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Effect of pH on floc properties and membrane fouling in coagulation–ultrafiltration hybrid process with different Al-based coagulants

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ABSTRACT

Impacts of pH on floc properties and membrane fouling in coagulation–ultrafiltration process with different Al-based coagulants were investigated. Polyaluminum chloride (PAC) was prepared with alkali-titration method and Al speciation distribution was tested with Al-Ferron method. Three kinds of coagulants (AC($AlCl_3$), PACb, and PACc) consisted primarily of Ala (monomeric species), Alb (medium polymer species), and Alc (colloidal or solid species), respectively, were used as coagulants under pH conditions of 4.0, 6.0, and 8.0. Floc properties were evaluated using a laser diffraction particle sizing device and ultrafiltration experiments were conducted by a dead-end batch unit. The results indicated that pH condition and aluminum species had significant influence on size and fractal dimension value of flocs. For the three Al species, relatively low pH condition was favorable to form larger flocs, while it would diminish the floc growth rate. And the loosest flocs were formed at pH 4.0. Under the same pH conditions, Ala tended to form the largest flocs and Alc achieved the loosest floc structure. For each coagulant, membrane fouling under different pH conditions was in the following order: pH 4.0 > pH 8.0 > pH 6.0. Alb and Alc showed a wider tolerance for changes of pH conditions than Ala. And under the same pH conditions, Alc achieved the lightest membrane fouling.

Keywords: Floc properties; Membrane fouling; pH; Al species

1. Introduction

Presently, application of membrane filtration processes (involving microfiltration, ultrafiltration, and nanofiltration) in potable water production has increased rapidly as an alternative to conventional drinking water treatment. As a low-pressure membrane process, ultrafiltration has been known to be effective to remove suspended solids, colloidal material (>0.1 μm), inorganic particulates, and fatal microorganisms [1]. However, flux decline due to the adsorption and deposition of foulants is normally experienced, which affects the practical application of

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the ultrafiltration [2–4]. Pretreatment such as coagulation, adsorption, and ozonation before membrane process to reduce natural organic matter (NOM) in the inflow is a useful approach to alleviate the problem of flux decline in ultrafiltration [5–7].

Due to low-cost and easy operation, coagulation/flocculation has been widely used as pretreatment of ultrafiltration. In coagulation–ultrafiltration hybrid process (C-UF), membrane fouling has been reported to be significantly affected by coagulant type, coagulation condition, and floc characteristics [8–10]. Choo et al. [11] stated that the degree of fouling reduction during C-UF process highly depended on the type of coagulants used. Gui et al. [12] reported that a reduction of coagulant dose induces an increase in the mass transfer resistance even in quasi-stable hydrodynamic operating conditions. Kabsch-Korbutowicz [13] stated that pH of feed water could strongly affect NOM removal and membrane fouling in C-UF hybrid process. Dong et al. [14] also reported that the irreversible fouling of membrane could be decreased at lower pH values in humic acid (HA) treatment by C-UF process. Moreover, the floc properties, including floc size and fractal dimension significantly affect the membrane fouling in C-UF hybrid process. Increase in particle size by coagulation would reduce foulant penetration into pores and formed a higher permeability cake on the membrane surface [15]. A specific cake theoretical model has been reported to predict the porosity and specific resistance of cake layer, based on which the specific cake resistance decreases upon increasing the floc size and decreasing the fractal dimension [16].

Aluminum-based coagulant is one of the most widely applied inorganic salt coagulants. Polyaluminum chloride (PAC) has been known to been superior to the traditional aluminum-based coagulants (e.g. $AlCl_3$ and alum) in particulate and/or organic matter removal [17–19]. Hydrolyzed species of PAC have been divided into three types based on their reaction time with Al-Ferron: monomeric species (Ala), medium polymer species (Alb), and colloidal or solid species (Alc) [20]. It has been recognized that the performance of polymeric aluminum coagulants greatly depends on their Al speciation characteristics [21]. Many studies have been performed to find the differences of coagulation performance of these Al species. The distinct coagulation feature of Ala, Alb, and Alc can be applied to develop tailor-made PAC (with the correct distribution of Al species) to match the characteristics of raw water for optimized coagulation. In addition, as an enhanced coagulation process, adjust of pH is a significant way to improve turbidity and NOM removal [13]. This was because pH of feed water could affect the characteristics of component it contains and change the speciation of coagulants [21,22]. However, the effect of pH on floc properties and membrane fouling during C-UF process coagulated by different Al species has not been completely understood.

The main objective of this study was to investigate the floc properties formed by Ala, Alb, and Alc and the membrane fouling performance in coagulation–ultrafiltration process under different pH conditions.

2. Materials and methods

2.1. Water sample

HA is ubiquitous and is the main organic constituent in the drinking water [22], so being used with Kaolin to simulate the actual surface water is meaningful. The preparation of HA stock solution was as follows: 1.00 g HA and 0.4 g NaOH were dissolved in about 750-mL deionized water with continuous agitation for 1 h, and then the suspension was diluted to 1 L with deionized water. The commercial HA was obtained from Jufeng Chemical Technology Co. Ltd, Shanghai, China.

Kaolin was used to simulate the suspension in the actual water. The stock solution of kaolin was prepared by dissolving 5.00 g kaolin (Tianjin, China) in about 750 mL deionized water. After 30 min stirring, the clay suspension was diluted to 1 L with deionized water and then settled for 30 min in a glass measuring cylinder. The top 500 mL was decanted for later use.

A HA-kaolin synthetic water was prepared by adding HA stock solution into tap water and the concentration of HA was 10 mg/L. Initial turbidity was adjusted by kaolin stock suspension to 15.0 ± 0.5 NTU. The properties of synthetic test water were shown in Table 1.

2.2. Coagulants

Reagents used in this study were all of analytical grade, and deionized water was used to prepare all solutions. Three kinds of coagulants ((AC($AlCl_3$), PACb, and PACc) containing high content Ala, Alb, and Alc, respectively, were used in all the tests and they were all 5 g Al/L. AC was prepared by dissolving 4.4709 g $AlCl_3 \cdot 6H_2O$ into deionized water to

Table 1
The properties of synthetic test water

Turbidity (NTU)	UV_{254} (cm^{-1})	DOC (mg/L)	pH
15.0 ± 0.5	0.308 ± 0.015	5.354 ± 0.783	8.28 ± 0.02

100 ml. And PACb was synthesized by titrating 90 ml NaOH solutions containing 3.2593 g NaOH to 90 ml $AlCl_3$ solutions with 8.9418 g $AlCl_3·6H_2O$ to make the B value (molar ratio of OH/Al^{3+}) equal to 2.2 at a constant speed at 72°C and the mixture was strong stirred during the experimental process. The titrating process lasted for about 1 h. Then the mixture solution was still strong stirred at the same temperature till the solution became clear and then was diluted to 200 ml. The procedure of preparing PACc was described as follows: 100 ml of PACb solutions was strong stirred in the flask at 95°C for 12 h. Al species distribution of the three coagulants was measured after 24 h aged time based on ferron method, and the results were shown in Table 2. The dosage of coagulant in this study was calculated as Al content (mg/L).

2.3. Jar tests

All coagulation experiments were conducted in a 1.0 L Plexiglas beaker using a programmable jar-test apparatus (ZR4-6; Zhongrun Water Industry Technology Development Co. Ltd, China). The coagulation process consisted of three sections in time sequence: rapid stirring for the solutions at 200 rpm for 1.5 min, slow stirring at 40 rpm for 15 min and sedimentation for 20 min. The coagulant was added into the solutions at the beginning of rapid stir. After sedimentation, supernatant samples were collected 3 cm below the water surface. Turbidity was measured using a 2100P turbidimeter (Hach, USA) immediately after sample collection. Zeta potential of the supernatant water was tested using a Zetasizer 3000 Hsa (Malvern Instruments, UK). The sample was filtered through 0.45 μm fiber membrane before DOC (dissolved organic carbon) analysis using a Shimadzu TOC-VCPH analyzer and UV_{254} (absorbance at 254 nm) measurement using a TU-1810 UV/vis spectrophotometer.

2.4. Floc properties

Dynamic changes of floc size and floc structure were determined by a Malvern Mastersizer 2000 (Malvern, UK). Silicone hose is used to connect the coagulation mixer, peristaltic pump, and laser particle size analyzer. Water sample flowed with the speed of 1.5 L/h from coagulation mixer to laser particle size analyzer and then flowed back by a peristaltic pump. Floc size were tested every 30 s. The mean size (d_{50}) was used to embody the floc size. Floc structure was represented by fractal dimension (D_f), which could be described by the following relationship:

$$I(q) \propto q^{-D_f} \tag{1}$$

where $I(q)$ is the aggregate clusters and q is the momentum transfer. The power relationship is linear on a log–log scale and the slope of the line is D_f. The D_f indicates the mass fractal scaling relationship within the aggregates and the degree of compaction of flocs. In general, compact aggregates have higher D_f values than loose structures.

Table 2
Al species distribution of three kinds of coagulants

Coagulant	Ala (%)	Alb (%)	Alc
AC	93.2	6.8	0
PACb	14.73	81.91	3.36%
PACc	9.13	21.51	69.36%

2.5. Coagulation–ultrafiltration procedure

All ultrafiltration experiments were conducted using a 300-mL capacity stirred batch unit and the sample water after coagulation without sedimentation process was gently transferred into the cell. At the top of the cell, there was an opening desired for pre-treated samples addition. Slow agitation was used to make a uniform suspension. A constant pressure was provided by nitrogen gas at 150 kPa. The cumulative mass of permeate was measured every 10 s by an electronic balance (MSU5201S-000-D0; SartoriusAG, Germany), which was connected to a computer with a data acquisition system. The schematic diagram of coagulation–ultrafiltration hybrid process was showed in Fig. 1.

The UF membrane (Mosu, China) used was polyethersulfone (PES) flat sheet membrane with

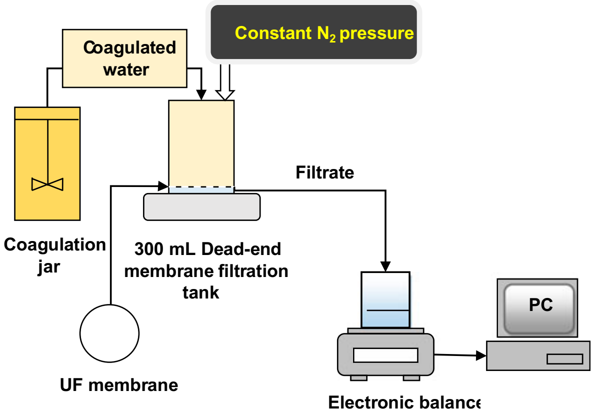

Fig. 1. Schematic diagram of coagulation–ultrafiltration hybrid process.

molecular weight cut-off of 100 kDa and the effective membrane area was 50.24 cm^2. The membrane was soaked in deionized water at least 24 h before use and a fresh piece of membrane was used for every single experiment.

3. Results and discussion

3.1. Coagulation test

3.1.1. Coagulation for optimal dose

Effect of dosage on coagulation performance of AC, PACb, and PACc was studied to choose the optimal dose. The results were showed in the Fig. 2.

Turbidity removal efficiencies of three coagulants all rose along with the increase in the dosage and then reached steady. The turbidity removal efficiencies of PACb and PACc were very similar and higher than that of AC during the dosage of 6–12 mg/L, which indicated that Alb and Alc were superior to Ala in turbidity removal when the feed water was alkalescent [21,23]. This may be because Alb has higher charge neutralization ability and Alc has higher sweep ability. The optimal coagulation dose of PACb and PACc for turbidity removal efficiencies was 6–10 mg/L, while that for AC was 4–10 mg/L.

UV_{254} characterizes organic matters with benzene ring, conjugated double bonds, or long molecular chain. UV_{254} removal trends of PACb and PACc were almost overlapped and UV_{254} removal was lower than that of AC during the investigated dosage range. So Ala had better performance in removing UV_{254} than the other species. The UV_{254} removal efficiencies rose with dosage increasing all the time, while when the dosage was more than 8 mg/L, the trend is not obvious. When the dosage of the coagulant was less than 8 mg/L, DOC removal efficiencies of AC, PACb, and PACc all rose with dosage increasing, and DOC removal efficiency of PACc was higher than that of AC and PACb, while the DOC removal difference between AC and PACb was very small. In other words, Alc had advantage on DOC removal. The optimal coagulation dose of these three coagulants for DOC removal efficiencies was about in range of 8–12 mg/L.

Based on the above experimental results and considering the principle of minimizing coagulant dose to reduce the reagent cost, 8 mg/L as Al was selected as the optimal dose to conduct the following experiments.

3.1.2. Coagulation for optimal pH conditions

The coagulation efficiencies of three different coagulants under different pH conditions were investigated to choose the optimal pH condition and the results were showed in Fig. 3.

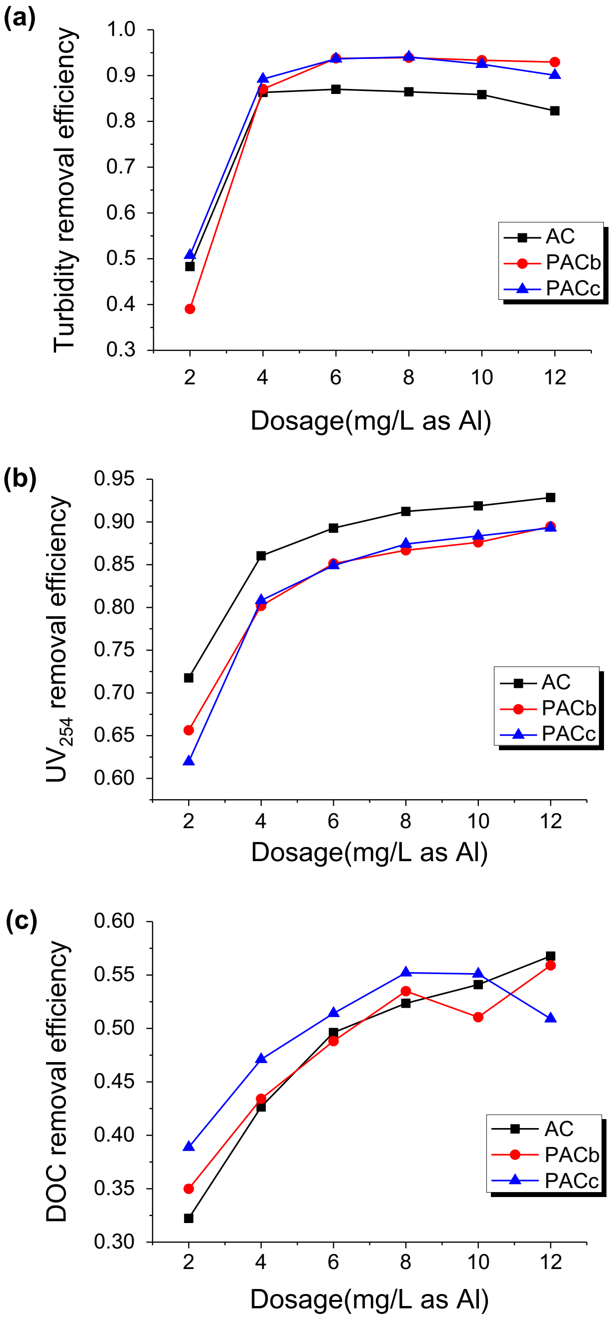

Fig. 2. Coagulation performance under different aluminum-based coagulants and doses conditions: (a) turbidity removal efficiency, (b) UV_{254} removal efficiency, and (c) DOC removal efficiency.

Turbidity removal efficiency of AC gradually rose with pH under acidic condition and almost remains the same in pH range of 7–9, while the turbidity removal efficiency of PACb and PACc were not sensitive to the variation of pH. This may be related with the stability of PACb and PACc under acid condition. Comparing with AC at the pH range of 4.0–5.0, PACb and PACc were relatively stable, which resulted in the similar turbidity removal efficiencies to neutral environment. The removal efficiency of UV$_{254}$ and DOC rose with the raise of pH and then descended which achieved the maximum value at pH 6.0.

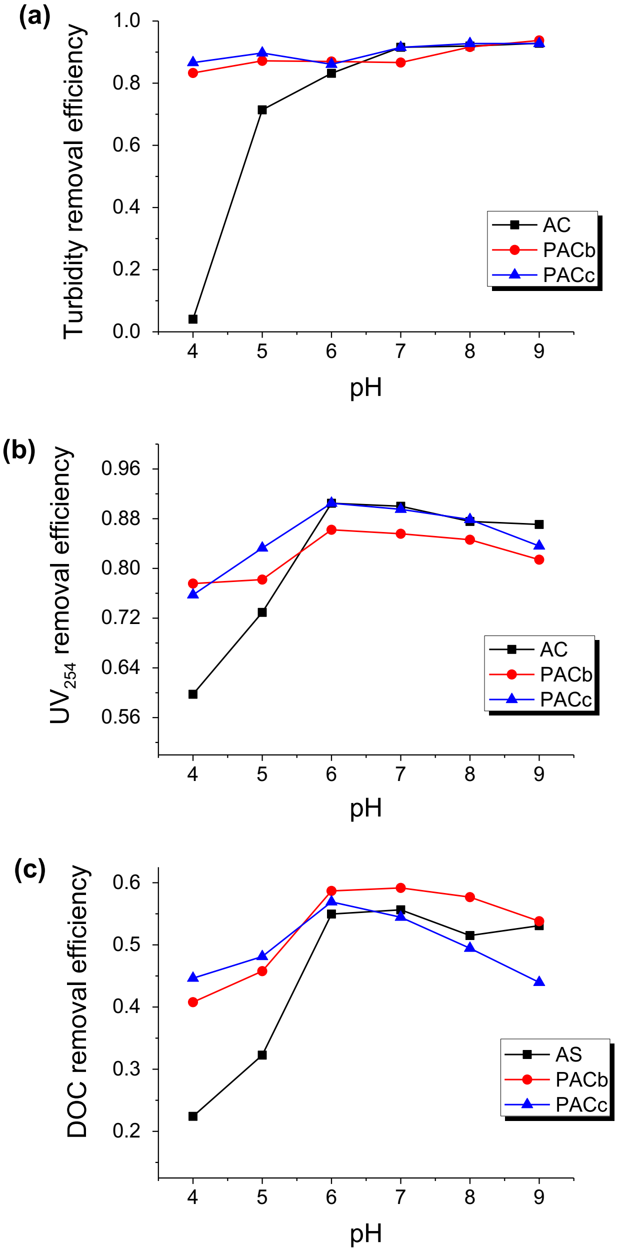

Fig. 3. Coagulation performance under different aluminum-based coagulants and pH conditions: (a) turbidity removal efficiency, (b) UV$_{254}$ removal efficiency, and (c) DOC removal efficiency.

At the pH range of 4.0–5.0, AC had the worse UV$_{254}$ and DOC removal performance than PACb and PACc, which was the same with the variation of turbidity removal efficiency. When the pH was less than 5.0, Al species of AC was mainly composed of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{3+}$, dimer ($Al_2(OH)_2^{4+}$), trimer ($Al_3(OH)_4^{5+}$) and some small polymer [24]. It complexes with negative functional groups and neutralizes HA to form Al-HA. As most of HA was not large enough to provide nuclei for floc formation with Ala, the Al-HA generated was hard to settle down. So when pH was 4.0–5.0, AC had poor coagulation performance.

Based on the performance of the coagulation of three different coagulants under different pH conditions, the selected optimal pH was 6.0, which corresponded with the previous articles [25,26].

3.2. Floc size and fractal dimension

Dynamic floc sizes with time for AC, PACb, and PACc at different pH were shown in Fig. 4.

For AC, the growth rate of flocs formed at pH 4.0 was lower than those when pH was 6.0 and 8.0, while the floc size at pH 4.0 was biggest. The floc growth curves with time at pH 6.0 and 8.0 were almost coincident, which means floc sizes and the growth rate at pH 6.0 were similar to those at pH 8.0. In the case of PACb, the floc sizes under different pH conditions were in the order: pH 4.0 > pH 6.0 > pH 8.0, while the floc growth rates order were exactly in the contrary: pH 8.0 > pH 6.0 > pH 4.0. For PACc, the smallest floc size was observed at pH 8.0, while the floc sizes at pH 4.0 was similar to that at pH 6.0. The floc growth rates were also in the order: pH 8.0 > pH 6.0 > pH 4.0.

The above results indicated that for performed Ala, Alb, and Alc (especially Ala), the growth rate of the flocs would be low under low pH condition. Acidic condition was favorable for them to form larger flocs. This may be mainly because of the effect of pH on the Al species. When pH was 4.0, AC was mainly composed of monomeric Al species (Ala) as the above text, and most of Al-HA and Al-kaolin were not large enough to settle down unless there was further hydroxylation and polymerization of Al or enough stirring time for collision. So the floc formation rate was low when pH was 4.0. At pH 6.0 or 8.0, Ala in AC would transform into Alb and finally Alc within minutes after dosing. Alb preferentially co-precipitated with HA in the form of Alb-HA complexes [27], which would increase the particle concentration and particle collision rate as Alb which had large size. So the floc growth rate of PACb was higher. The growth rate of PACc was also high as Alc is easy to precipitate

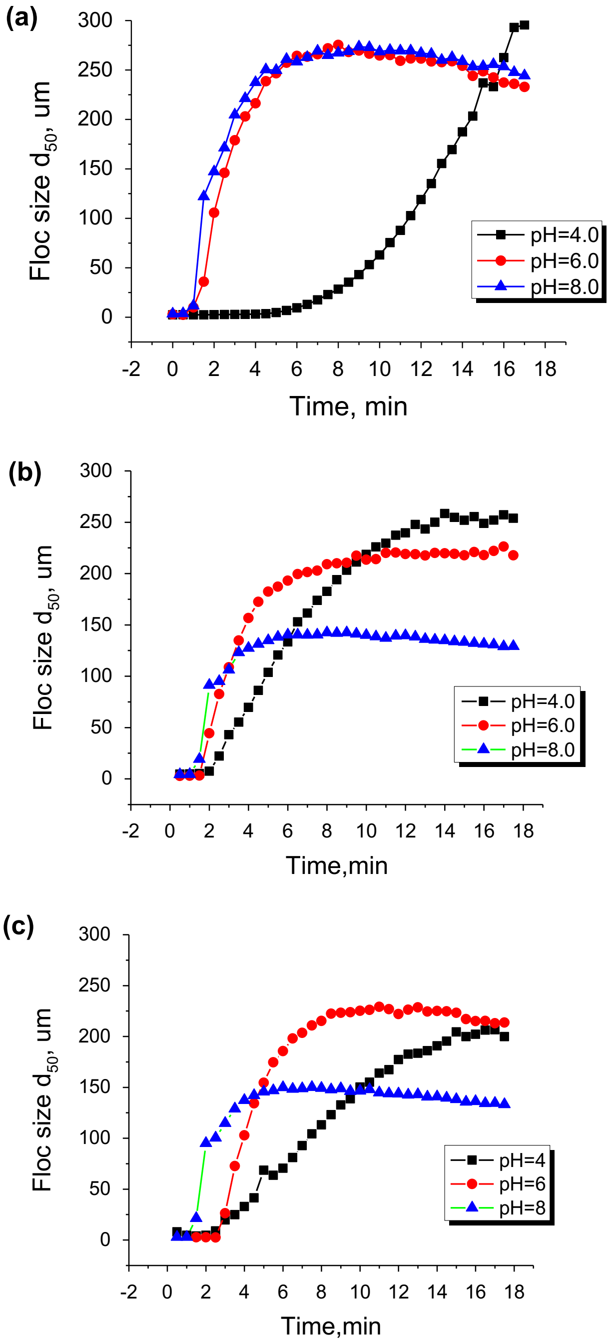

Fig. 4. Floc size variation under different aluminum-based coagulants and pH conditions: (a) AC, (b) PACb, and (c) PACc.

because of its large size. So when pH was 6.0 or 8.0, floc formation rates were higher than that at pH 4.0. The conclusion about the effect of pH on floc formation rate could also be applied to performed Alb and Alc, which was shown in Fig. 4. But the differences of floc formation rates between Alb and Alc under pH 6.0 and 8.0 were much smaller than that of Ala, which could be attributed to the relatively stability of Alb and Alc under acidic condition.

When pH was 6.0, the floc sizes of AC, PACb, and PACc were in the following order: AC > PACb ≈ PACc. This could be explained by the acting force between coagulants and impurity in the water. Coagulation mechanism of contaminants by Ala, Alb, and Alc follows complexation, neutralization, and adsorption, respectively [23]. The complexation force is stronger than force of the other two mechanisms, so that the floc size of AC was biggest.

The fractal dimension of flocs formed by coagulation was parameter of the floc structure. The fractal dimensions of flocs formed by AC, PACb, and PACc at different pH conditions were shown in Table 3. It could be seen that the fractal dimensions of flocs formed by PACb and PACc under different pH conditions was in the order: pH 4.0 < pH 8.0 < pH 6.0, which meant the flocs were loosest at pH 4.0 and most compact at pH 6.0. AC also formed loosest flocs at pH 4.0, but flocs have the similar fractal dimension at pH 6.0 and 8.0. The results indicated under significant acidic condition (pH 4.0) the aluminum-based coagulant tended to form loosest flocs comparing with neutral condition.

PACc tend to produce flocs with lower D_f value at pH 4.0, 6.0, or 8.0 compared with AC and PACb. This means the flocs formed by AC were looser, while the flocs formed by PACb and PACc have not much difference in fractal dimension.

3.3. Membrane fouling

UF experiments after coagulation (without precipitation) was conducted to study the effect of aluminum speciation distribution and pH on membrane fouling. The normalized membrane permeate fluxes (J/J_0) was used as a parameter of reflecting the membrane performance. Fig. 5 showed the normalized fluxes of different coagulants with the coagulant dose of 8 mg/L

Table 3
Fractal dimensions (D_f) of flocs formed by AC, PACb, and PACc at different pH conditions

Coagulant	AC			PACb			PACc		
pH	4	6	8	4	6	8	4	6	8
D_f	2.509 ± 0.009	2.532 ± 0.005	2.533 ± 0.006	2.493 ± 0.004	2.534 ± 0.004	2.513 ± 0.005	2.448 ± 0.004	2.482 ± 0.005	2.464 ± 0.005

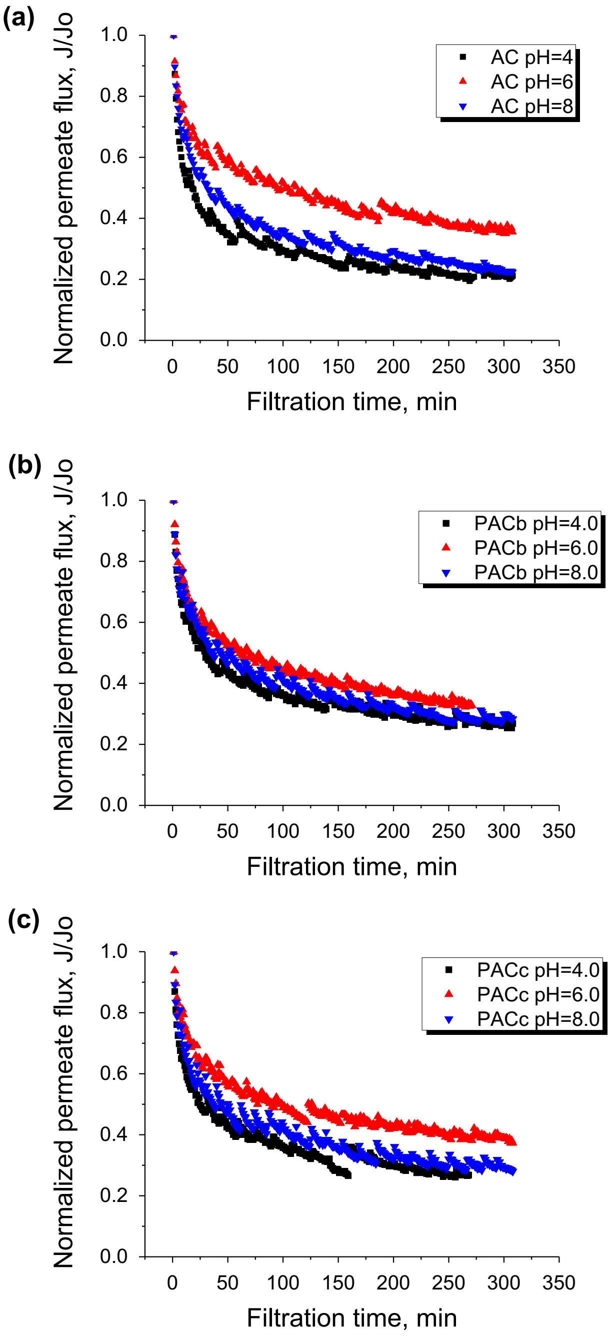

Fig. 5. The change of flux as a function of filtration time under different pH conditions: (a) AC, (b) PACb, and (c) PACc.

at different pH conditions as a function of filtration time. For all the conditions, after the filtration began, the normalized fluxes reduced dramatically and then the decay rate decreased gradually to zero till the normalized fluxes came to equilibrium. Table 4 showed the normalized fluxes when the normalized fluxes maintained stable.

In general, floc characteristics have important influence on membrane fouling and increasing floc size and decreasing fractal dimension would help to decrease the cake resistance and decrease membrane fouling. For all three coagulants, the normalized fluxes was the largest at pH of 6.0 (the optimal pH), followed by the normalized fluxes at pH 8.0. When pH was 4.0, the normalized fluxes were the lowest. Membrane fouling was severer when raw water was at pH 4.0, although the floc size and fractal dimensions did not show disadvantages on the membrane fouling. This was because the turbidity removal efficiency and HA removal efficiency of the pretreat coagulation process were very low. When coagulated suspension was ultra-filtered, the cake layer on surface of the ultrafiltration membrane could absorb some residual kaolin and HA, and too many residual impurities in the water samples would still cause serious membrane fouling no matter which coagulant was used at pH 4.0.

When the coagulant dose was 8 mg/L and pH was 6.0, the normalized fluxes of different coagulants were in the order of PACc > AC > PACb, as shown in Table 4. PACc gave the best ultrafiltration performance, which may be because PACc formed the loosest structure comparing with the other two coagulants. AC and PACb had the similar fractal dimensions, but the floc size of AC was larger than that of PACb, which could explain why AC showed the better membrane filtration performance than PACb. When the raw water was at pH 4.0 or 8.0, AC had the smallest normalized fluxes, while PACb and PACc had similar normalized flux. So when the pH of raw water deviated the optimal pH, Ala achieved severest membrane fouling. And membrane fouling of Alb and Alc was less sensitive to the change of pH than Ala.

Table 4
The normalized membrane permeate fluxes (J/J_0) of different coagulants at different pH conditions when the normalized fluxes maintained stable

Coagulant	AC			PACb			PACc		
pH	4.0	6.0	8.0	4.0	6.0	8.0	4.0	6.0	8.0
J/J_0 (%)	21.2	36.2	23.0	26.9	33.6	28.5	27.0	38.9	29.5

4. Conclusions

The experimental results indicated that aluminum speciation and pH condition of raw water had great impacts on the floc properties and the membrane fouling in ultrafiltration. Based on the results of this research, following conclusions were obtained:

(1) The optimal coagulation performance for Ala, Alb, and Alc was all gotten when the dose was 8 mg/L as Al and pH was 6.0.
(2) Under acidic condition the growth rate of flocs formed by Ala, Alb, and Alc was lower, while the flocs formed was larger and looser. Coagulant mainly containing Ala tended to form larger flocs than Alb and Alc, and Alc of coagulant was propitious to the formation of looser flocs.
(3) When the raw water was at pH 6.0, the filtration performance with Ala, Alb, and Alc as the pretreatment agent was the best, followed by pH 8.0. When the pH was 4.0, the filtration performance was the worst, which was because of the worst coagulation performance.
(4) Under investigated pH conditions, Alc had the best filtration performance as the pretreatment agent compared with Ala and Alb, while the difference of the latter two would depend on the special pH condition. Alb and Alc showed a wider tolerance for changes of pH conditions than Ala. Thus, Alc was the most efficient speciation for the coagulation–ultrafiltration hybrid process and could be used for further study.

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