Floc structure and membrane fouling affected by sodium alginate interaction with Al species as model organic pollutants

Xuejun Xiong1,2,3, Hui Xu2,3,⁎, Beiping Zhang1,⁎, Xiaohui Wu1, Hongyan Sun2,3, Dongsheng Wang2,3, Zhengyang Wang4

1. School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
2. Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18, Shuangqing Road, Beijing 100085, China
3. State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
4. Department of Civil and Environmental Engineering, University of Missouri, Columbia, MO 65211, USA

Abstract

Membrane filtration combined with pre-coagulation has advantages in advanced wastewater treatment. As a model of a microbial polysaccharide, research on the effect of sodium alginate (SA) on alum hydrolysis has been rare; therefore, it is necessary to gain insight into the interface interaction between SA molecules and Al species, and the role SA plays during floc formation. In this study, the interaction mechanism between SA and Al species has been investigated, by evaluating the effect of SA on floc characteristics and membrane fouling during coagulation–ultrafiltration with different Al species (AlCl3 and preformed Al13). Al 2p X-ray photoelectron spectroscopy (XPS) confirmed that the complexation of ligands and Al species strongly affects the reaction pathways for Al hydrolysis and the final nature of the flocs, as Al13 can be decomposed into octahedral precipitates when SA is added. The presence of SA can affect floc properties, which have important impacts on the characteristics of the cake layer and membrane fouling. Due to the bridging ability of SA, the floc strength increased by about 50% using Al₆, which was much better than preformed Al₁₃, with a percentage increase of only about 6%. Moreover, the recovery factor of HA-flocs was decreased from 96% to 43% with SA addition of 0.5 mg/L. It was concluded that SA can affect the characteristics of the cake layer and membrane fouling through participating in the formation of primary flocs and altering the Al hydrolysis pathway.

Keywords: Coagulation–ultrafiltration process Al species Interface interaction X-ray photoelectron spectroscopy Floc properties Membrane fouling

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Introduction

Increasing public health concern has grown in relation to the presence of micro-pollutants in the aquatic environment (Petrie et al., 2015). The discharge of treated effluent from municipal wastewater treatment plants (WWTP) is a major pathway for the introduction of micropollutants to surface water (Acero et al., 2016). Membrane filtration has been widely used after secondary treatment in order to remove suspended solids, organics and nutrients and produce high quality water suitable for reuse purposes (Filloux et al., 2012). However, a major issue is membrane fouling caused by effluent organic matter (EfOM), which results in reduction of membrane performance and the need for cleaning. Pre-coagulation has so far been the most successful method for controlling the fouling of low-pressure membranes employed in full-scale water treatment (Huang et al., 2009).

The performance of coagulation can affect membrane fouling directly and the strength factors of flocs exhibit a strong positive linear correlation with the cake compressibility index during direct microfiltration (Zhao et al., 2011). The porosity of the cake layer and the characteristics of the floc particulates are the main factors that control membrane resistance, i.e., floc particulates of larger size and better settling ability or loose cake layers can mitigate membrane fouling (Yao et al., 2015). Al-based coagulants have been most widely used in drinking water and wastewater treatment plants (Cui et al., 2016; Liu et al., 2013; Matilainen et al., 2010). However, the type of Al species used can affect floc properties, leading to different membrane flux declines (Feng et al., 2015). In addition to traditional aluminum salts (Al₃), such as Al₂(SO₄)₃ and AlCl₃, pre-hydrolyzed aluminum coagulants, e.g., Al₁₃ polycation ([Al₁₃O₉(OH)₅₄(H₂O)₁₂]⁷⁺), which has been recognized as the major species that can cause coagulation of negatively charged particles by charge neutralization (Lin et al., 2009), have been investigated in the coagulation process (Matilainen et al., 2010). The floc sizes of Al₃ were much larger than Al₁₃ and Al₃₀, but the structures were looser in flocs of Al₃ (Jiao et al., 2015; Xu et al., 2011). It was also observed that the strength factor of flocs formed by alum was higher than that of PACI, regardless of the coagulant dose or breakage rate (Yu et al., 2009).

The EfOM can be classified into two types: (A) biomass-associated products (e.g., proteins and polysaccharides), and (B) humic-type organic matter (Vakondios et al., 2014). Though these three forms of organic matter can be present together in secondary effluent, most studies have focused on either humic substance or protein removal, while little attention has been paid to the role played by polysaccharides during their simultaneous removal. Pivokonsky investigated the impact of interactions between protein and humic substances on coagulation (Pivokonsky et al., 2015). The study showed that the molecular interactions between humic substance and protein substantially impact the coagulation process, as these interactions lead to a decrease in coagulant dose and increase in coagulation effectiveness. Myat et al. (2014) found that humic acid (HA) interacts with alginate (used as a model compound for algal polysaccharides) via Ca²⁺-mediated interactions. However, among these contaminants, polysaccharides are responsible for membrane fouling in MBRs (Kim and Dempsey, 2013; Kimura et al., 2012), and some investigations have indicated that humic substances can interact with polysaccharides during membrane filtration, thus influencing the rate of flux decline (Katsoufidou et al., 2010; Myat et al., 2014). Taking these facts into consideration, it is necessary to gain insight into the impact of interactions between polysaccharides and humic substances or proteins on coagulation and membrane fouling. Considering the complicated composition of EfOM, commercially available sodium alginites (SA), bovine serum albumin (BSA), and humic acids (HA) extracted from soils or water have been used as surrogates for the polysaccharides, proteins and humic substances in EfOM, respectively (Kim and Dempsey, 2013). Due to the intermolecular cross-linking of polysaccharide chains, polysaccharides have significant effects on floc growth and floc properties (Zhao et al., 2012a, 2012b), which may affect the structure of the cake layer. As a model of polysaccharides, primary coagulants plus SA gave flocs with better recoverability but with more highly branched and loosely bound structure (Zhao et al., 2012b). The flocs generated in the PACI-Ep (PACI-Enteromorpha polysaccharides) system were stronger than those generated in PACI alone, and Ep addition led to better floc recovery performance. Large size and loosely structured flocs were generated in coagulation effluents when Ep was used, which resulted in less membrane fouling (Zhao et al., 2015).

The main coagulation mechanism to remove humic acid and protein with alum coagulants can be concluded to be charge-neutralization, complexation, co-precipitation, and adsorption (Duan and Gregory, 2003; Jin et al., 2018; Lin et al., 2014; Sillanpaa et al., 2018). However, investigations on the mechanism of interaction between sodium alginate and alum coagulants have been rare and research on the effect of sodium alginate on membrane fouling alleviation during inline coagulation is limited. In this study, the SA interfacial interaction with Al species were investigated and different concentrations of SA were introduced to examine the effects of SA on floc structure during in-line coagulation. The properties of aggregated flocs in synthetic wastewater were characterized in terms of floc size, floc growth rate, strength factor, recovery factor and fractal dimension. XPS spectra were utilized to analyze the interaction between organic matters and Al species. Based on experimental data, this study provides insight into the role SA plays in the pathway of Al hydrolysis and its effect on floc structure.

1. Materials and method

1.1. Chemical regents and materials

1.1.1. The preparation of stock solution and synthesis water

All chemicals used in this study were analytical reagent grade except where specified. All stock solutions and water samples were prepared with deionized water. Solution pH was adjusted with 0.1 mol/L HCl and 0.1 mol/L NaOH. The stock solutions of humic acids (Aldrich, USA), bovine serum albumin (Aladdin Industrial Corporation, China) and kaolin suspension (produced by Sigma–Aldrich) were prepared as described in the previous study (Jiao et al., 2015). 1.7 g sodium nitrate and 1.7 g potassium nitrate were prepared together.
alginate (Aladdin Industrial Corporation, China) was dissolved in 500 mL de-ionized water. All stock solutions were standardized according to the DOC concentration measured by a total organic carbon analyzer (TOC-V CPH/CPN, Shimadzu, Japan).

Kaolin-HA and kaolin-BSA water samples were prepared by mixing organic matter with the kaolin suspension, and the DOC and turbidity were 5.0 mg/L and 20 ± 1 NTU, respectively. The turbidity was measured by a turbidimeter (2100N, HACH, USA). In order to study the effect of the concentration of SA on coagulation performance and characteristics of flocs in HA and BSA water samples, the chosen DOC concentrations of SA were 0.2 and 0.5 mg/L. NaHCO3 and NaNO3 solutions with concentrations of 4.0 and 5.0 mmol/L were introduced to provide the desired levels of alkalinity and ion strength (Jiao et al., 2015).

1.2. Preparation and characterization of coagulants

Two Al-based coagulants, AlCl3 and Al13, which represented Al1-coagulant and Al6-coagulant, were selected to evaluate their coagulation performance. AlCl3 solution was prepared by dissolving AlCl3·6H2O in deionized water. Al13 polycation ([Al13O4(OH)24(H2O)12]13+), which is claimed to be the most active species in polyaluminum chloride (PACl), was used as a coagulant in this study. The procedures of preparing Al13 polycation can be described as follows: (1) PACl with a basicity value (B, [OH]/[Al3+] molar ratio) of 2.2 was synthesized by adding a pre-determined amount of NaOH solution slowly into AlCl3 solution under intense agitation. (2) A sulfate precipitate of Al13 was separated and purified by adding a pre-determined amount of Na2SO4 under gentle agitation. (3) A pre-determined amount of BaCl2 or Ba(NO3)2 solution was added to substitute for sulfate in the Al13 precipitate under gentle agitation (Duan et al., 2014; Shi et al., 2007a). Total Al concentration (AlT) was measured by the Al-Ferron method and the solution was diluted with deionized water to 0.025 mol/L. The Al species distributions of coagulants were provided the desired levels of alkalinity and ion strength (Jiao et al., 2015), and the results are summarized in Appendix A Table S1.

1.3. Coagulation experiment and characterization of floc properties

1.3.1. Coagulation process

Coagulation experiments were performed by a conventional jar test apparatus (MY3000-6F, Meiyu Instruments Co., LTD., China). 500 mL of synthetic water was transferred into a cylindrical beaker, then the procedure was started with rapid mixing at the speed of 250 r/min; after 30 sec, coagulant was added, followed by a mixing speed of 200 r/min for 1.5 min, and then samples were collected to measure the zeta potential. The mixing speed was reduced further to 40 r/min for 10 min to allow floc growth, finally followed by sedimentation for 30 min. After being settled, the supernatant was collected to measure DOC, turbidity, fluorescence and residual Al. The pH of the water was adjusted to 7.0 with 0.1 mol/L HCl and 0.1 mol/L NaOH.

1.3.2. Floc breakage and regrowth

A laser diffraction instrument (Mastersizer 2000, Malvern Instruments, UK) was used to measure dynamic floc size as the coagulation experiments proceeded. Coagulation procedures were conducted as described in Section 1.3.1 and a breakage phase of 5 min was introduced with shearing rates of 200 r/min; after the breakage phase, slow stirring at 40 r/min was reintroduced for 10 min (regrowth stage). The suspension was monitored by drawing water through the optical unit of the laser diffraction instrument and back into the beaker by a peristaltic pump. Size measurements were taken every 30 sec during the jar test and the results (the median volumetric diameter (d50)) were recorded on a computer. The relative breakage and regrowth of different flocculated systems have previously been compared by use of the floc strength factor (Sf) and recovery factor (Rf) (Jarvis et al., 2005), which may be calculated as follows:

\[ S_f = \frac{d_2}{d_1} \times 100 \]  

\[ R_f = \frac{d_3/d_2 - 1}{d_1/d_2 - 1} \times 100 \]

where \( d_1 \) (μm) is the average floc size at the plateau before breakage, \( d_2 \) (μm) is the floc size after the floc breakage period, and \( d_3 \) is the floc size after regrowth to the new plateau. Here, the Sf indicates resistance of the formed flocs to shear force, while the Rf refers to the re-aggregation of flocs to larger flocs again after being subjected to shear breakage.

1.3.3. Floc fractal dimension

The floc structure is simply described by the mass fractal dimension Df. Compact aggregates have larger Df, while aggregates with loose structures show smaller Df. The total scattered light intensity I has a certain functional relationship with the scattering vector Q, Q is the difference value between the incident and the scattered wave vectors of the radiation beam in the medium, which is given by:

\[ Q = \frac{4\pi n \sin \theta}{\lambda} \]

where n is the refractive index of the suspending medium, \( \theta \) is the scattering angle, and \( \lambda \) is the wave length of the radiation in a vacuum. The total scattered light intensity I can be calculated with the scattering vector Q and the sample fractal dimension Df, which is shown as:

\[ I \propto Q^{-D_f} \]  

1.3.4. X-ray photoelectron spectroscopy

An X-ray photoelectron spectrometer (PHI Quantera SXM, ULVAC-PHI, Japan) was used to analyze the surface Al species of HA-flocs and BSA-flocs up to depths of 10 nm. XPS analysis was performed on freeze-dried floc samples from experiments at optimal dosages. The flocs formed after sedimentation were withdrawn immediately from the beaker and then freeze-dried over 2 day(s) with a vacuum refrigeration instrument (LQJ-10, Songyuanhuaxing Technology Develop Co., LTD., China).
1.4. Coagulation-ultrafiltration hybrid process

Filtration experiments were carried out at bench-scale by using a flexible filtration system as described in a previous study (Huang et al., 2011). The ultrafiltration experiments were conducted using a dead-end batch ultrafiltration unit with a PVC, UF, hollow fiber membrane. The PVC membrane was purchased from the Litree Purifying Technology Co., Ltd., China. The properties of the PVC membranes are summarized in Appendix A Table S2. The membrane fibers were fabricated into mini-modules with an effective membrane area of approximately 0.0016 m². These mini-modules were then flushed with ultrapure water prior to use for the removal of wetting agent or other preservatives on the membrane. After coagulation, the coagulated samples were gently decanted from the coagulation tank to the dead-end filtration unit and filtered through the PVC ultrafiltration membrane. Stirring should be maintained in the filtration modules to prevent flocs from settling. Prior to the commencement of continuous UF, the trans-membrane pressure \( P_0 \) (MPa) was measured by the filtration of pure water. The trans-membrane pressure (TMP) of the membrane \( J \) was recorded continuously during the filtration process, in which the permeate flux was fixed at 73.81 L/(m² × H) by using a peristaltic pump (BL-100, Prefluid, China). During the experiment, the UF membrane system operated on a filtration cycle of 2 hr. \( J \) is defined as follows according to Huang et al. (2008):

\[
J = \frac{J_s}{J_0} = \frac{1}{P} = \frac{P}{P_0}
\]

The UF membrane fouling in this research was evaluated by membrane flux decline. With the accumulation of foulant on the surface and in the pores of the UF membrane, the normalized specific flux gradually decreased, indicating an increase in membrane fouling. A Field Emission Scanning Electron Microscope was used (Helios Nanolab 600i, FEI, USA) to acquire the surface images of original and fouled membranes.

2. Results and discussion

2.1. Effect of SA on coagulation performance of HA and BSA at neutral pH

2.1.1. Effects of coagulant dosage on the removal efficiency for turbidity and DOC

Effects of coagulant dosages on the removal efficiency of turbidity and DOC using AlCl₃ and Al₁₃ were investigated. The dosages were adjusted from 0.02 to 0.24 mmol/L calculated as Al and the results are summarized in Figs. 1 and 2.

![Fig. 1 - Turbidity removal efficiency as function of coagulant dosage at neutral pH.](image)
Results in Fig. 1 showed that the turbidity removal efficiencies increased with increasing coagulant dosage. Different Al species had different effects on the turbidity removal efficiency of HA and BSA samples. The removal efficiency for turbidity showed a sharp increase when the AlCl₃ dosage was larger than 0.14 mmol/L for both HA and BSA. For BSA, the Al₁₃ coagulant

Fig. 2 – DOC removal as function of coagulant dosage at neutral pH.

Fig. 3 – Zeta potential of HA and BSA samples with different SA concentrations: (a) AlCl₃; (b) Al₁₃.
Fig. 4 - XPS Al-2p spectra and ratios of $\text{Al}^{VI}/\text{Al}^{IV}$: (a) $\text{AlCl}_3$ flocs; (b) $\text{Al}_{13}$ flocs.

Fig. 5 - The floc size ($d_{50}$) and fractal dimension of flocs with breakage strength of 200 r/min with different SA concentrations.
showed better removal efficiency of turbidity compared to AlCl₃, as better removal efficiency was acquired at lower dosage. However, opposite results were found for HA, as AlCl₃ exhibited better removal efficiency. During the coagulation of AlCl₃, the turbidity removal of kaolin-HA increased from 20% to more than 90% at a dosage of 0.14 mmol/L when SA was added (Fig. 1a), while the turbidity removal of kaolin-BSA decreased from 38% to 0% (Fig. 1c). This may mean that the interaction of SA molecules with HA and BSA during the coagulation was quite different.

DOC removal efficiency increased with coagulant dosage as shown in Fig. 2. For HA samples, there was not much difference in DOC removal between different SA concentrations, which indicated that the presence of SA had little effect on DOC removal in HA samples (Fig. 2a and b). Nevertheless, the trend of DOC removal was different between Ala and Al₁₃ in BSA samples (Fig. 2c and d). When AlCl₃ was used as coagulant (coagulant dosage was larger than 0.12 mmol/L), the existence of SA could significantly decrease the removal efficiency of DOC. The required coagulant dosage for optimal DOC removal of HA and BSA with different SA concentrations is summarized in Appendix A (Fig. S1). For BSA, the required coagulant dosage for optimal DOC removal by Ala was higher than for Al₁₃. According to previous studies, the major pre-hydrolyzed species of PACl is Al₁₃ polycations, which possess high positive charge. Al₁₃ can subsequently destabilize organic matter by strong charge neutralization at lower dosage compared to Ala and effectively remove contaminants from water through the coagulation/sedimentation process (Jiao et al., 2015; Liu et al., 2009). However, a different result was found during coagulation of HA, such that Ala exhibited better performance in removing HA than Al₁₃. A similar phenomenon was also found by Shi et al., 2007b), that coagulants with preformed Al₁₃ were less effective than conventional Al salt in removing humic acid with large molecular weight and hydrophobic properties. In conclusion, Ala and Al₁₃ exhibited different coagulation performance between HA and BSA and the addition of SA had a positive effect on the removal of HA with Ala, but negative effect on removing HA with Al₁₃, and the removal efficiency of BSA was independent of the coagulant species.

2.1.2. The variation of zeta potential in HA and BSA with SA addition

The zeta potential is an interfacial parameter related to the stability of primary flocs that are formed by hydrolysis of coagulants. In order to understand the effect of SA concentration on HA and BSA destabilization by AlCl₃ and Al₁₃, the changes of zeta potential at various dosages with different SA concentrations were determined and shown in Fig. 3.

A quick increase of zeta potential was found in BSA at low dosage (Fig. 3a) when using Ala and Al₁₃ as coagulants, and this may due to the presence of Al₁₃ and the hydrolysis of Ala coagulants at neutral pH. Ala can form metastable Al₁₃ at neutral pH, which has high positive charge on the surface and can be strongly adsorbed on negative particles, giving some increase in the zeta potential (Duan and Gregory, 2003). The zeta potential of Al₁₃ with BSA samples kept increasing with dosage addition due to the high positive charge on the surface of Al₁₃ (Fig. 3b), and the DOC removal efficiency reached the highest value when the zeta potential of flocs was close to the isoelectric point at 0.16 mmol/L without SA addition. This is the main process of the charge neutralization mechanism. Compared with BSA samples, the hydrolysis of Al₄ could be significantly affected by organic ligands for HA coagulation (Fig. 3a). Al₄ species would not substantially undergo hydrolysis and transform into Al₁₃ at low dosage initially but instead complex with HA, resulting in a slow increase of the zeta potential compared to BSA samples (Dempsey, 2006a). In this study, DOC removal was obtained in HA samples while zeta potentials were still negative regardless of the coagulants used (Fig. 3), and the coagulation mechanisms were suspected to be a combination of precipitate charge neutralization and entrapment/adsorption of organic matters onto metal precipitates. As the carboxyl groups of SA molecules can cause decomposition of Al₁₃ and affect the formation of Al₄, the increase of zeta potential in BSA became less significant as the concentration of SA increased, especially at low dosage. This was consistent with the DOC and turbidity removal.

### Table 1 – The strength factor (S₄) of HA-flocs and BSA-flocs during Ala and Al₁₃ coagulation under different concentrations of SA.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Sample</th>
<th>No SA</th>
<th>0.2 mg/L SA</th>
<th>0.5 mg/L SA</th>
<th>Percentage increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₄</td>
<td>HA</td>
<td>52.0</td>
<td>73.6</td>
<td>77.6</td>
<td>49.2</td>
</tr>
<tr>
<td></td>
<td>BSA</td>
<td>46.3</td>
<td>60.3</td>
<td>70.0</td>
<td>51.2</td>
</tr>
<tr>
<td>Al₁₃</td>
<td>HA</td>
<td>67</td>
<td>70.9</td>
<td>71.1</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>BSA</td>
<td>44.3</td>
<td>44.6</td>
<td>45.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

HA: humic acid; BSA: bovine serum albumin; SA: sodium alginate.

### Table 2 – The recovery factor (R) of HA-flocs and BSA-flocs during Ala and Al₁₃ coagulation under different concentrations of SA.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Sample</th>
<th>No SA</th>
<th>0.2 mg/L SA</th>
<th>0.5 mg/L SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₄</td>
<td>HA</td>
<td>70.8</td>
<td>96.3</td>
<td>43.7</td>
</tr>
<tr>
<td></td>
<td>BSA</td>
<td>47.7</td>
<td>31.9</td>
<td>18</td>
</tr>
<tr>
<td>Al₁₃</td>
<td>HA</td>
<td>79.5</td>
<td>91.9</td>
<td>53.3</td>
</tr>
<tr>
<td></td>
<td>BSA</td>
<td>31.2</td>
<td>22.9</td>
<td>20.1</td>
</tr>
</tbody>
</table>
(0.4 eV) in the characteristic peaks of tetrahedral Al or octahedral Al, as shown in Fig. 4. A shift less than 0.5 eV is within the range of the typical precision of the instrument.

As shown in Fig. 4a, the AlVI/AlIV ratios of HA flocs and BSA flocs in Ala coagulation were 3.1:1 and 1.5:1 respectively, suggesting the occurrence of tetrahedral Al (AlIV) on the surface of HA-flocs and BSA-flocs. As mentioned before, AlIV species could substantially transform into Al13 in situ which contains the AlIV structure in the absence of organic ligands (Lin et al., 2009). The metastable Al13 could convert to solid Al(OH)3 via the condensation of Al13 and retain the AlIV structure (Sposito, 1996). Therefore, the Al(OH)3-rich flocs contain a large amount of colloidal Al(OH)3 crystals with an AlIV center (Lin et al., 2009). Theoretically, the AlIV/AlIV ratio in Al13 molecules should be approximately 12:1 (Lin et al., 2014). The AlIV/AlIV ratios of HA flocs and BSA flocs were 3.1 and 1.5, indicating that voluminous Al13 do not exist and Al(OH)3 was the main Al species on the surface. Moreover, the conversion from AlIV to Al13 was slower than the formation of AlIV via complexation (Dempsey, 2006b) and the presence of organic ligands impeded the formation of AlIV. As HA molecules contain more organic ligands (carboxyl groups) than BSA molecules, the AlVI/AlIV ratio of HA flocs (3.1) was higher than that of BSA flocs (1.5). However, the AlVI/AlIV ratios in Al13-flocs were much different from AlIV-flocs, as shown in Fig. 4b. For Al13-flocs, the AlVI/AlIV ratio in BSA flocs was 11, which was very close to the theoretical value in Al13 molecules (12). This indicated that preformed Al13 species played an important role in coagulation. According to Lin et al. (2009), some outer octahedral structures could decompose from Al13 molecules during the formation of Al13 aggregates. In this study, due to the decrease in AlIV during Al13 aggregation, the AlVI/AlIV ratio was less than 12. By contrast, the AlVI/AlIV ratio in HA flocs was 22.1. This ratio was much higher than the theoretical ratio, which means that decomposition of the Al13 structure occurred in preformed Al13 species (Lin et al., 2014).

The interaction mechanisms of SA molecules with coagulants were different among Al species. As mentioned before, the metastable species Al13 could convert to solid Al(OH)3 via the condensation of Al13 and retain the AlIV structure (Sposito, 1996). However, there are many carboxyl structures in the SA molecule which can interact with AlIV and impede the conversion from AlIV to Al13 and the formation of AlIV. Compared to the absence of SA molecules, the increase in the AlVI/AlIV ratios of HA flocs (3.6) and BSA flocs (2.3) when 0.2 mg/L SA was added provides evidence that SA molecules can affect the reaction pathway of AlIV hydrolysis by complexation and impeding the formation of the AlIV structure (Fig. 4a). Nevertheless, the effect of SA molecules on Al13 was quite different. The addition of SA molecules can accelerate the dissolution of Al13 by complexation. Due to the decomposition of the Al13 structure, the AlVI/AlIV ratios of both HA flocs and BSA flocs increased to 22.6 and 12.5 with 0.2 mg/L SA addition, respectively (Fig. 4b). The change in ratios confirmed that the presence of SA molecules can result in the decomposition of the Al13 structure. The decomposition of the Keggin structure can explain why the charge neutralization ability of preformed Al13 species was decreased when SA was added, as discussed in Section 2.1.2. Therefore, SA molecules can affect the reaction pathway of Al13 hydrolysis by accelerating the dissolution of Al13.

2.3. Effect of SA molecules on floc properties

2.3.1. Breakage and regrowth of flocs

A series of jar tests were conducted to investigate the effect of SA concentration on floc growth and breakage as a function of dosage. The floc size and fractal dimension of flocs at different SA concentrations are shown in Fig. 5. The results demonstrated that SA gave apparent improvement in floc size regardless of which kind of coagulant was used, especially for HA samples. It can be seen that the growth rates increased with SA addition, and micro flocs aggregated into larger ones due to the bridging ability of SA.

As floc characteristics may influence membrane filtration, the strength factor (Sf) and recovery factor (Rf) were calculated using Eqs. (1) and (2) to evaluate floc strength and recoverability and shown in Table 1. The floc structures during floc
formation were investigated in terms of fractal dimension \( D_f \) and are shown in Fig. 5. It can be seen from Table 1 that the floc strength improved with SA addition during Al coagulation, especially for kaolin–HA and kaolin–BSA samples, with the percentage increases of 49.2\% and 51.2\%, respectively. The increase in floc strength was attributed to the chemical structure of SA. The structures of flocs formed by Al were needle-like, which were more open so that primary flocs could easily aggregate into larger ones through the bridging ability of SA, but Al\(_{13}\) aggregates had a denser structure and a smoother surface, which made it harder for flocs to contact with each other and grow into larger flocs through the bridging ability of SA when SA was added (Lin et al., 2009, 2014). The results in this study indicated that the influence on floc characteristics when SA was added as a contaminant was much different from that as a coagulant aid. Previous results showed that the percentage increases of \( S_f \) were lower than 20\% both in aluminum salts and PACl, when SA was added 30 sec later after the addition of Al coagulants (Zhao et al., 2012a, 2012b). This different phenomenon may due to the participation of SA molecules in the formation of primary flocs when SA molecules are taken as a contaminant. According to Jarvis et al. (2005), the floc strength is related to the strength and number of the bonds holding the floc together. Without SA, complexation and adsorption were the main interaction forces holding the flocs together during Al coagulation. However, the ability of cross-linking by SA provided another stronger type of bond for aggregation (Lee and Mooney, 2012), and resulted in significant improvement of floc strength. From Table 2, it can be seen that the recoverability

Fig. 7 – Images of original membrane and membrane fouled by different contaminants: (a) original membrane; (b) BSA; (c) BSA + 0.2 mg/L SA; (d) BSA + 0.5 mg/L SA; (e) HA; (f) HA + 0.2 mg/L SA; (g) HA + 0.5 mg/L SA.
of HA-flocs was significantly increased with low SA concentration (0.2 mg/L), but decreased dramatically as the concentration kept increasing to 0.5 mg/L. However, the recoverability of BSA-flocs decreased with SA addition at all concentrations. This may be attributed to the reason that a higher dose of negatively charged SA (about $-88.0 \text{ mV}$) would inhibit micro flocs from growing into bigger ones due to strong repulsive forces between micro flocs and the SA molecules. As the molecular weight and size of BSA were larger than those of HA, the effect of charge repulsion on BSA was much more apparent.

2.3.2. Floc structural analysis

Changes in the $D_f$ of flocs under different SA concentrations with Al and Al$_{13}$ are presented in Fig. 5. The $D_f$ of flocs was derived from the relationship between the scattered light intensity $I$ and the scattering vector $Q$ as shown in Eqs. (3) and (4). From Fig. 5a and Fig. 5b it can be seen that, for kaolin-HA samples, the presence of SA gave flocs with denser structure as reflected by the higher $D_f$ values during the coagulation process. This result was much different from that reported by previous studies, in which primary coagulants plus SA gave flocs with more highly branched and loosely bound structures (Zhao et al., 2012a, 2012b). This may due to the participation of SA molecules in Al hydrolysis and the formation of primary flocs. As discussed above, for HA, complexation was the main way to form primary flocs due to the plentiful ligands in HA molecules. Due to the carboxyl groups and negative charge on the surface, the complexation process and charge neutralization was enhanced when SA was introduced in the coagulation process (Guo et al., 2015). Together with the bridging ability of SA molecules, more compact flocs with higher $D_f$ value were produced. However, the value of $D_f$ decreased at higher SA concentration (0.5 mg/L) during Al$_{13}$ coagulation due to the repulsive force.

As discussed in Section 2.1, sweep and charge neutralization were the main coagulation mechanisms during Al$_4$ and Al$_{13}$ coagulation for kaolin–BSA samples, respectively. Based on the different coagulation mechanisms, the fractal dimension varied in the following sequence: sweep $>$ charge neutralization $>$ bridging (Li et al., 2006). When sweep coagulation dominated, the particles were enmeshed in the precipitate of amorphous aluminum hydroxide; therefore, the floc structure was most compact. This can explain why the value of $D_f$ during Al$_4$ coagulation was higher (Fig. 5c and Fig. 5d). However, amorphous aluminum hydroxide is the main Al species in kaolin–BSA samples during Al$_4$ coagulation at neutral pH, so the adsorption and bridging of SA molecules on the surface of amorphous aluminum hydroxide resulted in a

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**Fig. 8** – The effect of SA concentration on normalized flux with different Al species: (a) HA samples; (b) BSA samples.

**Fig. 9** – Images of membrane fouled by HA-Al$_{13}$ flocs with different SA concentrations: (a) None; (b) 0.2 mg/L SA; (c) 0.5 mg/L SA.
more open structure. That was the reason why \( D_1 \) values decreased with SA addition in Al\(_4\) flocs (Fig. 5c). Similar phenomena have also been found in other studies (Wu et al., 2002; Zhao et al., 2012b). Charge neutralization was the main coagulation mechanism for BSA during Al\(_{13}\) coagulation. As the carboxyl groups in the alginate backbone became protonated (Lee and Mooney, 2012), the charge neutralization process was enhanced with SA addition and resulted in denser flocs with higher \( D_1 \) (Fig. 5d).

### 2.4 Membrane fouling

SA has been used as a model microbial polysaccharide in membrane fouling research (Xie et al., 2017); the impact of SA concentration on normalized flux \( (J/J_0) \) is presented in Fig. 6. The addition of SA molecules caused a visible decrease in normalized flux, especially in BSA samples. According to previous studies, SA can cause severe membrane fouling (Kim and Dempsey, 2013). When SA was added into HA or BSA samples, deposition of a cake layer occurred on the membrane surface with low SA concentration, and the negatively charged SA chains were most likely separated, allowing their migration inside the membrane pores (Charfi et al., 2017). The images obtained by scanning electron microscopy confirm the fouling pattern. As shown in Fig. 7, the morphology of the cake layer on the surface of an HA-fouled membrane (Fig. 7e) was different from that of a BSA-fouled membrane (Fig. 7b), which was more porous. When SA molecules were added, the cake layer became more compact and the porosity decreased (Fig. 7c–d and Fig. 7f–e) which led to a significant decline in membrane flux.

As presented in Fig. 6, both HA and BSA cause significant membrane fouling, and the flux decline was about 70% percent in the presence of SA. Therefore, pre-coagulation was applied to alleviate membrane fouling. After water samples were coagulated by Al\(_{13}\) and Al\(_4\) at the optimal dosage, the coagulated waters were filtered through the membrane directly without sedimentation. The result (Appendix A Fig. S2) showed that coagulation can effectively alleviate membrane fouling and increase flux compared to direct filtration. The flocs, which were larger than the membrane pores, were intercepted by the membrane surface to form a cake layer. According to previous studies (Feng et al., 2015; Kimura et al., 2015), the fractal dimension and strength factor of flocs have important effects on membrane fouling. The effect of SA on the relation between floc properties and membrane fouling is discussed in this section. The influence of SA on membrane fouling with different Al species of HA or BSA flocs is compared in Fig. 8.

As shown in the SEM image (Fig. 9), flocs firstly deposited on the surface and formed a sponge-like structure, which was the support layer, and then flocs kept accumulating to form the cake layer. Therefore, the strength of the sponge-like structure determined the ability of the cake layer to resist pressure and remain porous. Compared with BSA-flocs, the floc strength of HA-flocs was stronger (Table 1) and resisted pressure better, so the fractal dimension of flocs was more important in affecting membrane fouling for HA-flocs. The variation of flux was consistent with the variation in fractal dimension, as mentioned in Fig. 5. Membrane flux decreased as the concentration of SA increased with HA-flocs (Fig. 8a), except for Al\(_{13}\). In the presence of SA molecules, the complexation process was enhanced, which would result in higher fractal dimension for HA-flocs, which meant a tighter floc structure, and finally led to more a compact cake layer on the surface (Appendix A Fig. S3). However, due to the electrostatic repulsion between SA molecules, the value of floc \( D_1 \) decreased in HA-Al\(_{13}\) flocs with 0.5 mg/L SA, which meant a more porous cake layer, and improvement in flux decline was obtained. The sponge-like structure of the cake layer is shown distinctly by the SEM image in Fig. 9, and an obvious change in porosity can be observed from Fig. 9a to Fig. 9c that was consistent with \( D_1 \). However, the floc strength of BSA-flocs without SA addition was weak, which means the sponge-like support was weak and easily compressed, causing pore blocking. As presented in Table 1, the strength factor of BSA-flocs increased with the addition of SA due to the carboxyl groups in SA, which can complex with Al species and lead to bridging ability and better strength, especially during Al\(_{13}\) coagulation. A previous study indicated that cake layers formed by flocs with improved strength were not easily compressed and less porous (Feng et al., 2015). Due to the increase in floc strength, even though the floc \( D_1 \) also increased with SA addition, the results in Fig. 8b indicated that less flux decline was obtained, and greater porosity can be observed on the surface of a membrane fouled by BSA-Al\(_{13}\) with 0.5 mg/L SA in the image in Appendix A Fig. S5. Therefore, floc strength became the main factor that affects membrane fouling by BSA-flocs. In conclusion, the variation in floc properties with SA addition was different between HA and BSA due to different coagulation mechanisms and hydrolysis pathways of Al species.

### 3. Conclusion

The interfacial interaction between SA molecules and Al species and the role SA played during floc formation were investigated. Moreover, the influence of SA on alleviating membrane fouling when combined with coagulation was also assessed. It could be concluded that SA can react with aluminum coagulants and affect coagulation performance and membrane fouling, which is significant for quality control and advanced treatment of surface water. The following conclusions can be drawn: (1) SA molecules can participate in the pathway of Al hydrolysis and affect the Al\(^{3+}/\text{Al}^{3+}\) ratios on the surface of flocs by accelerating the decomposition of the Al\(_{13}\) structure. The floc structure was more compact in kaolin-HA samples due to complexation by SA molecules, as the values of \( D_1 \) were increased markedly. (2) SA can participate in the formation of primary flocs and the bridging ability of SA provides another type of bond for aggregation, resulting in significant improvement of floc strength and size. Floc recoverability was decreased in BSA-flocs due to the strong repulsive force between micro flocs and SA molecules. (3) Floc properties have effects on membrane fouling through affecting the structure of the cake layer on the surface. Floc strength was the main factor that affected membrane fouling by BSA-flocs, while the fractal dimension of flocs was more important for HA-flocs.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2019.02.022.

REFERENCES


