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Effect of low dosage of coagulant on the ultrafiltration membrane performance in feedwater treatment

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ABSTRACT

One of the critical issues for the widely application of ultrafiltration (UF) in water treatment is membrane fouling owing to the dissolved organic matter. The aim of the present study is to explore the effect of various particle sizes caused by low dosages of coagulant with dissolved organic matter on the UF membrane performance. Aluminum chloride was added to the synthetic water with the hydrophobic humic acid (HA), the hydrophilic bovine serum albumin (BSA) – a protein- and their 1:1 (mass ratio) mixture. The results showed that there was a critical dose of Al that could cause dramatic flux reduction by blocking the membrane pores after coagulating with HA/BSA. For HA or BSA, the critical dose of Al was relatively lower at pH 6.0 than that at pH 8.0. After coagulation, the flux decline caused by HA was slightly varied as a function of pH while that caused by BSA was greatly affected by pH. The flux decline caused by the 1:1 (mass ratio) HA/BSA mixture after coagulation was similar to that caused by HA after coagulation because BSA could be encapsulated by HA. In addition, the peak value of the molecular weight (MW) distribution of HA coagulated with Al was changed more drastically compared to that of BSA after filtration.

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1. Introduction

Ultrafiltration (UF) membrane has been widely used in drinking water treatment due to its excellent properties, such as removing a variety of waterborne viruses and much of the dissolved organic matter, etc. (Kimura et al., 2004; Jermann et al., 2007; Porcelli and Judd, 2010). However, a major impediment in the application of UF membrane technology is membrane fouling. The UF membrane could be polluted by three different ways: pore constriction, pore blocking and cake

layer (Jucker and Clark, 1994; Yuan and Zydney, 1999; Aoustin et al., 2001; Katsoufidou et al., 2007). The occurrence of different mechanisms of membrane fouling is related to particle size relative to membrane pore size (Huang et al., 2008) and other influence factors (Maximous et al., 2009; Katsoufidou et al., 2010; Masatoshi et al., 2011). The particle sizes which are close to the diameter of membrane pores can cause pore blocking, resulting in the most severe membrane fouling.

There are many different substances which co-exist in the complex natural water. Now more and more studies have

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focused on two or more contaminants in the solution, and some different pollution mechanisms have really been found compared to only one single pollutant in feed water (Jermann et al., 2007; Katsoufidou et al., 2010; Zazouli et al., 2010). Humic acid (HA) and bovine serum albumin (BSA) are used as model contaminants for their widely application in many studies (Tang and Leckie, 2007; Mo et al., 2008; Listiarini et al., 2009; She et al., 2009; Huber et al., 2011; Wang and Tang, 2011).

Coagulation remains the most common process to remove turbidity and nature organic matter (NOM) in water treatment, and Al/Fe salts are widely used as coagulants for pretreatment (Shon et al., 2004, 2005; Lee et al., 2009; Wang et al., 2009). Al-based or Fe-based salts could form a series of cationic hydrolytic species and weakly charged or uncharged precipitates after reacting with water (Stumm and Morgan, 1996; O'Melia, 1998). Al-Malack and Anderson (1996) determined the optimal coagulation conditions for wastewater which was 200 mg/L FeCl_3 at pH 9.0, and the chemical oxygen demand (COD) removal efficiency by this optimal dose of FeCl_3 was about 99.3%. Aguiar et al. (1996) found that the optimal dose of coagulant was 2.1 ± 0.2 mg Fe per mg of total organic carbon (TOC). In recent years, some studies have focused on finding an optimal dose in order to dramatically reduce the membrane fouling in the downstream treatment of membrane filtration. Tran et al. (2006) found that a specified dose of Al which could remove dissolved organic carbon (DOC) effectively also reduced the polyvinylidene fluoride (PVDF) micro-filtration (MF) membrane fouling. Lee et al. (2009) reported that there was an optimal PACl dosage with respect to fouling minimization, depending on the specific characteristics of wastewater. The optimal PACl dose was shifted to a higher level with increasing the ionic strength. They found that 0.0371 mM PACl (calculated as Al) was needed to achieve the highest UF membrane flux with a low ionic strength (546 $\mu\text{S}/\text{cm}$) while approximately 0.5 mM PACl could achieve the maximal flux when the ionic strength was much higher (2390 $\mu\text{S}/\text{cm}$). According to the results presented by Shon et al. (2005), there was an optimal dose of FeCl_3 which did not cause any flux decline during the whole operation of UF in 6 h. Finally they showed that at least 50 mg/L FeCl_3 was found to be necessary to avoid any significant flux decline and to obtain a better DOC removal efficiency. Up to now, more and more studies are focused on finding an optimal dose of coagulant to reduce the membrane fouling in the downstream treatment. However, few have been paid attention to the phenomenon that whether the membrane will be fully blocked by a critical dose of coagulant or not. Herein the key issue that we concern about is to know the membrane flux decline induced by the various particle sizes formed by HA/BSA coagulated with low dosages of Al.

This research focuses on the fouling mechanism of UF membrane at the low dosage coagulant. It aims at: (1) whether there is a critical dose of Al that can cause membrane flux reduce significantly or even fully block the membrane pores as a function of time, pH, etc. after coagulating with the hydrophobic HA or the hydrophilic BSA; if there is, then, (2) whether the critical dose of Al would be different for HA or BSA; and (3) what the critical dose of Al would be if the feed water is mixed by HA and BSA.

2. Materials and methods

2.1. Chemical reagents and materials

All chemicals were analytical reagent except for specific illustration and the deionized (DI) water was used for preparation of all stock solutions and membrane performance experiments. pH was adjusted by 0.1 M HCl or 0.1 M NaOH by pre-determined. Humic acids, sodium salt (HA, Aldrich, USA) was dissolved by DI water while BSA (Electrophoresis Pure, Sinopharm Chemical Reagent Co., Ltd, China) was dissolved by solutions of 0.15 M ionic strength phosphate buffered salt (Sean et al., 1993). Stock solutions of HA and BSA at a total concentration of 10 g/L were prepared. BSA working solutions were used within two days (Sean et al., 1993). Aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, calculated as Al) was used as coagulant here and the stock concentration was 0.1 M. Working solutions were stored in the dark at 4 °C and all experiments were repeated for 2 or 3 times.

2.2. UF experiments

The UF membrane (PVDF) was used here with nominal molecular weight cutoff of 100 kDa. Each membrane was placed in DI water for at least 24 h to remove impurities and production residues. Immediately before the stirred cell test the DI water flux of the membrane was determined by filtering DI water through the membrane until reached a stable permeate flux. Normalized flux J/J_0 as a function of time was shown for the flux decline results from the stirred cell experiments, and J_0 was the initial membrane flux. Using UF stirred cell (Milipore, Amicon 8400) and keeping the pressure stable (0.1 MPa) by nitrogen gas, the fouling characteristics of the flat sheet UF membrane were studied by filtering dilute HA and BSA in the presence of different doses of Al in feed solution.

For the tests, the aluminum chloride stock solution was diluted in DI water (300 ml), in the UF stirred cell, with 0.1 M NaHCO_3 to give test solution. During the test, the pH of final solution was maintained by prior addition of a predetermined amount of 0.1 M NaOH or 0.1 M HCl. Afterward 10 ppm HA, 1:1_{ratio} 5 ppm HA/BSA mixture or 10 ppm BSA were formed by adding the corresponding stock solution to the feed water. Rapid mixing (250 rpm) lasted for 1 min while slow mixing (100 rpm) lasted for 14 min to allow floc growth to occur and taking out the stirrer carefully finally.

2.3. Analytical methods

pH was measured by Orion pH Benchtop; Variation of UF membrane flux as a function of time was recorded by data logger; Molecular weight distribution was determined by Gel Permeation Chromatography (GPC, Agilent Technologies, USA; Detector: UV₂₅₄; Column: TSK; Temperature: 25 °C); Particle size was measured by Zeta Sizer (Malvern Instrument, Nano Series, Nano-ZS, Model: ZEN3600); Ultrafiltration membrane pore size was analyzed by IB-FT, GmbH (POROLUX 1000, Germany).

3. Results

3.1. Flux decline caused by the critical dose of Al

In order to investigate whether there was a critical dose of Al that would cause the membrane flux decline significantly as a function of time after coagulating with HA or BSA, different low doses of Al were added to the feed water at pH 7.0 with 10 ppm HA, 1:1_{ratio} 5 ppm HA/BSA mixture or 10 ppm BSA, respectively. For HA, 1:1_{ratio} 5 ppm HA/BSA and BSA, their J/J_0 values reduced firstly and then increased with increasing the dose of Al (Fig. 1). It clearly showed that there was indeed a critical dose of Al that could cause the flux reduce dramatically after coagulation, especially for BSA. Ye et al. (2005a,b; 2006) found that membrane flux decline was induced by pore constriction in a short time, and by cake layer over a long period of time. In fact, the critical dose of Al was a boundary point, which meant that the main flux decline was caused by adsorption when the dose of Al was lower than the critical dose, and that was caused by cake layer when the dose of Al was higher than the critical dose. Compared to the flux decline caused by HA after coagulation with Al, the flux decline caused by BSA after coagulation was much more significant. Fig. 1 showed the minimal J/J_0 value caused by HA coagulated with Al was about 0.64 while that caused by BSA after coagulation was about 0.36. The wide MW distribution of HA (Yuan and Zydney, 1999) inferred that it was difficult to reach a particle size which could cause serious flux decline compared to that of BSA, of which the MW distribution was relatively much narrow (electrophoresis pure).

Studies have demonstrated that protein could be encapsulated by humic substances (HS) because of the protein-HS electrostatic attraction (Knicker and Hatcher, 1997; Zang et al., 2000; Hsu and Hatcher, 2005, 2006; Tan et al., 2008; Tan et al.,

2009). Thus, the J/J_0 value caused by 1:1_{ratio} 5 ppm HA/BSA mixture was similar to that caused by HA after coagulation. However, things would be different when there was little HA in the mixture solution because more BSA molecules were free.

3.2. Critical dose influenced by pH

To know exactly whether the pH of the feed water could inference the critical dose of Al or not, fouling experiments were performed with solutions at pH 6.0, 7.0 and 8.0 (Figs. 1 and 2). It was presented that the flux declines caused by HA or 1:1_{ratio} 5 ppm HA/BSA mixture were almost the same after coagulation. However, the membrane flux decline caused by BSA after coagulation was much more serious than those caused by HA or 1:1_{ratio} 5 ppm HA/BSA mixture after coagulation. The flux decline caused by BSA coagulated with Al at pH 6.0 ($J/J_0 = 0.24$) or 7.0 ($J/J_0 = 0.46$) was smaller than that at pH 8.0 ($J/J_0 = 0.66$). Palacio et al. (2003) have demonstrated that BSA always polluted the membrane by internal pollution, and Al species were not the same as a function of pH which would form various particle sizes (Wanget al., 2008). Therefore, the minimal J/J_0 value induced by BSA coagulated with Al was varied as a function of pH after coagulation (Figs. 1c and 2c,f). Furthermore, BSA could cause serious flux decline at its iso electric point (IEP, pH 4.7) because there was no electrostatic interaction between BSA and membrane while the membrane fouling was mitigated when the pH was far away from its IEP (Palacio et al., 2003).

Fig. 3 described the minimal J/J_0 value induced by the critical dose of Al after coagulating with HA or BSA as a function of pH. It showed that the minimal membrane flux caused by BSA after coagulation was significantly affected as a function of pH while that caused by HA or 1:1_{ratio} 5 ppm HA/BSA mixture was changed little after coagulation. According

Fig. 1 – Normalized flux decline as a function of time with various doses of Al at pH 7.0. (a) 10 ppm HA; (b) 1:1_{ratio} 5 ppm HA/BSA mixture (i.e., 1:1 HA/BSA); (c) 10 ppm BSA.

Fig. 2 – Normalized flux decline as a function of time with different doses of Al. (a) 10 ppm HA at pH 6.0; (b) 1:1_{ratio} 5 ppm HA/BSA mixture (i.e., 1:1 HA/BSA) at pH 6.0; (c) 10 ppm BSA at pH 6.0; (d) 10 ppm HA at pH 8.0; (e) 1:1_{ratio} 5 ppm HA/BSA mixture (i.e., 1:1 HA/BSA) at pH 8.0; (f) 10 ppm BSA at pH 8.0.

to Figs. 1 and 2, the critical dose of Al was lower at pH 6.0 than that at pH 8.0. For HA, BSA or their 1:1_{ratio} 5 ppm HA/BSA mixture, 5 μ M Al could induce membrane flux reduce drastically at pH 6.0 while 10 μ M Al was needed at pH 8.0. However, no dramatic flux decline at pH 8.0 was found because Al hydrolysis species was not sufficient (Wang et al., 2008). For the 1:1_{ratio} 5 ppm HA/BSA mixture, its minimal J/J_0 value was similar to that caused by HA as a function of pH because protein (BSA) could be encapsulated by HA, and that was stable at pH 5.0 to 8.0 (Jeanne et al., 2011).

3.3. Change of molecular weight distribution

The MW distribution of HA and BSA was also investigated to know whether it would be changed or not before and after the filtration (Fig. 4). Three main doses of Al were chosen, which represented the minimum, the critical and the maximum dose of Al used. As seen from Fig. 4, the MW distribution of HA was from 41,477 Da to 2181 Da before filtration, while the MW

Fig. 3 – Minimal J/J_0 value caused by the critical dose of Al after coagulating with HA/BSA as a function of pH.

Fig. 4 – Molecular weight distribution of HA or BSA coagulated with Al before and after the filtration at pH 7.0. (a) 10 ppm HA; (b) 10 ppm BSA.

distribution of HA was from 22,134 Da to 1802 Da, from 20,899 Da to 1683 Da, and from 19,965 Da to 1498 Da when the dose of Al was 2.5 μM, 10 μM and 30 μM in the feed, respectively. It clearly showed that HA with large MW were rejected, and the peak value of the MW distribution of HA were shifted to a smaller one with increasing the dose of Al. For BSA, however, its peak value of the MW distribution was varied little after coagulation, which might be due to the single chemical characteristic of BSA. In general, the variation of the peak value (from 12,071 Da to 7196 Da) of the MW distribution of HA was much more significant than that of BSA (from 67,000 Da to 65,590 Da) after filtration because there were some large MW of HA which were easily rejected when coagulated with various doses of Al.

4. Discussion

To know the effect of various particle sizes caused by the low doses of coagulant on the UF membrane filtration behavior, different doses of Al were added to the feed water with HA, BSA or 1:1_{ratio} 5 ppm HA/BSA mixture. Wang and Tarabara (2008) reported that pore blocking was an important fouling mechanism for porous MF and UF membranes. The fact was that the size of particles which were close to the diameter of membrane pores could cause serious membrane fouling, while smaller than the pore size or larger than the pore size cannot because particles could either filtrate or form a relatively loose layer on the membrane surface. Fig. 5 showed the particle size distribution of HA/BSA coagulated with different low doses of Al. For HA, there were two peak values (3.77 nm, volume: 6.01%; 82.09 nm, volume: 53.54%) of the particle size distribution due to a portion of non-dissolved particles. The particle size increased with increasing the dose of Al in the feed solution. One peak value of the particle size was 28.24 nm (volume: 17.40%) when the dose of Al was 2.5 μM, while the peak values of the particle size were 39.41 nm (volume: 12.70%) and 55.37 nm (volume: 10.60%) when the doses of Al were 10 μM (critical dose) and 30 μM, respectively. As analyzed by IB-FT, GmbH, the average diameter of the UF membrane pores used in the experiment was about 41.51 nm. Therefore, serious flux decline was induced by the particle size of HA coagulated with 10 μM Al because of higher chances of

blocking the membrane pores. Owing to the wide MW distribution of HA, its particle size was difficultly equal to the diameter of the membrane pore after coagulation. Although a number of particles would block some membrane pores after coagulation, the amount was fractional and that cannot cause dramatic flux reduction. Thus, the main fouling mechanism would be induced by cake layer as there were numbers of particles larger than 100 nm. For BSA, the peak value of the particle size distribution was 7.7 nm. The particle size also increased with increasing the dose of Al in the feed solution. The peak value of the particle size distribution after coagulation was 28.21 nm when the dose of Al was 1 μM, while the peak values of the particle size distribution were 37.84 nm and 105.70 nm when the doses of Al were 5 μM (critical dose) and 20 μM, respectively. Thus, the particle size of BSA which was coagulated with the 5 μM Al could cause drastic flux decline by blocking the membrane pores during the filtration. In comparison with the flux decline caused by HA after coagulation, BSA coagulated with Al could cause a much more serious membrane fouling due to the similarity of the particle size distribution to the membrane pore size distribution.

When there was a low dosage of Al in feed solution, especially when the dose was lower than the critical dose, most flocs were nano-scale, leading to a less serious flux decline because a large number of flocs could pass through the membrane pores. However, some micro-flocs were formed at the critical dose and would grow gradually with increasing the dose of Al. Therefore, more and more flocs could fully block the membrane pores and that could cause significant flux reduction, especially for the narrower MW distribution of BSA. When the dose of Al was higher than the critical dose, cake layer was formed. For the 1:1_{ratio} 5 ppm HA/BSA mixture, the flux decline was dominated by HA because BSA was encapsulated by HA, which induced a rare chance of the pore blocking. The MW distribution of HA were relatively wide and it was difficult to cause serious flux decline because the chances of fully blocking the membrane pores were rare (Fig. 6).

5. Conclusions

Up to now, more studies have focused on finding an optimal dose of coagulant in order to drastically mitigate the

Fig. 5 – Particle size distribution of HA/BSA coagulated with Al at pH 7.0. (a) 10 ppm HA; (b) 10 ppm BSA.

Fig. 6 – Schematic diagram of the membrane fouling mechanism. (a) HA; (b) 1:1 (mass ratio) HA/BSA; (c) BSA.

membrane fouling in the downstream treatment of membrane filtration. However, the most serious membrane fouling was investigated when there was HA or BSA in the feed water with low doses of coagulant. There was indeed a critical dose of Al that could exacerbate membrane fouling after coagulation, especially for BSA. The fouling mechanism was mainly induced by the particle size of HA or BSA coagulated with Al. For HA or BSA, the critical dose of Al was relatively lower at pH 6.0 than that at pH 8.0. HA/BSA coagulated with the critical dose of Al behaved conformably except the flux. The flux decline caused by HA after coagulation was slightly affected by pH while that caused by BSA after coagulation was varied significantly as a function of pH. In addition, the flux decline caused by the 1:1_{ratio} 5 ppm HA/BSA mixture after coagulation was inclined to that caused by HA after coagulation because BSA could be encapsulated by HA in feed solution. The peak value of

the MW distribution of HA coagulated with Al was changed much more drastically compared to that of BSA after filtration.

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