Kellogg, G.J. Joseph, H.O. Huang, Modification of low pressure membranes with carbon nanotube layers for fouling control, Water Res. 46 (2012) 5645–5654.

[11] Z.X. Cai, M.M. Benjamin, NOM fractionation and fouling of low-pressure membranes in microgranular adsorptive filtration, Environ. Sci. Technol. 45 (2011) 8935–8940.

[12] A. Felder, R. Epsztein, N. Villensky, V. Gitis, Optimization of coagulation step in membrane treatment of municipal secondary effluents, Desalin. Water Treat. 35 (2011) 62–67.

[13] G.S. Ajmani, D. Goodwin, K. Marsh, D.H. Fairbrother, K.J. Schwab, J.G. Jacangelo, H.O. Huang, Modification of low pressure membranes with carbon nanotube layers for fouling control, Water Res. 64 (2011) 4634–4642.

[14] B.W. Ma, W.Z. Yu, H.J. Liu, J.B. Yao, J.H. Qu, Effect of iron/aluminum hydrolyzed precipitate layer on ultrafiltration membrane, Desalination 330 (2013) 16–21.

[15] J. Kim, Z.X. Cai, M.M. Benjamin, NOM fouling mechanisms in a hybrid adsorption/membrane system, J. Membr. Sci. 349 (2010) 35–43.

[16] Z.X. Cai, C. Wee, M.M. Benjamin, Fouling mechanisms in low-pressure membrane filtration in the presence of an adsorbent cake layer, J. Membr. Sci. 433 (2013) 32–38.

[17] M.M. Zhang, C. Li, M.M. Benjamin, Y.J. Chang, Fouling and natural organic matter removal in adsorbent/membrane systems for drinking water treatment, Environ. Sci. Technol. 37 (2003) 1663–1669.

[18] J. Kim, Z.X. Cai, M.M. Benjamin, Effects of adsorbents on membrane fouling by natural organic matter, J. Membr. Sci. 310 (2008) 356–364.

[19] B.W. Ma, W.Z. Yu, W.A. Jefferson, H.J. Liu, J.H. Qu, Modification of ultrafiltration membrane with nanoscale zerovalent iron layers for humic acid fouling reduction, Water Res. 71 (2015) 140–149.

[20] H.A. Andrianisa, A. Ito, A. Sasaki, J. Aizawa, T. Umita, Biotransformation of arsenic species by activated sludge and removal of bio-oxidised arsenate from wastewater by coagulation with ferric chloride, Water Res. 42 (2008) 4809–4817.

[21] A. Malakahmad, S.Y. Chuan, Application of response surface methodology to optimize coagulation–flocculation treatment of anaerobically digested palm oil mill effluent using alum, Desalin. Water Treat. 51 (2013) 6729–6735.

[22] G.D. Bella, M.G. Giustra, G. Freni, Optimisation of coagulation/flocculation for pre-treatment of high strength and saline wastewater: Performance analysis with different coagulant doses, Chem. Eng. J. 254 (2014) 283–292.

[23] M. Habuda-Stanić, M. Nujić, Ž. Romić, A. Lončarić, M.E. Ravancić, E. Kralj, Arsenic preoxidation and its removal from groundwater using iron coagulants, Desalin. Water Treat. 56 (2015) 2105–2113.

[24] P. Jarvis, B. Jefferson, S.A. Parsons, Breakage, regrowth, and fractal nature of natural organic matter flocs, Environ. Sci. Technol. 39 (2005) 2307–2314.

[25] W.Z. Yu, C.Z. Hu, H.J. Liu, J.H. Qu, Effect of dosage strategy on Al-humic flocs growth and re-growth, Colloids Surf., A 404 (2012) 106–111.

[26] T.D. Waite, J.K. Cleaver, J.K. Beattie, Aggregation kinetics and fractal structure of γ-alumina assemblages, J. Colloid Interface Sci. 241 (2001) 333–339.

[27] J.H. Ahn, Shedding and size distributions of suspended sediments in an urban watershed, Desalin. Water Treat. 38 (2012) 396–400.

[28] Z.X. Zhong, D.Y. Li, B.B. Zhang, W.H. Xing, Membrane surface roughness characterization and its influence on ultrafine particle adhesion, Sep. Purif. Technol. 90 (2012) 140–146.

[29] L. Wang, D.E. Giammar, Effects of pH, dissolved oxygen and aqueous ferrous iron on the adsorption of arsenic to lepidocrocite, J. Colloid Interface Sci. 448 (2015) 331–338.

[30] M. Cherifi, S. Hazourli, S. Pontvianne, J.P. Leclerc, F. Lapicque, Electrokinetic removal of aluminum from water potabilization treatment sludge, Desalination 281 (2011) 263–270.

[31] E.M. Vrijenhoek, S. Hong, M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, J. Membr. Sci. 188 (2001) 115–128.

[32] A. Weis, M.R. Bird, M. Nyström, C. Wright, The influence of morphology, hydrophobicity and charge upon the long-term performance of ultrafiltration membranes fouled with spent sulphite liquor, Desalination 175 (2005) 73–85.

[33] N. Park, B. Kwon, S.D. Kim, J. Cho, Characterizations of the colloidal and microbial organic matters with respect to membrane foulants, J. Membr. Sci. 275 (2006) 29–36.

[34] S.A. Lee, A.G. Fane, T.D. Waite, Impact of natural organic matter on floc size and structure effects in membrane filtration, Environ. Sci. Technol. 39 (2005) 6477–6486.

[35] M.H. Cho, C.H. Lee, S.H. Lee, Effect of flocculation conditions on membrane permeability in coagulation–microfiltration, Desalination 191 (2006) 386–396.

[36] W.Z. Yu, N. Graham, H.J. Liu, J.H. Qu, Comparison of $FeCl_3$ and alum pre-treatment on UF membrane fouling, Chem. Eng. J. 234 (2013) 158–165.

[37] A.B.M. Giasuddin, S.R. Kanel, H. Choi, Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal, Environ. Sci. Technol. 41 (2007) 2022–2027.