



Coagulation performance evaluation of sodium alginate used as coagulant aid with aluminum sulfate, iron chloride and titanium tetrachloride

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ABSTRACT

Coagulation–flocculation was applied to humic acid–kaolin synthetic water samples, using sodium alginate (SA) as a coagulant aid with primary coagulants used: aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), iron chloride (FeCl_3) and titanium tetrachloride (TiCl_4). The corresponding dual-coagulants were denoted as $\text{Al}_2(\text{SO}_4)_3$ –SA, FeCl_3 –SA and TiCl_4 –SA by dosing SA 30 s after primary coagulants addition. Coagulation performance was investigated in terms of turbidity reduction and dissolved organic carbon (DOC) removal and the flocs were characterized in terms of size, growth rate, strength, recoverability and structure through on-line monitoring of the coagulation process using Mastersizer 2000. The results showed that dual-coagulants could remove HA effectively with appropriate SA doses. Primary coagulants plus SA exhibited an apparent improvement in both floc growth rate and floc size. Besides, floc recoverability was significantly increased. It was suspected that SA addition may have a positive effect on the solid/liquid separation process. However, dual-coagulants gave the flocs with more open structure.

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1. Introduction

Humic acid (HA) has been recognized as a significant generator of disinfection-byproducts (DBPs) [1–3] and coagulation and flocculation processes are commonly used to remove HA and colloidal particles [4]. Flocculating agents are generally divided into three groups: (1) inorganic flocculants, such as aluminum sulfate, polyaluminum chloride, ferric chloride and polyferric sulfate; (2) organic synthetic flocculants, such as polyacrylamide derivatives and polyethylene imine; and (3) naturally occurring flocculants, such as chitosan, sodium alginate (SA) and bioflocculant [5,6]. Chemical flocculants resulted in some health and environmental problems, such as Alzheimer's disease [7]. Polyacrylamide derivatives and the acrylamide monomer are neurotoxic, carcinogenic and non-biodegradable in the nature [8]. The main drawback of using inorganic and organic synthetic flocculants is that they usually generate a large amount of sludge, which requires disposal either at landfills and/or dumping into the ocean. Recently, titanium tetrachloride (TiCl_4) was used as a coagulant, the most significant advantage of which is the possibility of recovering the sludge to produce a valuable by-product namely titanium dioxide (TiO_2) [9]. TiO_2 is the most widely used metal oxide, whose applications include photocatalysts, cosmetics, paints, electronic paper, and solar cells

[10,11]. Therefore, recycling of Ti-flocculated sludge not only produces TiO_2 , but also solves the problem of disposal of sludge generated from water and wastewater treatment plants. The naturally occurring flocculants are considered safe and biodegradable [12]. However, so far none of the bioflocculants has been put into practical applications because of the low flocculating capacity, low yields and high production cost [13,14].

To overcome these limitations, dual-coagulants (naturally occurring flocculant used as coagulant aid with inorganic coagulants) are used as a cost reduction method. It reduces the dose of naturally occurring flocculants together with the enhancement of the flocculation activity. Moreover, the risk induced by the chemical flocculants can be reduced as their doses could be cut down. Yang et al. [15] studied the treatment of kaolin suspension by the composite flocculant of MBFGA1 and polyaluminum chloride (PAC) using response surface methodology. Until now, there have been few reports on the effect of SA used as coagulant aid with inorganic coagulants, such as $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 and TiCl_4 .

Characteristics of flocs after flocculation cause a critical effect on the solid/liquid separation process [16]. Boller and Blaser [17] showed that small particles generally have lower removal efficiency by flocculation. Floc strength and recoverability are also considered important parameters for overall process optimization as flocculation process is often prevalent with regions of high shear force during the separation technique such as the removal of aggregated particles [18]. Some researchers found that regrowth of chalk aggregates could be reversible after high shear force was applied [19]. Chaignon et al. reported that the

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flocs formed by charge neutrality had complete recoverability [20]. Fractal dimension of flocs is also an important parameter influencing solid/liquid separation, since it corresponds to the space-filling capacity of an object and influences floc density [21,23]. It has been reported that the floc properties, such as density and settling velocity, are non-integral function of size, but exhibit the structure of flocs [22].

The aim of this study was to evaluate the effect of SA used as a coagulant aid with $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 and TiCl_4 . Three dual-coagulants, $\text{Al}_2(\text{SO}_4)_3$ -SA, FeCl_3 -SA and TiCl_4 -SA, were prepared by dosing SA at 30 s after the addition of $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 and TiCl_4 . The coagulation performance of the dual-coagulants was investigated in comparison with that of $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 and TiCl_4 alone in terms of residual turbidity and dissolved organic carbon (DOC) removal as well as zeta potential. In addition, the evolution of floc size vs. coagulation time was measured by a laser diffraction instrument. Floc aggregates were characterized in terms of floc size, growth rate, fractal dimension, breakage and subsequent regrowth potential. The relationship between floc properties and coagulation mechanisms was also discussed.

2. Experimental

2.1. Water used in this study

A stock solution of HA was prepared by dissolving 1.0 g of HA in 0.01 mol/L sodium hydroxide (NaOH) solution under continuous stirring for 30 min. Coagulation experiments were performed with synthetic water containing 10 mg/L of HA prepared in deionized water and tap water [24]. The initial turbidity was adjusted to approximately 15 ± 0.2 NTU by adding kaolin. The UV_{254} absorbance, DOC, temperature and pH of the suspension was $0.430 \pm 0.020 \text{ cm}^{-1}$, $5.000 \pm 0.500 \text{ mg/L}$, $18.0 \pm 1.0^\circ\text{C}$ and 78.38 ± 0.03 , respectively.

2.2. Coagulants

TiCl_4 stock solution (20%, density = 1.148 g/mL) was obtained from Photo & Environment Technology Co. Ltd (South Korea), and was used as received without any further purification. Stock solutions of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were prepared at a concentration of 1 g/L by Al and 2 g/L by Fe, respectively. SA was provided by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Zeta potential of SA was about -88.0 mV . Stock solution of SA was prepared at a concentration of 1.0 g/L and was stored in 4°C . Deionized water was used for all the reagents preparation.

2.3. Jar test

Standard jar tests were conducted on a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) at $18 \pm 1^\circ\text{C}$ of room temperature. During the rapid stirring of 200 rpm, predetermined amount of coagulants were dosed to give a certain $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 and TiCl_4 concentration. Doses of $\text{Al}_2(\text{SO}_4)_3$ ranged from 0.5 to 3.0 mg/L as Al, while doses of FeCl_3 and TiCl_4 ranged from 2.0 to 12.0 mg/L as Fe and Ti, respectively. Bratby reported that when organic polymer was used as coagulant aids, best results were obtained when the polymer was added after the addition of the primary coagulant [25]. In the comparative experiment, $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 and TiCl_4 , respectively, was added first at the start of rapid mixing phase (200 rpm) and followed by SA addition after 30 s. The dual-coagulants were denoted as $\text{Al}_2(\text{SO}_4)_3$ -SA, FeCl_3 -SA and TiCl_4 -SA, respectively. Rapid mixing (200 rpm) of 1 min continued after the coagulants addition, then, the stirring speed was changed to 40 rpm with duration of 15 min, followed by 15 min of quiescent settling. After sedimentation, supernatant samples were collected using a syringe from about 2 cm below the water surface for subsequent measurements. Collected samples were prefiltered through a $0.45 \mu\text{m}$ fiber membrane before testing for DOC (measured by a Shimadzu

TOC-VCPH analyzer), while the turbidity was measured without filtration using a 2100P turbidimeter (Hach, USA) and zeta potential was analyzed with a Zetasizer 3000HSa (Malvern Instruments, UK).

2.4. On-line monitoring of floc size

The dynamic floc sizes were measured using a laser diffraction instrument (Mastersizer 2000, Malvern, UK). The suspended flocs were monitored through the optical unit of the Mastersizer and transferred back into the jar by a peristaltic pump (LEAD-1, Longer Precision Pump, China) with a tube of 5 mm internal diameter. Size measurements of the formed flocs were taken every 0.5 min during jar test process and the corresponding data were recorded automatically.

2.5. Floc breakage and regrowth

The aggregated flocs after each flocculation were exposed to shear force at 200 rpm for 5 min after the slow mixing phase. After the shear mixing phase, slow mixing was reintroduced for a further 20 min at 40 rpm. Floc sizes were monitored as stated in Section 2.4. Strength factor (S_f) and recovery factor (R_f) to compare the floc strength and recoverability were calculated as follows [4,26,27]:

$$S_f = \frac{d_2}{d_1} \times 100 \quad (1)$$

$$R_f = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \quad (2)$$

where d_1 is the average floc size of the steady phase before breakage or shear phase, d_2 is the floc size after the floc breakage period, and d_3 is the floc size after regrowth to the new steady phase.

Here, the S_f indicates resistance of the formed flocs to shear force, while the R_f refers to the re-aggregation of flocs to form larger flocs again after being subjected to shear breakage.

2.6. Floc fractal dimension

Light scattering method is widely used for the determination of aggregate mass fractal dimension. Details in the theory of the mass fractal dimension have been reported in a few literatures [18,28]. The light scattering technique involves measurement of light intensity I as a function of the scatter vector Q . The vector is defined as the difference between the incident and scattered wave vectors of the radiation beam in the medium [28], which is given by Eq. (3):

$$Q = \frac{4\pi n \sin(\theta/2)}{\lambda} \quad (3)$$

where n , θ , and λ are the refractive index of the medium, the scattered angle, and the wavelength of radiation in vacuum, respectively.

For independently scattering aggregates, the relationship among I , Q and the fractal dimension D_f can be represented by Eq. (4):

$$I \propto Q^{-D_f} \quad (4)$$

D_f is the fractal dimension and can be determined by the slope of a plot of I as a function of Q on a log-log scale. High D_f means the primary particles in an aggregate are arranged compactly, while low D_f results from highly branched and loosely bound structure.

3. Results and discussion

3.1. Effect of SA on coagulation performance

In this study, when SA was used as coagulant alone, coagulation performance with various SA dosages was investigated, with the

results suggesting that the turbidity and DOC removal was barely observed and the flocs formed were hardly visible (data not shown). When SA was used as coagulant aid with different coagulants, the dual-coagulants were obtained by adding SA 30 s after the primary coagulants addition, and the effect of dosing sequence of the coagulants on coagulation performance was not investigated. That may be because i) when SA was added firstly, the system was exposed to a higher absolute value of zeta potential, since both HA-kaolin particles and SA were negatively charged with the zeta potential of ca. -17 mV and -88.0 mV, respectively; ii) SA may partially act as impurities like HA that could need to be coagulated by $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 and TiCl_4 , which may result in problematic coagulation of the colloids with SA due to strong repulsion between them. This was also the reason why the coagulation performance with SA alone was barely observed.

Coagulation performance of different coagulants was evaluated in terms of residual turbidity and DOC removal as well as zeta potential and the results are shown in Fig. 1. In this study, dose range of 0.5–

3.0 mg/L was selected for $\text{Al}_2(\text{SO}_4)_3$, while dose range of 2.0–12.0 mg/L was for both FeCl_3 and TiCl_4 , as no significant increase in removal efficiency was observed with further addition of the coagulants. Doses of SA varied from 0.5 to 2.0 mg/L. The main finding was that the DOC removal was not enhanced with SA addition compared with $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 and TiCl_4 when they were used alone. For $\text{Al}_2(\text{SO}_4)_3$ and FeCl_3 , the increase or decrease in the DOC removal was barely observed, while, for TiCl_4 , the DOC removal presented comparatively apparent reduction with SA addition. Specifically, when TiCl_4 doses of 2.0 and 4.0 mg/L were used combined with 0.5 mg/L of SA, the DOC removal decreased from 39.6% and 55.7% to 23.0% and 36.8%, respectively. And, further decrease in DOC removal was observed when TiCl_4 was used combined with SA of 2.0 mg/L. This was not consistent with the previous reports that better removal performance could be achieved when polymer is used in combination with conventional coagulants [29–31]. In addition, it can be seen from Fig. 1 that the residual turbidity increased to different degrees with

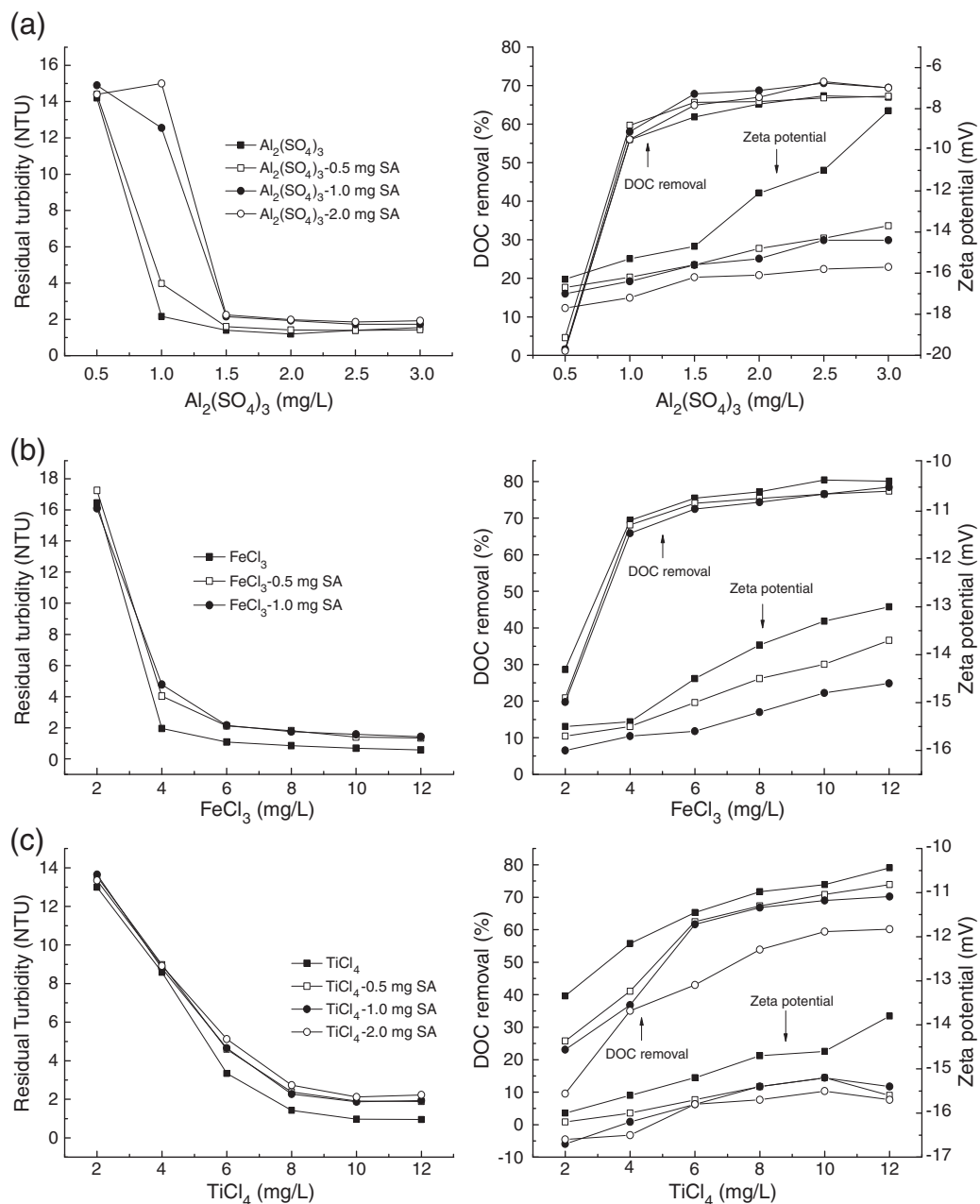


Fig. 1. Effect of SA doses on residual turbidity, DOC removal and zeta potential with different coagulants: (a) $\text{Al}_2(\text{SO}_4)_3$; (b) FeCl_3 ; (c) TiCl_4 .

SA addition for different coagulants. The apparent decrease in DOC removal when 2.0 mg/L SA was used combined with TiCl_4 could be explained as follows: (i) the negatively charged particles may inhibit the flocs formation due to the mutual repulsion, which may further result in the poor coagulation performance; (ii) the residual SA, which was essentially a kind of organic polymer, might be another

considerable reason for the decrease of DOC removal when SA was overdosed. The high DOC removal efficiency by the dual-coagulants could be attributed to the bridging ability of SA molecules. Microflocs formed when the primary coagulants were added in the initial rapid mixing stage. When SA was dosed, it quickly adsorbed on the surface of the microflocs and large flocs gradually formed due to the bridging ability of SA. Therefore, like coagulant agents, doses of SA as coagulant aid should also be optimized. Lower SA doses meant that no enough chain molecules to adsorb the microflocs and to further bridge between them, while higher doses of SA may increase the zeta potential to a higher absolute value, which further resulted in the particles repulsion. This may explain why the residual turbidity of the effluent showed certain increase with SA addition, because the particles with repulsion force were difficult to settle down. Only appropriate doses of SA may possibly have positive effect on coagulation performance.

Fig. 1 also shows the relationship of zeta potential vs. different coagulants and the corresponding dual-coagulants. It can be observed that, FeCl_3 and TiCl_4 flocs showed a slight increase in zeta potential with the increasing coagulant dosages, while the increase in zeta potential was quite sharp for $\text{Al}_2(\text{SO}_4)_3$. Flocculation with $\text{Al}_2(\text{SO}_4)_3$ has been suggested to be achieved by charge-neutralization and the bridge-formation mechanism [32]. In this study, the high HA removal efficiency by $\text{Al}_2(\text{SO}_4)_3$ was achieved at the optimal dosage of 1.5 mg/L, which probably due to bridge-aggregation, since zeta potential was rather negative (approx. -15 mV) under this concentration. As to FeCl_3 and TiCl_4 , charge neutralization was not the dominant coagulation mechanism due to the low zeta potential of flocs after coagulation and sedimentation. In case of FeCl_3 , adsorption might play an important role since Cheng et al. [33] reported that the fraction of HA removed by charge neutralization was less than that removed by adsorption in the pH range of 7.5–9 and pH of the synthetic water was about 8.38. In case of TiCl_4 , adsorption, entrapment, sweep and complexation were the possible dominant mechanisms [34,35]. That could be one of the reasons why FeCl_3 and TiCl_4 achieved better organic matter removal even though the charge neutralization was comparatively weak. In case of the dual-coagulants, zeta potentials of flocs decreased with increasing SA doses for all the three coagulants. When primary coagulants ($\text{Al}_2(\text{SO}_4)_3$, FeCl_3 and TiCl_4) were added in water samples, it was suspected that the primary coagulants hydrolyzed instantaneously. The hydrolyzates reacted with HA to form the negatively charged

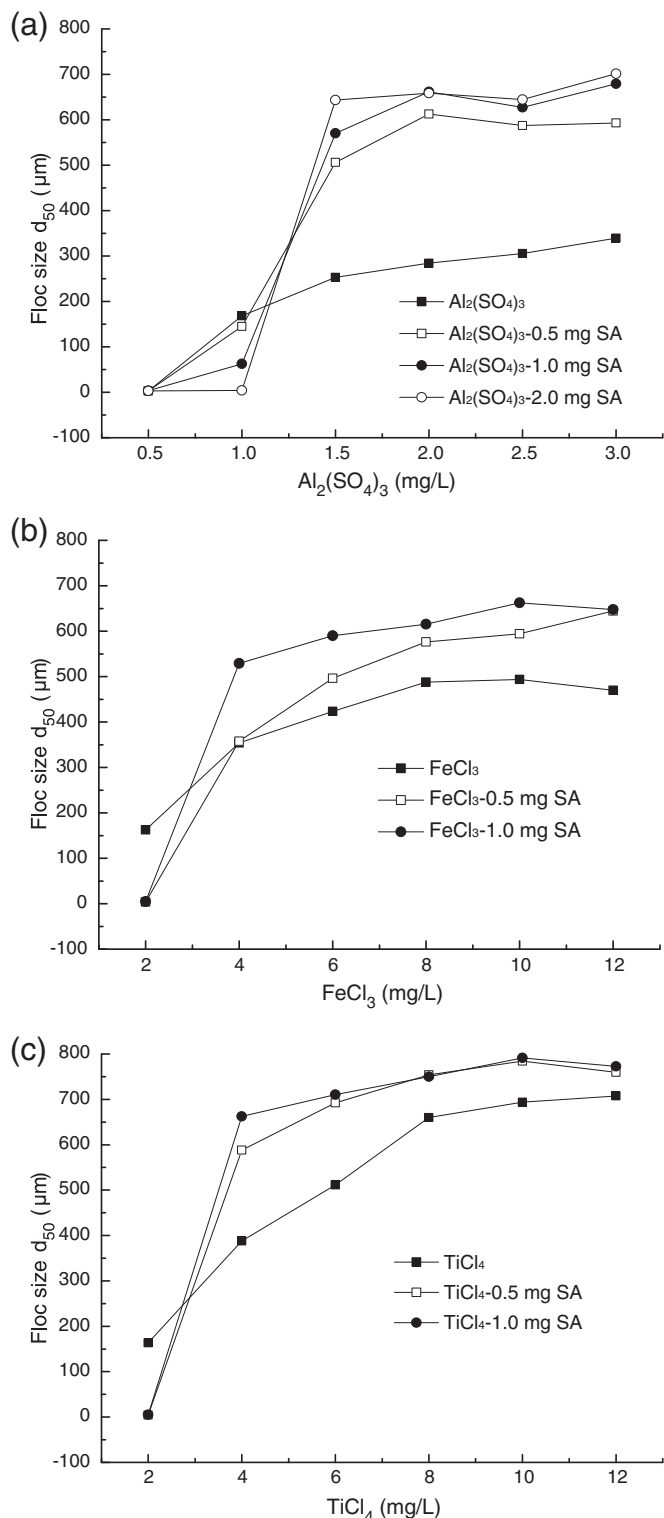


Fig. 2. Variation of floc size d_{50} with different coagulants as a function of coagulant dose during floc growth phase: (a) $\text{Al}_2(\text{SO}_4)_3$; (b) FeCl_3 ; (c) TiCl_4 .

Table 1

Grow rates of HA flocs formed by $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 and TiCl_4 combined with different SA doses in floc formation processes.

Coagulant dose (mg/L)	Floc grow rate ($\mu\text{m}/\text{min}$)			
	$\text{Al}_2(\text{SO}_4)_3$	$\text{Al}_2(\text{SO}_4)_3$ -0.5 mg SA	$\text{Al}_2(\text{SO}_4)_3$ -1.0 mg SA	$\text{Al}_2(\text{SO}_4)_3$ -2.0 mg SA
1.5	25.3	40.5	40.7	47.7
2.0	37.9	61.3	66.1	82.3
2.5	50.9	97.9	104.5	107.4
3.0	52.2	98.8	150.9	155.8
	FeCl_3	FeCl_3 -0.5 mg SA	FeCl_3 -1.0 mg SA	
4	29.5	46.7	47.1	
6	60.5	82.7	89.2	
8	88.7	96.1	112.5	
10	98.7	118.8	165.6	
12	117.4	214.9	215.8	
	TiCl_4	TiCl_4 -0.5 mg SA	TiCl_4 -1.0 mg SA	
4.0	32.3	46.9	47.4	
6.0	60.8	115.4	177.6	
8.0	101.5	167.6	214.3	
10.0	231.2	261.5	263.9	
12.0	283.0	303.8	309.2	

complex, or part of the primary coagulants hydrolyzed to form $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$ and $\text{Ti}(\text{OH})_4$ flocs. The complex and $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$ and $\text{Ti}(\text{OH})_4$ flocs constituted the microflocs in the initial stage of rapid mixing. When the highly negatively charged SA was dosed, it quickly adsorbed on the surface of the microflocs, resulting in the higher absolute zeta potential values of the flocs (Fig. 1) due to adsorption of the SA molecules on the surface of the microflocs.

3.2. Effect of SA on floc characteristics

Floc formation, breakage and re-formation with different coagulants were monitored using Mastersizer 2000. The same general trend was seen for d_{10} , d_{50} and d_{90} floc sizes, and d_{50} (the 50 percentile floc size) was selected as represent floc size.

3.2.1. Dynamic analysis of floc formation process

The suspensions was stirred at 200 rpm for 1 min after the coagulants addition, followed by slow stirring at 40 rpm for 15 min (no significant change in the floc size and thus no further floc growth occurred after 15 min of slow stirring). Variation of the floc size in steady state and floc growth rate vs. coagulant dose was investigated as suggested by Wang et al. [36], and the results are shown in Fig. 2 and Table 1. From Fig. 2, it can be seen that the floc size increased with increasing coagulant doses for all the three coagulants and the corresponding dual-coagulants, and the primary coagulants plus anionic polymer SA exhibited apparent improvement in floc size under certain coagulant concentrations regardless of which kind of coagulant was used. The floc sizes increased from 253 μm , 423 μm and 511 μm to 570 μm , 580 μm and 710 μm , respectively, when 1.5 mg/L of $\text{Al}_2(\text{SO}_4)_3$ and

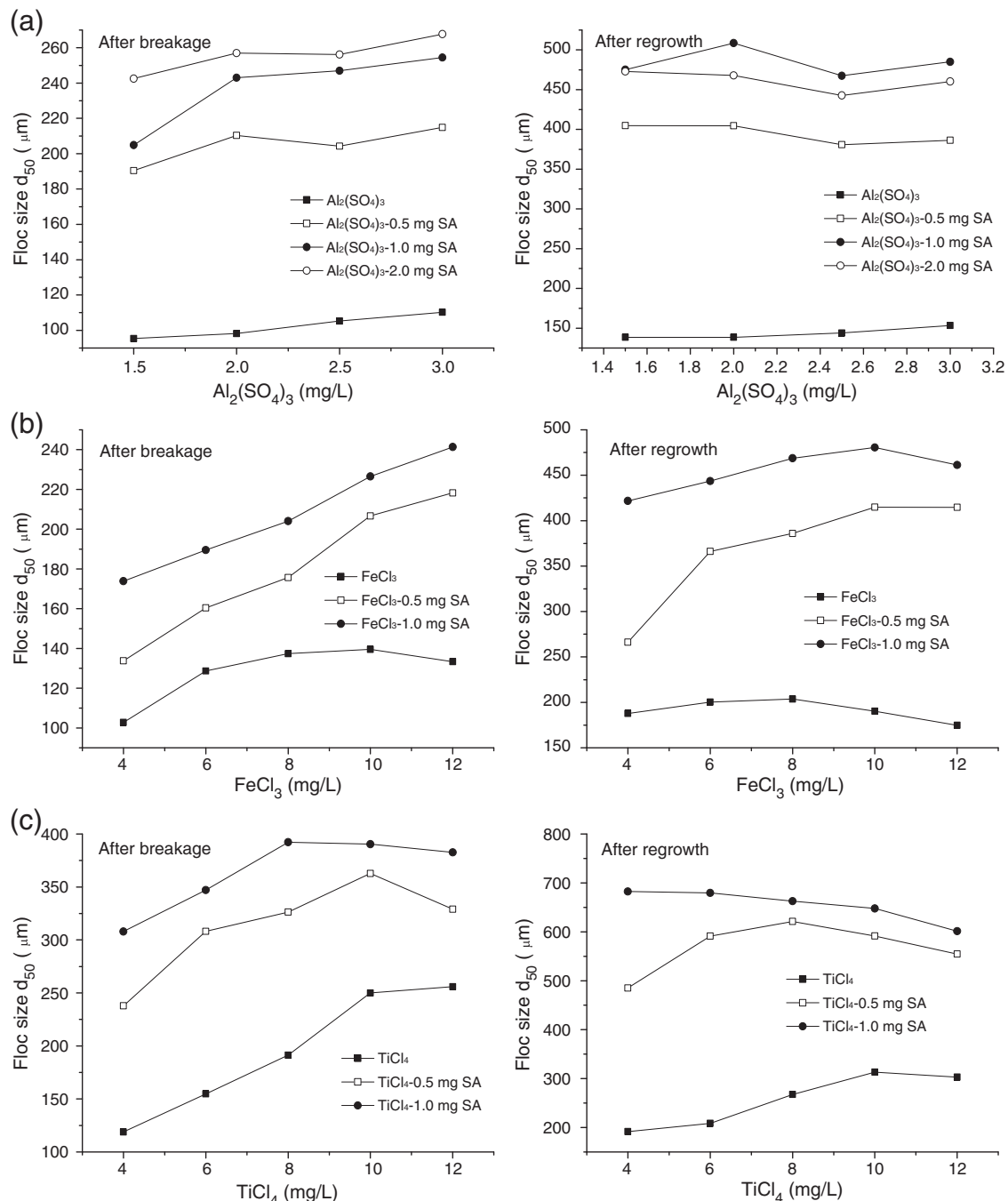


Fig. 3. Effect of SA on floc size with (a) $\text{Al}_2(\text{SO}_4)_3$, (b) FeCl_3 and (c) TiCl_4 and as a function of coagulant dose after floc breakage and regrowth.

6.0 mg/L of FeCl_3 and TiCl_4 were used combined with 1.0 mg/L SA. However, when 2.0 mg/L of FeCl_3 and TiCl_4 were used with SA, the flocs growth was hardly observed, and floc sizes decreased with increasing SA doses when 1.0 mg/L of $\text{Al}_2(\text{SO}_4)_3$ was used. In this study, a steady-state size of flocs did not appear within the coagulation time investigated when 0.5 and 1.0 mg/L of $\text{Al}_2(\text{SO}_4)_3$, 2.0 mg/L of FeCl_3 and TiCl_4 were used. Therefore, the growth rates of flocs formed by the above concentrations were not calculated in Table 1. In this study, floc growth rate was denoted as the slope of rapid growth region and was calculated in the same way as previously described [37]:

$$\text{Growth rate} = \frac{\Delta \text{size}}{\Delta \text{time}} \quad (5)$$

It can be observed from Table 1 that the dual-coagulants gave obviously faster floc formation within the dosages investigated. Also, the floc growth rates increased not only with increasing SA doses but also with coagulant doses, regardless of the coagulants used. When 1.0 mg/L SA was used as coagulant aid with 1.5 mg/L of $\text{Al}_2(\text{SO}_4)_3$, 2.0 mg/L of FeCl_3 and TiCl_4 , the floc growth rates increased by 61.0%, 47.5% and 192.0%, respectively.

The results mentioned above indicated that i) the negatively charged SA could result in the repulsion among microflocs, for which reason, SA inhibited the microflocs from growing into bigger ones and, therefore, reduced the floc growth rate and floc size; ii) the adsorption and bridge ability of SA could produce a positive effect on floc growth rate and floc size. Ray and Hogg [38] also reported that flocs produced by bridging flocculation can be much larger than those formed simply by charge neutralization and hence further aggregation. The analysis above showed that the doses of SA used as coagulant aid should be optimized, which corresponded well with the conclusions obtained in Section 3.1. However, it should be noted that doses of the primary coagulants must also be optimized even though with the same SA addition. For example, in case of TiCl_4 , TiCl_4 doses of 2.0 and 4.0 mg/L yielded the flocs with sizes of 163 μm and 388 μm , respectively. When TiCl_4 was used with 1.0 mg/L SA, growth rate of the flocs formed by 4.0 mg/L of TiCl_4 increased from approx. 32.3 $\mu\text{m}/\text{min}$ to 46.9 $\mu\text{m}/\text{min}$ with the resulted floc size of ca. 662.4 μm . While the flocs formed by 2.0 mg/L of TiCl_4 combined with 1.0 mg/L SA were hardly observed to naked eyes.

3.2.2. Floc breakage and floc recovery

Floc growth tests were programmed similarly as aforementioned, and the floc size significantly increased after floc growth period, suggesting that the appropriate balance between floc growth and breakage reached [39]. After 15 min of the floc growth period at 40 rpm, the shear force was introduced by increasing the mixing speed up to 200 rpm for 5 min. Then, the original slow stir speed of 40 rpm was reintroduced for 15 min for floc regrowth. In this section, 1.5 to 3.0 mg/L of $\text{Al}_2(\text{SO}_4)_3$ and 4.0 to 12.0 mg/L of FeCl_3 and TiCl_4 were selected for floc properties investigation. Fig. 3 shows the variation of floc size with (a) $\text{Al}_2(\text{SO}_4)_3$, (b) FeCl_3 and (c) TiCl_4 and the corresponding dual-coagulants as a function of coagulant doses after floc breakage and floc regrowth. It can be clearly seen that dual-coagulants yielded the flocs with larger sizes after both floc breakage and regrowth periods, and size of the flocs increased with increasing SA doses except the condition that when 2.0 mg/L of SA was used in combination with $\text{Al}_2(\text{SO}_4)_3$, improvement of floc size decreased after floc regrowth period, which might be ascribed to the repulsion forces between particles caused by the overdosed anionic polymer SA.

Aggregates formed by coagulation were not uniform in size after floc growth phase, and varied over a wide range after floc breakage and floc regrowth. To investigate floc variations in detail, floc S_f and R_f were calculated using Eqs. (1) and (2) to interpret the floc strength and recoverability (Table 2). The increased percentages were calculated by comparison floc S_f s and R_f s of the dual-coagulants

Table 2
Comparison of floc S_f and R_f with different coagulants.

Coagulant dose (mg/L)	$\text{Al}_2(\text{SO}_4)_3$	$\text{Al}_2(\text{SO}_4)_3$ –0.5 mg SA	$\text{Al}_2(\text{SO}_4)_3$ –1.0 mg SA	$\text{Al}_2(\text{SO}_4)_3$ –2.0 mg SA	Increased percentage (%)
S_f					
1.5	37.7	37.6	37.9	37.7	0.5
2.0	34.5	34.3	36.7	39.0	6.4
2.5	34.5	34.8	39.4	38.2	14.2
3.0	32.5	36.2	37.5	38.2	15.4
R_f					
1.5	27.4	67.9	73.9	57.5	169.7
2.0	21.7	48.3	63.4	52.5	192.2
2.5	19.2	46.1	58.0	49.4	202.1
3.0	18.8	45.4	54.3	44.4	188.8
S_f					
	FeCl_3	FeCl_3 –0.5 mg SA	FeCl_3 –1.0 mg SA		
4	29.0	37.4	32.8	13.1	
6	29.4	32.3	34.1	16.0	
8	28.1	30.5	33.2	18.1	
10	28.3	34.8	34.2	20.8	
12	28.4	33.9	37.3	31.3	
R_f					
4	33.8	59.1	69.7	106.2	
6	24.3	61.3	60.9	150.6	
8	18.9	52.5	64.4	240.7	
10	14.3	53.8	58.3	307.7	
12	12.3	46.1	54.1	339.8	
S_f					
	TiCl_4	TiCl_4 –0.5 mg SA	TiCl_4 –1.0 mg SA		
4.0	30.6	40.5	46.5	52.0	
6.0	30.3	44.5	48.9	61.4	
8.0	29.0	43.3	52.3	80.3	
10.0	36.0	46.2	49.3	36.9	
12.0	36.2	43.3	49.5	36.7	
R_f					
4.0	27.0	52.0	105.7	291.5	
6.0	15.1	61.4	91.5	506.0	
8.0	16.3	80.3	75.6	363.8	
10.0	14.2	36.9	64.1	351.4	
12.0	10.4	36.7	56.1	439.4	

(with 1.0 mg/L SA used as coagulant aid) with those of the coagulants used alone. It was found from Table 2 that the floc recoverability was significantly improved with SA addition no matter which kind of coagulant was used, as reflected by the high increased percentages of floc R_f s. As to the floc S_f s, the increased percentages were not that obvious as floc R_f s. Compared with the $\text{Al}_2(\text{SO}_4)_3$ –SA and FeCl_3 –SA, TiCl_4 –SA gave the flocs with relatively higher increased percentages of both S_f s and R_f s. Even though recoverability of flocs was apparently improved after SA addition, the flocs could not regrow to anywhere near their previous size for all the dual-coagulants, for the R_f s of flocs were all still below 100%. It has been reported that recoverability of flocs gives some indication of the floc internal bonding structure [24]. And, Yukselen and Gregory [27] have reported that the chemical bonds broken during floc breakage process may lead to the irreversibility of flocs for hydrolyzing coagulants. It was suspected that, the flocs may be held together by chemical rather than physical bonds, which may be a possible reason for the poor recoverability of flocs. It was also reported that the flocs formed by charge neutralization should give complete recovery, while the flocs formed by sweep coagulation showed poor regrowth after floc breakage [20,40,41].

Therefore, the irreversibility of the flocs was seen as evidence that the flocs formed were not dominated by pure charge-neutralization mechanisms. This was in accordance with the analysis in Section 3.1, which concluded that charge neutralization was not the dominant coagulation mechanisms for the three coagulants due to the low zeta potential of flocs after coagulation. For the dual-coagulants, it was suspected that the adsorption and bridging ability of SA gave the flocs with larger floc size and resulted in the floc strength

improvement. Then the flocs were broken under high shear force, followed by 15 min of floc regrowth under 40 rpm. During the floc regrowth period, floc fragments with newly exposed surface may be bonded together by SA with the electrostatic attraction and *Van der Waals*, resulting in the good recoverability of the flocs formed by the dual-coagulants. It was worth noting that synergistic improvement in floc R_f s decreased when 2.0 mg/L SA was used with $Al_2(SO_4)_3$, which might be ascribed to the repulsion forces between floc

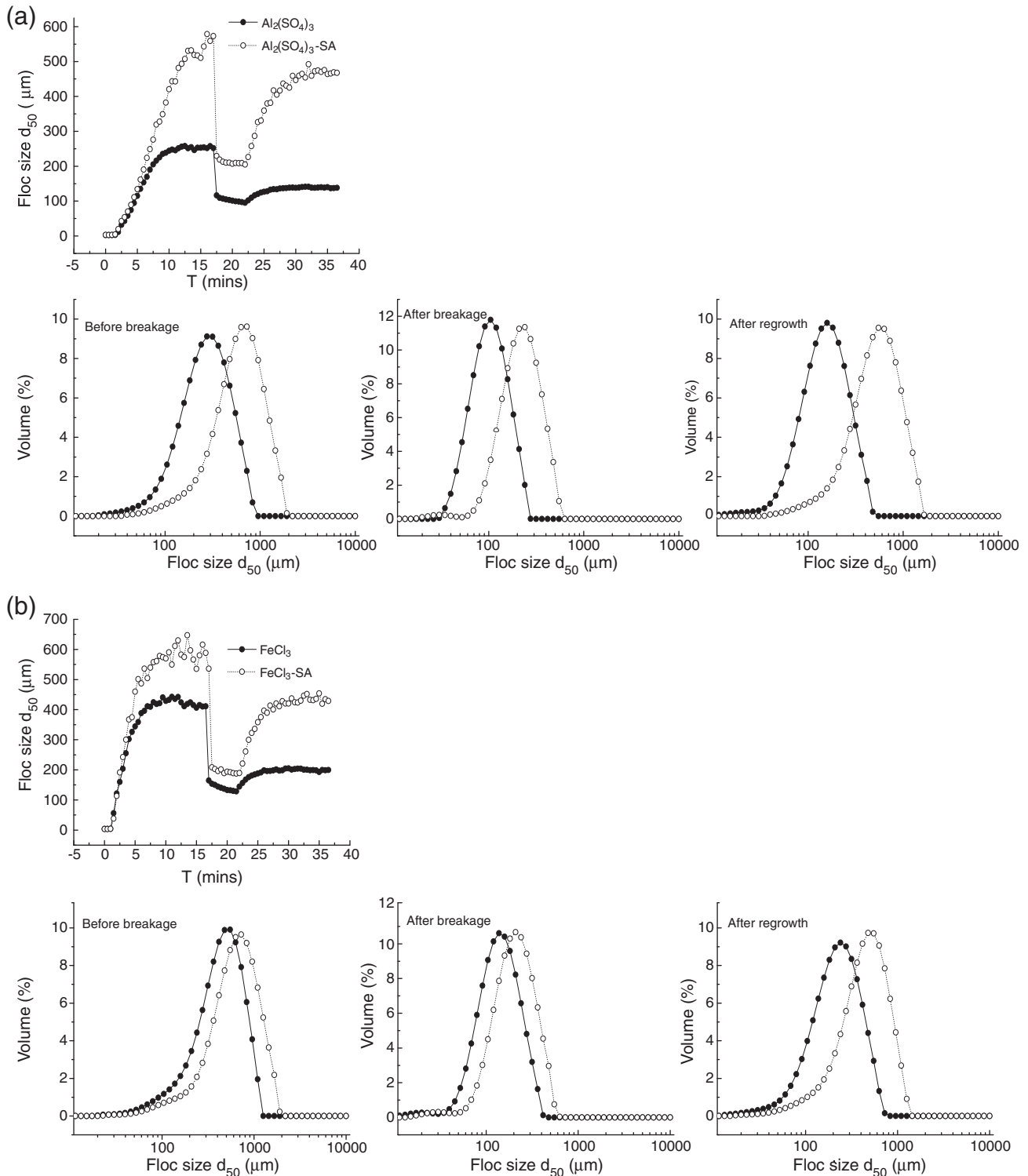


Fig. 4. Growth, breakage and regrowth profile of the NOM flocs formed by different coagulants and the corresponding particle size distributions of the flocs before breakage, after breakage and after regrowth after 5 min of high shear time: (a) $Al_2(SO_4)_3$; (b) $FeCl_3$; (c) $TiCl_4$.

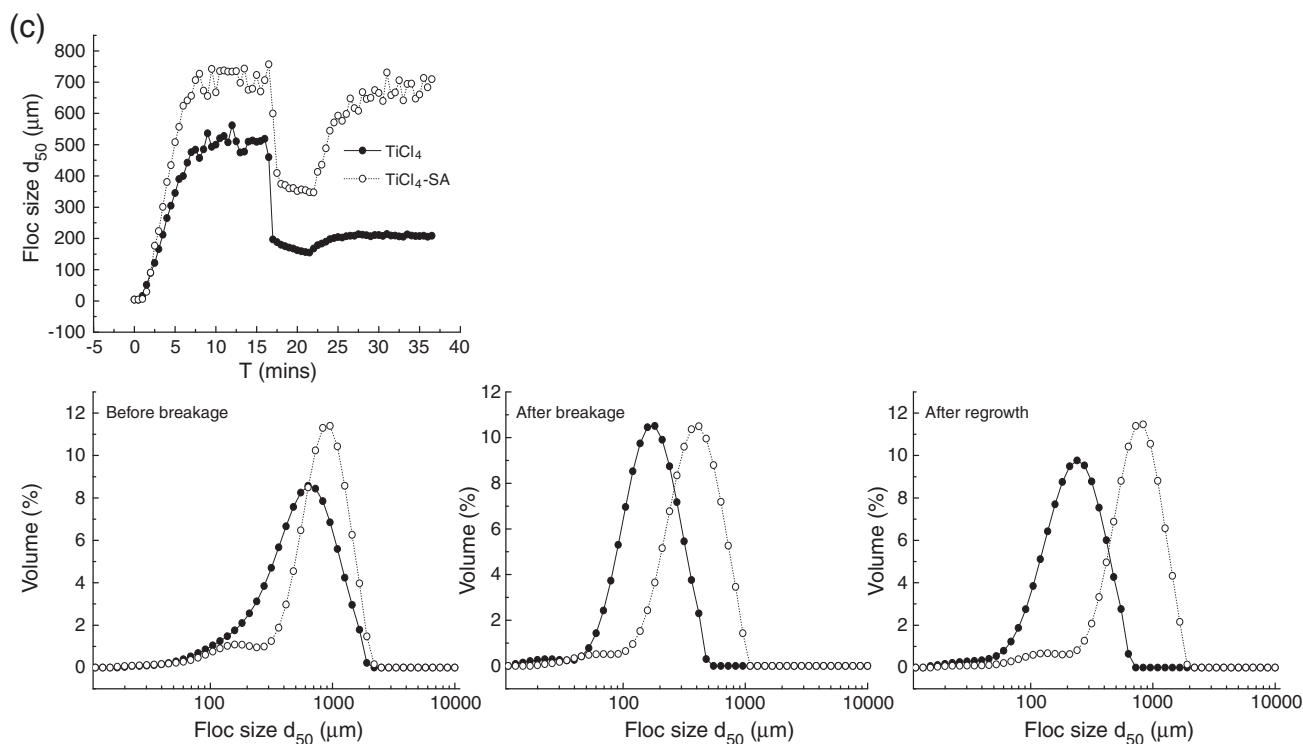


Fig. 4 (continued).

fragments and the overdosed anionic polymer SA. This corresponded well with the decrease in improvement of the floc size after floc regrowth period when 2.0 mg/L was used as coagulant aid (Fig. 3(a)). Based on the above speculation, reduction of the R_f s increased percentages may also be possible if SA was overdosed for both $FeCl_3$ and $TiCl_4$. Thus, doses of SA used as coagulant aid should be optimized as discussed in Section 3.1.

3.2.3. Particle size distribution

Particle size distribution (PSD) was analyzed in this section. For $Al_2(SO_4)_3$ and the corresponding dual-coagulants, the DOC removal reached ca. 62.0% under the $Al_2(SO_4)_3$ concentration of 1.5 mg/L and no significant increase was observed with further coagulant addition (Fig. 1(a)). In addition, when 1.0 mg/L SA was used combined with 1.5 mg/L of $Al_2(SO_4)_3$, the floc size increased from 253 μm to 570 μm (Fig. 2(a)), and the floc recoverability was significantly improved (with the R_f increased from 27% to 74% as shown in Table 2). So, in this section, 1.5 mg/L of $Al_2(SO_4)_3$ combined with 1.0 mg/L SA were selected for investigation. Likewise, 6.0 mg/L of $FeCl_3$ and $TiCl_4$ with 1.0 mg/L SA were selected. Growth, breakage and regrowth profile of the flocs formed by different coagulants and the corresponding PSD of the flocs before breakage, after breakage and after regrowth are presented in Fig. 4. From the growth, breakage and regrowth profile of the flocs, it can be seen that, for all the coagulants investigated, size of the flocs after growth period was obviously improved with SA addition. Then, the flocs showed an apparent decrease immediately with increasing the shear force at 200 rpm, followed by the regrowth of flocs as the shear was reduced. It was clear that irreversibility breakage was observed for all the coagulants, even though size of the flocs formed by the dual-coagulants was larger than those by the coagulants used alone. As to the dual-coagulants, analyzed results of the corresponding PSD found that there was an apparent shift in the major peak to the right of the original value no matter before floc breakage, after floc breakage or after floc regrowth. Besides, there was an obvious decrease in the volume of the flocs with size below ca. 100 μm when the dual-coagulants were used. That is, SA

addition not only improved the average floc size but also reduced the flocs with small size. Boller and Blaser [17] showed that small particles generally have lower removal efficiency by flocculation. Besides, smaller particles generally settle down more slowly than larger particles of similar density. In addition, according to the profiles in Fig. 4 and the PSD analysis, flocs formed by the dual-coagulants showed better recoverability, which was in accordance with the conclusions obtained in Section 3.2.2. As flocculation unit is often prevalent with high shear force regions during the separation technique such as the removal of aggregated particles [18]. Therefore, SA addition may have a positive effect on solid/liquid separation process.

3.2.4. Floc structural analysis

Variation of floc D_f values during floc formation, breakage and regrowth processes was investigated under two doses of each coagulant combined with 1.0 mg/L SA, and the results are shown in Fig. 5. Generally, it was found from Fig. 5 that D_f values of the flocs increased with increasing coagulant doses for each coagulant for both dual-coagulants and the coagulants used alone. Also, the D_f values of the flocs followed the order of $TiCl_4 > FeCl_3 > Al_2(SO_4)_3$ within the doses investigated. The main finding was that, for all the three coagulants, the dual-coagulants gave the flocs with more open structure as reflected by lower D_f values compared with the coagulants used alone, regardless of floc growth, breakage or regrowth process. As discussed in Sections 3.1 and 3.2.1, bridging ability of SA play an important role in DOC removal and large flocs formation under the concentrations of the three coagulants investigated in this section. It was speculated that the larger the floc size, the smaller the floc D_f was. A similar phenomenon was also reported by Cao et al. [42]. Wu et al. [43] found the decreasing in fractal dimension as bridging increased for activated sludge flocs, which was conducted by a similar technique. So, decrease in floc D_f values may be attributed to the bridging of the SA chain molecules on the negatively charged microflocs. Gregory [21] reported that fractal dimension of flocs is an important parameter influencing floc density, which further influences solid/liquid separation. Analyze results of this section indicated that, when SA was used as coagulant aid, the corresponding dual-coagulants of $Al_2(SO_4)_3$,

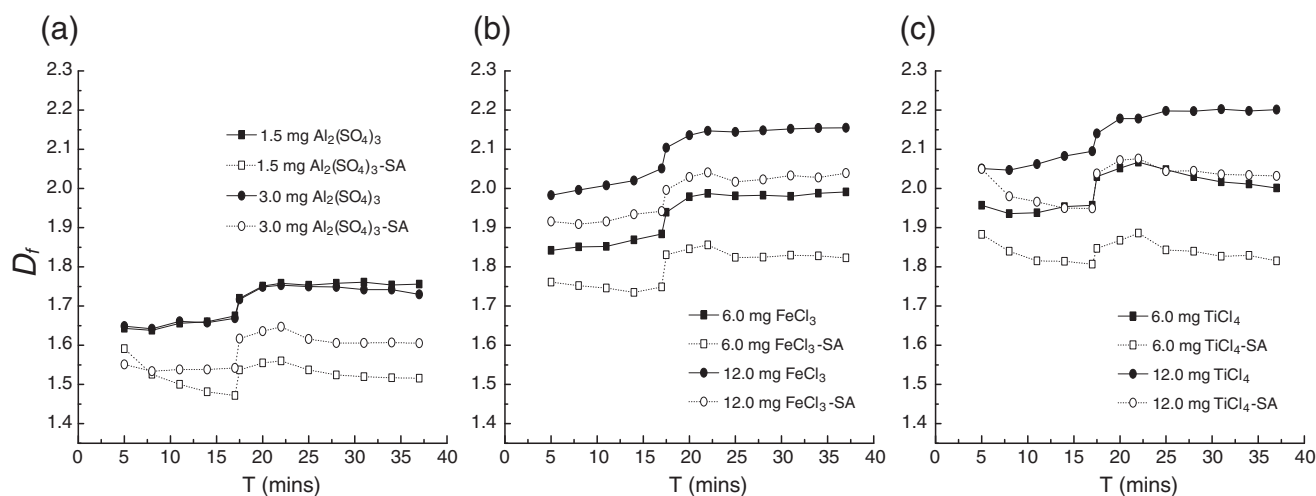


Fig. 5. Change in fractal dimension of flocs with time for (a) $\text{Al}_2(\text{SO}_4)_3$, (b) FeCl_3 and (c) TiCl_4 after floc growth (40 rpm) and breakage (200 rpm) followed by a return to the initial 40 rpm for floc regrowth.

FeCl_3 and TiCl_4 yielded the flocs with highly branched and loosely bound structure. For that reason, it needed carefully handling of the flocs formed by the dual-coagulants during solid/liquid separation process. In addition, it should be noted that D_f values increased substantially when high speed of 200 rpm was applied, and the values increased with time during floc breakage period, which may be possibly ascribed to the reason that the weak points of aggregates were ruptured under high shear speed and were rearranged at more favorable points [44,45]. Subsequently, rearrangement resulted in the flocs with more compact and stable structure with high D_f values.

4. Conclusions

It was concluded that appropriate doses of SA did not obviously influence the coagulation efficiency while floc properties could be significantly changed. Dual-coagulants gave faster floc formation and yielded the flocs with larger size. Primary coagulants plus SA gave the flocs with better recoverability but with more highly branched and loosely bound structure. It was supposed that using SA as a coagulant aid could be beneficial during solid/liquid separation process due to the flocs with larger size and better recovery. However, the flocs still needed to be carefully handled as the structure was not that compact due to SA addition.

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References

- [1] C.Z. Hu, H.J. Liu, J.H. Qu, D.S. Wang, J. Ru, Coagulation behavior of aluminum salts in eutrophic water significance of Al_{13} species and pH control, *Environ. Sci. Technol.* 40 (1) (2006) 325–331.
- [2] V. Kazpard, B.S. Lartiges, C. Frochet, J.B. d'Espinose de la Caillerie, M.L. Viriot, J.M. Portal, T. Görner, J.L. Bersillon, Fate of coagulant species and conformational effects during the aggregation of a model of coagulation of humic acid: the performance of preformed and non-preformed Al species, *Water Res.* 40 (10) (2006) 1965–1974.
- [3] B.Y. Shi, Q.S. Wei, D.S. Wang, Z. Zhu, H.X. Tang, Coagulation of humic acid: the performance of preformed and non-preformed Al species, *Colloids Surf., A Physicochem. Eng. Asp.* 296 (1–3) (2007) 141–148.
- [4] P. Jarvis, B. Jefferson, S.A. Parsons, Breakage, re-growth, and fractal nature of natural organic matter flocs, *Environ. Sci. Technol.* 39 (7) (2005) 2307–2314.
- [5] H. Salehzadeh, S.A. Shojasodati, Extracellular biopolymeric flocculants: recent trends and biotechnological importance, *Biotechnol. Adv.* 19 (2001) 371–385.
- [6] Z.Q. Zhang, B. Lin, S.Q. Xia, X.J. Wang, A.M. Yang, Production and application of a bioflocculant by multiple-microorganism consortia using brewery wastewater as carbon source, *J. Environ. Sci. China* 19 (2007) 660–666.
- [7] C. Arezoo, The potential role of aluminium in Alzheimer's disease, *Nephrol. Dial. Transplant* 17 (Suppl. 2) (2002) 17–20.
- [8] C. Rudén, Acrylamide and cancer risk—expert risk assessments and the public debate, *Food Chem. Toxicol.* 42 (2004) 335–349.
- [9] H.K. Shon, S. Vigneswaran, J. Kandasamy, M.H. Zareie, J.B. Kim, D.L. Cho, J.-H. Kim, Preparation and characterization of titanium dioxide (TiO_2) from sludge produced by TiCl_4 flocculation with FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$ and $\text{Ca}(\text{OH})_2$ coagulant aids in wastewater, *Sep. Sci. Technol.* 44 (7) (2009) 1525–1543.
- [10] T.N. Obee, R.T. Brown, TiO_2 photocatalysis for indoor air applications: effects of humidity and trace contaminant levels on the oxidation rates of formaldehyde, toluene, and 1, 3-butadiene, *Environ. Sci. Technol.* 29 (5) (1995) 1223–1231.
- [11] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95 (1) (1995) 69–96.
- [12] S.B. Deng, R.B. Bai, X.M. Hu, Q. Luo, Characteristics of a bioflocculant produced by *Bacillus mucilaginosus* and its use in starch wastewater treatment, *Appl. Microbiol. Biotechnol.* 60 (2003) 588–593.
- [13] N. He, Y. Li, J. Chen, Production of a novel polygalacturonic acid bioflocculant REA-1 by *Corynebacterium glutamicum*, *Bioresour. Technol.* 94 (2004) 99–105.
- [14] Z. Li, S. Zhong, H.Y. Lei, R.W. Chen, Q. Yu, H.L. Li, Production of a novel bio-flocculant by *Bacillus licheniformis* X14 and its application to low temperature drinking water treatment, *Bioresour. Technol.* 100 (2009) 3650–3656.
- [15] Z.H. Yang, J. Huang, G.M. Zeng, M. Ruan, C.S. Zhou, L. Li, Z.G. Rong, Optimization of flocculation conditions for kaolin suspension using the composite flocculant of MBFGA1 and PAC by response surface methodology, *Bioresour. Technol.* 101 (2009) 1044–1048.
- [16] W.Z. Yu, G.B. Li, Y.P. Xu, Breakage and re-growth of flocs formed by alum and PACI, *Powder Technol.* 189 (3) (2009) 439–443.
- [17] M. Boller, S. Blaser, Particles under stress, *Water Sci. Technol.* 37 (10) (1998) 9–29.
- [18] K. McCurdy, K. Carlson, D. Gregory, Floc morphology and cyclic shearing recovery: comparison of alum and polyaluminum chloride coagulants, *Water Res.* 38 (2) (2004) 486–494.
- [19] P.A. Shamlou, A.T. Gierczycki, N.J. Titchener-Hooker, Breakage of flocs in liquid suspensions agitated by vibrating and rotating mixers, *Chem. Eng. J.* 62 (1) (1996) 23–34.
- [20] V. Chaignon, B.S. Lartiges, A. El Samrani, C. Mustin, Evolution of size distribution and transfer of mineral particles between flocs in activated sludges: an insight into floc exchange dynamics, *Water Res.* 36 (3) (2002) 476–484.
- [21] J. Gregory, The role of floc density in solid-liquid separation, *Filtrat. Separ.* 35 (1998) 571–575.
- [22] S.M. Glover, Y.D. Yan, G.J. Jameson, S. Biggs, Dewatering properties of dual-polymer-flocculated systems, *Int. J. Miner. Process.* 73 (2004) 145–160.
- [23] D.G. Lee, J.S. Bonner, L.S. Garton, A.N.S. Ernest, R.L. Autenrieth, Modeling coagulation kinetics incorporating fractal theories: comparison with observed data, *Water Res.* 36 (2002) 1056–1066.
- [24] Z.L. Yang, B.Y. Gao, Q.Y. Yue, Y. Wang, Effect of pH on the coagulation performance of Al-based coagulants and residual aluminum speciation during the treatment of humic acid-kaolin synthetic water, *J. Hazard. Mater.* 178 (2010) 596–603.
- [25] J. Bratby, *Coagulation and Flocculation*, Upland Press, Croydon, UK, 1980.
- [26] R.J. Francois, Strength of aluminium hydroxide flocs, *Water Res.* 21 (9) (1987) 1023–1030.

- [27] M.A. Yukselen, J. Gregory, The reversibility of floc breakage, *Int. J. Miner. Process.* 73 (2–4) (2004) 251–259.
- [28] J. Guan, T.D. Waite, R. Amal, Rapid structure characterization of bacterial aggregates, *Environ. Sci. Technol.* 32 (23) (1998) 3735–3742.
- [29] B. Bolto, D. Dixon, R. Eldridge, S. King, Cationic polymer and clay or metal oxide combinations for natural organic matter removal, *Water Res.* 35 (2001) 2669–2676.
- [30] E.E. Chang, P.C. Chang, W.Y. Tang, S.H. Chao, H.J. Hsing, Effects of polyelectrolytes on reduction of model compounds via coagulation, *Chemosphere* 58 (2005) 1141–1150.
- [31] H.W. Walker, E.K. Kim, Influence of flocculant aids and NOM characteristics on the removal of DPB precursors during enhanced coagulation, *Proceedings of the Water Quality Technology Conference, American Water Works Association, Nashville, USA, 2001*.
- [32] B.-Y. Gao, Y.B. Chu, Q.Y. Yue, B.J. Wang, S.G. Wang, Characterization and coagulation of a polyaluminum chloride (PACl) coagulant with high Al_{13} content, *J. Environ. Manage.* 76 (2) (2005) 143–147.
- [33] W.P. Cheng, Comparison of hydrolysis/coagulation behavior of polymeric and monomeric iron coagulants in humic acid solution, *Chemosphere* 47 (9) (2002) 963–969.
- [34] Y.X. Zhao, B.Y. Gao, B.C. Cao, Z.L. Yang, Q.Y. Yue, H.K. Shon, J.-H. Kim, Comparison of coagulation behavior and floc characteristics of titanium tetrachloride ($TiCl_4$) and polyaluminum chloride (PACl) with surface water treatment, *Chem. Eng. J.* 166 (2011) 544–550.
- [35] Y.X. Zhao, B.Y. Gao, H.K. Shon, B.C. Cao, J.-H. Kim, Coagulation characteristics of titanium (Ti) salt coagulant compared with aluminum (Al) and iron (Fe) salts, *J. Hazard. Mater.* 185 (2011) 1536–1542.
- [36] Y. Wang, B.Y. Gao, X.M. Xu, W.Y. Xu, G.Y. Xu, Characterization of floc size, strength and structure in various aluminum coagulants treatment, *J. Colloid Interface Sci.* 332 (2) (2009) 354–359.
- [37] F. Xiao, P. Yi, X.R. Pan, B.J. Zhang, C. Lee, Comparative study of the effects of experimental variables on growth rates of aluminum and iron hydroxide flocs during coagulation and their structural characteristics, *Desalination* 250 (2010) 902–907.
- [38] D.T. Ray, R. Hogg, Agglomerate breakage in polymer-flocculated suspensions, *J. Colloid Interface Sci.* 116 (1987) 256–268.
- [39] C.A. Biggs, P.A. Lant, Activated sludge flocculation: on-line determination of floc size and the effect of shear, *Water Res.* 34 (9) (2000) 2542–2550.
- [40] M.I. Aguilar, J. Saez, M. Llorens, A. Soler, J.F. Ortuno, Microscopic observation of particle reduction in slaughterhouse wastewater by coagulation–flocculation using ferric sulphate as coagulant and different coagulant aids, *Water Res.* 37 (9) (2003) 2233–2241.
- [41] P. Jarvis, B. Jefferson, S.A. Parsons, The duplicity of floc strength, *Proceedings of the Nano and Micro Particles in Water and Wastewater Treatment Conference, International Water Association, Zurich, Switzerland, 2003*, pp. 63–70.
- [42] B.C. Cao, B.Y. Gao, X. Liu, M.M. Wang, Z.L. Yang, Q.Y. Yue, The impact of pH on floc structure characteristic of polyferric chloride in a low DOC and high alkalinity surface water treatment, *Water Res.* 45 (18) (2011) 6181–6188.
- [43] R.M. Wu, D.J. Lee, T.D. Waite, J. Guan, Multilevel structure of sludge flocs, *J. Colloid Interface Sci.* 252 (2002) 383–392.
- [44] D.C. Hopkins, J.J. Ducoste, Characterizing flocculation under heterogeneous turbulence, *J. Colloid Interface Sci.* 264 (1) (2003) 184–194.
- [45] C. Selomulya, R. Amal, G. Bushell, T.D. Waite, Evidence of shear rate dependence on restructuring and breakup of latex aggregates, *J. Colloid Interface Sci.* 236 (1) (2001) 66–77.