Antifouling by pre-deposited Al hydrolytic flocs on ultrafiltration membrane in the presence of humic acid and bovine serum albumin

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ABSTRACT

Pre-deposition technology is a promising method for alleviating membrane fouling, and in situ hydrolytic flocs have strong adsorption ability. In comparison with iron salts, less corrosiveness is induced by aluminum salts. Here, flocs formed by aluminum salts were pre-deposited onto the surface of an ultrafiltration (UF) membrane, aimed at investigating the antifouling performance with humic acid (HA) or bovine serum albumin (BSA). The results showed that Al-based flocs were well distributed onto the membrane surface, and a relatively dense and homogeneous deposition layer was formed. Both HA and BSA could largely be adsorbed/rejected by the pre-deposited layer during filtration. In comparison to results for solution pH of 8.0, the floc layer was much denser with a larger surface specific area and smaller average pore diameter at pH 6.0. Due to the existence of Al_{13} species, a more positively charged floc layer occurred at lower pH values, leading to stronger adsorption abilities toward the negatively charged HA and BSA molecules. The floc layer significantly reduced the possibility of HA and BSA molecules reaching the UF membrane, which helped alleviate membrane fouling under lower pH conditions. Furthermore, the results for effluent with pH between 6.0 and 8.0 showed that the removal efficiency of HA molecules with small molecular weight (< 3 kDa) was also higher, especially at pH 6.0.

1. Introduction

Ultrafiltration (UF) membranes have been applied in water treatment worldwide, due to the better effluent quality obtained even with varying feed-water properties. Membrane fouling is, however, inevitable because the membrane pores will gradually adsorb and be blocked by particles, followed by cake layer formation during filtration [1–4]. Larger molecular weight (MW) organic matter, such as humic substances and proteins, always tend to induce serious UF membrane fouling to some extent, owing to the pore blocking and cake layer formation [5–9].

To alleviate membrane fouling effectively, three membrane processes combined with adsorption technology have been investigated to remove pollutants: (1) pre-adsorption process, in which a sedimentation tank is required after adsorption and the adsorbents are deposited before the membrane system; (2) direct-filtration process, in which raw water is flowed into the membrane tank directly after adsorption; (3) pre-deposition process, in which adsorbent layers are pre-deposited onto the membrane surface before filtration [10,11].

The first two processes have been investigated in detail, and have already been applied in many water plants. However, the last process

has only been tested in the laboratory with flat sheet microfiltration/ultrafiltration membranes [12,13]. In comparison with the pre-adsorption process, the pre-deposition process further reduces land use, owing to the lack of a need for sedimentation. Additionally, serious membrane fouling is often caused when using the pre-adsorption process because of the higher chance of membrane pore blocking after the sedimentation process [14]. For the direct-filtration process, larger sludge discharge always occurs due to the lack of a sedimentation tank. Compared with the other two processes, the pre-deposition technology has demonstrated much better removal of organic compounds [11,15].

Up to now, various kinds of adsorption materials have been coated or layered onto the surface of membranes to investigate their adsorption/rejection properties with various target pollutants, and less membrane fouling was indeed observed. However, the use of powdered activated carbon (PAC) alone could cause severe membrane damage by shearing the membrane surface, especially after long running time [16], while the high cost of other adsorbents prohibited their use in actual operations, for example carbon nanotubes (CNTs) [13], heated iron oxide particles (HIOPs) [17], heated aluminum oxide particles (HAOPs) [18], nanoscale zerovalent iron (NZVI) [19], and so on. In addition, some adsorbents were found to exhibit preferential removal ability

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toward specific pollutants, while performing worse on removal of other types. It has been demonstrated that PAC preferentially adsorbs many non-fouling natural organic matter (NOM) molecules during filtration [18].

It is known that aluminum salts and iron salts have been successfully used in drinking water and wastewater treatment, and their favorable performance is due to the strong adsorption capability of their flocs [20–22]. For the combined process of coagulation and UF membrane, Al-based and Fe-based flocs have been shown to play an important role in alleviating membrane fouling [7,14,22]. In comparison to iron salts, however, aluminum salts have lower corrosiveness in water treatment [22,23]. In addition, humic substances and proteins are formed by the decomposition of plants/animals and are commonly present in natural waters [7,24,25]. The concentration of humic substances and proteins are in the range of a few mg/L to a few hundred mg/L C [26,27]. Owing to their large molecular weight distributions and physical properties, severe UF membrane fouling is inevitably induced [19,28,29]. Herein, this study focuses on an UF membrane with pre-deposited Al-based flocs, aiming to understand the characteristics of membrane fouling caused by humic substances and proteins. Furthermore, some influencing factors were also investigated, such as dosage and solution pH, and the membrane fouling alleviation mechanisms were elucidated finally.

2. Materials and methods

2.1. Chemical reagents

All chemicals used were analytical reagent grade unless otherwise specified, and the stock solutions were prepared using deionized (DI) water (Millipore, Milli-Q). Humic acid sodium salt (HA, Aldrich, USA) is typically used to represent HS [6,19], and was stored in the dark at 4 °C (10 g/L). Bovine serum albumin (BSA, Sinopharm Chemical Reagent, Co., Ltd, China; 67 kDa) is usually used as a representative of protein [30]. It was dissolved in a phosphate-buffered salt solution (PBS, composed of 0.03 M $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and 0.03 M KH_2PO_4) and was used within 8 h [31]. The concentration of BSA stock solution was also 10 g/L, and 0.02 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution was freshly prepared each time.

2.2. UF membrane process

A polyvinylidene fluoride (PVDF) flat sheet UF membrane was used with a molecular weight cut-off (MWCO) of 100 kDa. The membranes were obtained from Tianjin Motimo Membrane Tech. Co., Ltd, China. All membranes were firstly immersed in DI water for 24 h, and the water was changed three times. To keep membrane flux constant, fresh

membranes were firstly filtrated with DI water (300 mL). The Millipore UF stirred cell (Amicon 8400, USA) was driven by N_2 , which was maintained at 0.1 MPa during filtration.

For the tests, the aluminum solution was diluted by DI water to the specific concentration with NaHCO_3 (0.1 M, 3 mL) as buffer. The final solution pH was determined by prior addition of a corresponding amount of HCl or NaOH (0.1 M). In order to form flocs gradually, the rapid mixing of 300 rpm lasted for 1 min, while the slow mixing of 100 rpm lasted for 14 min. Afterward, the stirrer was taken out carefully, and the UF cell was maintained under static conditions to let the Al-based flocs settle naturally (20 min), forming a homogeneous layer on the membrane surface. Finally, the corresponding HA or BSA stock solution was added into the aforementioned water, and allowed to dissolve completely by keeping the cell static for 30 min.

2.3. Floc size measurement

A beaker (1.0 L) with a flocculator device was used in the jar tests without HA or BSA. 300 rpm (rapid mixing) was maintained for 1 min, followed by decreasing the speed to 100 rpm for another 14 min to allow flocs to grow. The properties of flocs were measured by a laser particle size analyzer (Mastersizer 2000, Malvern, UK) during the coagulation process, including particle size and fractal dimension (D_f). The particle size of flocs was automatically recorded by computer every 0.5 min. Fractal dimension was measured by using small angle-light scattering [32,33], which has been successfully used in previous studies [34,35]. Moreover, the specific surface area of the Al-based flocs was analyzed by the Brunauer-Emmett-Teller method (BET, ASAP2020HD88).

2.4. Other measurement methods

An Orion pH meter (USA) was used to measure the solution pH; The variation of membrane flux as a function of time was recorded by computer; The zeta potential was analyzed by a Malvern Zetasizer 2000 (UK); The concentration of HA or BSA and the MW distributions were measured by gel permeation chromatography (GPC, Agilent Technologies, USA); The morphology of the membrane surface was measured by scanning electron microscopy (SEM, JEOL Ltd., Tokyo, Japan). The average pore size of the pre-layered membrane was analyzed by ImageJ software, which measured the apparent pore size on the surface (without considering the 3-dimensional structure of the membrane and Al-based floc layer) [13].

Fig. 1. Concentration of (a) HA or (b) BSA for membrane with pre-deposited flocs formed by different doses of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at pH 7.0. The original concentration of HA or BSA was 20 mg/L.

Fig. 2. Membrane specific flux caused by HA or BSA for membrane with pre-deposited flocs formed by different doses of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at pH 7.0: (a) 20 mg/L HA; (b) 20 mg/L BSA.

Fig. 3. Variation of the concentration and peak value with flocs formed by 0.3 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in effluent under different pH conditions: (a) 20 mg/L HA; (b) 20 mg/L BSA.

3. Results

3.1. Effect of floc dosage and backwashing

To investigate the removal properties, different dosages of flocs were deposited onto the UF membrane surface. The variations of HA or BSA concentrations before and after filtration are shown in Fig. 1. The results showed that the concentration of HA or BSA in the effluent gradually decreased with increasing dose of flocs. The removal rate of HA was 20.3% when there were no flocs deposited onto the membrane surface, while the rate increased to 73.2%, 91.2%, 95.1% and 96.5% in the presence of flocs formed by 0.1, 0.3, 0.9 and 1.5 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, respectively. For BSA, however, 29.8% was removed by the UF membrane alone. When flocs were pre-layered onto the UF membrane surface, the removal efficiency of BSA was 60.7%, 76.3%, 78.8% and 82.4% in the presence of flocs formed by 0.1, 0.3, 0.9 and 1.5 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Fig. 1 clearly shows that both HA and BSA molecules were largely removed by the pre-deposited membrane, especially the wide MW range HA molecules.

With the removal of HA or BSA by the pre-deposited flocs during filtration, the corresponding membrane specific flux increased (Fig. 2). For comparison, the membrane specific flux induced by HA or BSA was investigated in the absence of flocs at pH 7.0. The results showed that the final membrane specific flux (600 s, similarly hereinafter) induced by 20 mg/L HA or BSA was 0.23 or 0.52. For HA, however, the final membrane specific fluxes increased to 0.61, 0.71, 0.73 and 0.64 in the presence of flocs formed by 0.1, 0.3, 0.9 and 1.5 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. For BSA, the corresponding final membrane specific fluxes increased to 0.74, 0.78, 0.70 and 0.67, respectively. Although both the membrane specific fluxes improved, pre-deposited Al-based flocs could alleviate

membrane fouling better in the presence of HA. As seen from Fig. 1, the final membrane specific flux increased 0.48 for HA with flocs formed by 0.3 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, and only increased 0.26 for BSA.

In addition, backwashing is one of the main running conditions, and the “dynamic” pre-layered membrane was investigated by pushing 10 mL permeate at a roughly flowrate after filtering half feed water. Fig. S1 shows that little variation was observed before and after backwashing in the presence of 0.3 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and 20 mg/L HA at pH 7.0. The possible reason was due to the strong adhesion force between the pre-layered floc layer and the UF membrane. Similar results have been observed in previous studies [13,19].

3.2. Effect of solution pH

Characteristics of flocs were significantly influenced by solution pH [36,37]. To understand the properties of membrane fouling under different pH conditions, fouling experiments were investigated between pH 6.0 and 8.0 when flocs were formed by 0.3 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (similarly hereinafter). Fig. 3 presents the variation of the concentration and the corresponding peak values as a function of pH. The removal rate of HA was 98.9% at pH 6.0, while the rates were gradually reduced to 91.2% and 64.2% at pH 7.0 and 8.0, respectively. For BSA, however, the removal rates were 95.8%, 76.3% and 62.7% at pH 6.0, 7.0 and 8.0.

With the rejection of HA or BSA, the MW distribution peak values in effluent decreased. The peak values of HA and BSA molecules alone were 11,826 Da and 66,496 Da. After filtration, the values were reduced to 5779, 9859 and 10,911 Da for HA at pH 6.0, 7.0 and 8.0. Compared with HA, less variation occurred regarding the peak values of the BSA MW distribution in effluent, which were 63943, 64,684 and 64,684 Da at pH 6.0, 7.0 and 8.0.

Fig. 4. Membrane specific flux for pre-deposited flocs formed by 0.3 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ under different pH conditions: (a) 20 mg/L HA; (b) 20 mg/L BSA.

As seen from Fig. 3, both HA and BSA molecules were largely removed at pH 6.0, resulting in less possibility of HA or BSA molecules reaching the UF membrane. Thus, less serious membrane fouling occurred (Fig. 4). For HA, the final membrane specific fluxes were 0.79, 0.71 and 0.65 at pH 6.0, 7.0 and 8.0. For BSA, the final membrane specific fluxes were 0.81, 0.78 and 0.73 at pH 6.0, 7.0 and 8.0, respectively. The membrane specific flux induced by 20 mg/L HA or BSA was 0.23 and 0.52 (pH 7.0), indicating that the pre-deposited flocs could improve membrane specific flux more for HA in comparison to BSA.

3.3. HA MW fraction in effluent

A previous study showed that the HA MW distribution ranges from a few thousands to hundreds of thousands of Daltons [6]. As seen in Figs. 1a and 3a, a higher removal rate of HA occurred, and the corresponding peak value was also dramatically changed. To investigate the properties of HA removal, the MW results in effluent as a function of pH were investigated and are shown in Fig. 5.

In contrast, the results from the original PVDF membrane are shown at pH 7.0. Fig. 1a shows that the removal rate of HA by the membrane alone was only 20.3%. The removal rate of HA molecules with large MW (> 30 kDa) was $37.2\% \pm 2.3\%$, while the removal rates of HA molecules with medium MW (3–30 kDa) and small MW (< 3 kDa) were $17.8\% \pm 1.2\%$ and $5.9\% \pm 0.7\%$, respectively. However, as seen from Figs. 1a and 3a, the deposited layer provided a large advantage in removing/rejecting HA molecules, especially in acidic solution. For pH 6.0, The specific removal rate of HA molecules with large MW (> 30 kDa) was $99.4\% \pm 0.9\%$, and the removal rates of HA molecules

with medium MW (3–30 kDa) and small MW (< 3 kDa) were $99.1\% \pm 1.1\%$ and $98.2\% \pm 0.6\%$, respectively. With rising solution pH, relatively fewer HA molecules were removed by the floc layer. Therefore, the removal rate of HA molecules with large MW (> 30 kDa) was reduced to $79.4\% \pm 5.6\%$ at pH 8.0, while the rates for medium MW (3–30 kDa) and small MW (< 3 kDa) were reduced to $67.3\% \pm 4.8\%$ and $45.9\% \pm 4.1\%$. Fig. 5 clearly shows that different MW distribution HA molecules were largely removed at pH 6.0.

Because the properties of flocs were significantly influenced by solution pH, the removal rates of HA molecules with different MW distributions also varied. Compared with pH 8.0, smaller differences were observed in the removal rate between large MW HA molecules (> 30 kDa) and small MW HA molecules (< 3 kDa) at pH 6.0. The difference in the removal rate regarding the large MW HA molecules (> 30 kDa) and small MW HA molecules (< 3 kDa) was only 1.2% at pH 6.0, and was significantly higher at 33.5% at pH 8.0.

4. Discussion

It has been reported that serious fouling is caused by pore blocking for porous UF membranes [38]. Owing to the variation in the HA MW distribution [6], severe fouling was always induced during filtration. The BSA used was electrophoresis pure and its molecular weight was about 67 kDa, which was smaller than the membrane pores (100 kDa). Thus, most BSA molecules passed through the membrane pores, causing less severe membrane fouling.

When flocs formed by Al hydrolysis were pre-deposited onto the membrane surface, HA and BSA molecules could be removed by the pre-deposited layer. It has been demonstrated that homogeneous deposition layers always perform better due to the UF membrane being more exposed to the solution with a heterogeneous layer [13]. The surface morphology of the virgin and pre-deposited membranes was investigated in the presence of brown HA (Fig. 6; morphology of the colorless BSA is not shown in the absence/presence of the pre-deposition layer). As seen from Fig. 6a and b, homogeneous aluminum floc deposition layers were formed at pH 7.0. Thus, HA and BSA molecules could largely be removed in the presence of flocs, especially with the much denser pre-deposited layer formed at pH 6.0 (Fig. S2). With increasing floc dosage, the pre-deposited layer became thicker, leading to more HA and BSA molecules being adsorbed/rejected. Owing to the different properties of HA and BSA, the removal efficiency of HA was higher (Fig. 1), and will be discussed later.

Fig. S3 shows that the membrane fouling induced by flocs alone was more severe with a larger dose of flocs at pH 7.0. Therefore, the membrane specific flux induced by HA or BSA increased first and decreased thereafter with increased floc dosage (Fig. 2), even though more HA or BSA molecules were rejected. On the other hand, Fig. 1 shows that more HA molecules were removed than BSA molecules. As a

Fig. 5. Removal rate of different molecular weight HA molecules with flocs formed by 0.3 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at pH 6.0, 7.0 and 8.0.

Fig. 6. Morphology of membrane surface at pH 7.0: (a) after filtration with 20 mg/L HA; (b) after filtration with 20 mg/L HA with pre-layered flocs formed by 0.3 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.

Fig. 7. SEM of the floc layer formed by 0.3 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at: (a) pH 6.0; (b) pH 8.0.

Fig. 8. Characteristics of flocs formed by 0.3 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at pH 6.0, 7.0 and 8.0: (a) particle size; (b) fractal dimension.

result, the pre-deposited membrane performed much better in the presence of HA (Fig. 2).

SEM of the pre-coated membrane surface was investigated to further understand the specific properties of the pre-deposited layer (Fig. 7). It was observed that relatively uniform deposition layers were formed on the membrane surface under different pH conditions (Fig. 7a and b). However, the pre-deposited layer formed at pH 6.0 was a little denser than that formed at pH 8.0. The average pore diameter of the pre-deposited layer was 9.47 ± 0.18 nm at pH 6.0, while it increased to 11.36 ± 0.07 nm at pH 8.0. Therefore, the chance of rejecting HA or BSA molecules was higher under lower pH conditions, especially the large MW HA molecules (> 30 kDa).

Solution pH significantly influenced the morphology of the pre-coated membrane surface [36,37]. As shown in Fig. 8, the median size (d_{50}) of flocs rapidly increased during the early coagulation period (< 4 min) at pH 6.0, 7.0 and 8.0. The d_{50} value increased to a maximum value after 5 min. However, it can be seen that the d_{50} value at lower pH values was much smaller compared to that at higher pH values. The specific d_{50} value of the flocs was 60.3 ± 10.2 μm at pH 6.0, while it was 422.3 ± 23.1 μm at pH 8.0. The floc fractal dimension was 2.45 ± 0.21 at pH 8.0, which was larger than that at pH 6.0 (1.98 ± 0.09). Although larger fractal dimension flocs were more easily compressed [39,40], the morphology of the membrane surface was denser at pH 6.0 (Fig. 7a). A potential reason for the difference at pH

Fig. 9. Zeta potential of flocs formed by 0.3 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ before and after coagulation with HA (20 mg/L) or BSA (20 mg/L) under different pH conditions.

6.0 might be due to the much smaller particle size flocs, which were roughly one seventh the particle size of the flocs at pH 8.0. In fact, the smaller floc particle size also led to larger specific surface area, which was $297.1 \pm 28.3 \text{ m}^2/\text{g}$ at pH 6.0, and $247.6 \pm 19.8 \text{ m}^2/\text{g}$ at pH 8.0. All the aforementioned characteristics of the pre-deposited layer indicated a larger adsorption/rejection ability at pH 6.0, despite the relatively thin layer formed (Fig. S4).

The adsorption ability of flocs was also analyzed to understand the fouling mechanism in detail (Fig. 9). A previous study demonstrated that the flocs formed by $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at pH 6.0 contained in-situ formed positively charged Al_{13} polymer ($[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$), and these flocs exhibited higher adsorption ability [41]. The zeta potentials of flocs alone were $7.03 \pm 0.14 \text{ mV}$ (pH 6.0), $2.52 \pm 0.21 \text{ mV}$ (pH 7.0) and $0.31 \pm 0.16 \text{ mV}$ (pH 8.0). It was determined that both HA and BSA molecules were negatively charged between pH 6.0 and pH 8.0. The corresponding zeta potentials of HA were -0.43 ± 0.08 , -0.83 ± 0.05 and $-1.74 \pm 0.16 \text{ mV}$ at pH 6.0, 7.0 and 8.0. The corresponding zeta potentials of BSA were -0.33 ± 0.06 , -0.58 ± 0.19 and $-1.12 \pm 0.15 \text{ mV}$ at pH 6.0, 7.0 and 8.0, respectively. Therefore, more HA or BSA molecules were adsorbed by the flocs under lower pH conditions, especially more negative HA molecules (Fig. 9). Additionally, it has been found that HA molecules could make fuller use of the active adsorption sites of flocs in comparison to BSA molecules, due to the wide MW distribution [7]. Thus, the pre-deposited layer alleviated the membrane fouling induced by HA better compared to that of BSA under different pH conditions (Figs. 1 and 4).

Regarding the removal rate of HA molecules, the UF membrane alone could not reject HA molecules effectively because of the large membrane pore diameter (100 kDa). When Al-based flocs were pre-layered onto the UF membrane surface, large MW HA molecules ($> 30 \text{ kDa}$) and medium MW HA molecules (3–30 kDa) were easily removed because of the dense pre-deposited layer, leading to higher removal efficiency. However, the floc layer was relatively dense and electropositive, leading to more small MW HA molecules being ($< 3 \text{ kDa}$) removed, especially at pH 6.0.

Based on the foregoing observations, the properties of the floc layer played an important role in the UF membrane performance. The larger the dose of Al-based flocs, the thicker the layer and higher removal efficiency induced. For the same total amount of flocs, the characteristics of the pre-deposited layer played an important role in the higher removal efficiency, such as the properties of density and uniformity. The larger specific surface area and higher positive zeta potentials of the pre-deposited layer were also key factors in removing HA and BSA molecules. Owing to the more negatively charged and wide MW range HA molecules, the corresponding removal rate was higher than that of BSA molecules. The specific schematic diagram of the pre-deposited membrane removing pollutants and resisting membrane fouling is illustrated in Fig. 10.

Although HA and BSA molecules could be largely removed by the pre-deposited layer, they would break through and membrane fouling could still be serious when the concentration of HA or BSA was higher than the maximum adsorption capacity. To fully understand the antifouling properties of the pre-deposited UF membrane, further research will be focused on hollow fiber UF membranes to investigate the practicability at pilot scale, in which the flocs are suspended in the membrane tank with aeration from the bottom.

5. Conclusions

Aluminum salts have been successfully applied in water treatment, and pre-deposition technology is a promising method for alleviation of membrane fouling. This study focused on the performance of membranes with pre-deposited in situ flocs formed by aluminum salts in the presence of humic substances or proteins. The overall findings are as follows:

1. Al-based flocs were well distributed onto the membrane surface, and had strong adsorption/rejection abilities, resulting in significant alleviation of membrane fouling. With increased pre-deposited floc dosage, the pre-deposited layer was thicker and higher removal

Fig. 10. Schematic diagram of the removal of HA and BSA by the pre-deposited layer under different pH conditions.

efficiency was induced.

2. Solution pH significantly influenced the properties of the pre-deposited layer. Owing to the smaller floc size under lower pH conditions, a denser deposition layer was formed with larger specific surface area. Additionally, the corresponding pre-deposited layer had a higher positive charge and smaller pore diameter, all of which indicated stronger adsorption abilities.
3. HA molecules with large MW (> 30 kDa) were much more easily rejected by the pre-layered flocs. In comparison to the removal rate of HA molecules with large MW (> 30 kDa), the removal rate of small MW HA molecules (< 3 kDa) was also higher, especially under lower pH conditions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2017.05.029>.

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