



Effect of second coagulant addition on coagulation efficiency, floc properties and residual Al for humic acid treatment by Al₁₃ polymer and polyaluminum chloride (PACl)

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ABSTRACT

Influence of second dose on coagulation efficiency, floc re-growth, fractal structure and residual Al of the effluent in humic acid (HA) coagulation with Al₁₃ polymer ([Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺) and PACl were comparatively investigated in this study. Effects of breakage shear on the floc properties generated in the coagulation with and without additional dose were also investigated. The results indicated that additional dose during breakage could essentially improve the HA removal efficiency and floc re-growth in both Al₁₃ and PACl coagulations. Second doses of Al₁₃ at 0.5 and 1.0 mg/L resulted in better turbidity and UV₂₅₄ removal as well as floc re-growth rather than higher additional dose of 1.5 and 2.0 mg/L; while in PACl coagulation, more efficient HA removal and better floc re-growth were obtained at higher additional doses (1.0, 1.5 and 2.0 mg/L). Small additional Al₁₃ could apparently increase the *D_f* of re-formed flocs while the additional PACl displayed inconspicuous effect on floc *D_f*. The additional coagulant dose could alleviate the further decrease of re-grown floc size with increased breakage shear for both coagulants. The residual Al analysis implied that two-stage addition contributed to lower residual Al in effluent than one-time addition mode with the same total coagulant concentration.

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1. Introduction

Coagulation and flocculation remain the most important steps in water treatment, allowing the removal of particles and natural organic matter (NOM). Recently, several researches have been devoted to improving the efficiency of coagulation–flocculation process, and a main trend is the production of coagulants with improved properties than the conventional ones, such as AlCl₃ or Al₂(SO₄)₃ (alum). In recent years, polyaluminum chloride (PACl) has been widely used and taken the place of many traditional aluminous coagulants. Al₁₃ polycation ([Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺), recognized as the most active species in PACl and a novel coagulant, has attracted much attention from researchers [1,2]. Previous investigation demonstrated that Al₁₃ species displayed higher charge neutralization ability than other Al-based coagulants, and thus could improve the coagulation efficiency and reduce consumption of coagulant dose in water treatment [3]. Our previous studies [4,5] have confirmed that Al₁₃ polymer could effectively enhance the particles aggregation and improve the floc structure,

which generally led to significant removal efficiency for contaminants in solid/liquid separation process [6].

The research to increase coagulation–flocculation efficiency also focuses on the improvement of operation parameters, such as dosing method, dosing time and shear force applied. Recently, Yu et al. [7,8] found that two-stage coagulant addition of alum could enhance floc re-growth after breakage due to freshly precipitated aluminum hydroxide. The result was meaningful because it overcame the disadvantage of irreversible breakage of flocs, which has been confirmed by many previous researches [9–11]. The poor re-growth ability of flocs was undesirable because the resultant small particles would pose a challenge to the solid/liquid separation process [12]. However, the positive effect of two-stage addition is supposed to be dependent on the characteristics of coagulants according to the study by Yu et al. [13], which found that different PACl species gave very different floc re-growth when added as the second coagulant. Taking into consideration of the distinct Al species distributions in pre-hydrolyzed aluminum coagulants and alum, their coagulation behaviors and mechanisms as the second coagulants may obviously differ, which is worth studying. Another important consideration is that the high velocity gradient (*G*) involved in coagulation has a fairly great influence on the floc break-up and re-growth, which has been previously suggested by other researchers [14,15]. Consequently, the impact of rapid

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Table 1
Properties of Al₁₃ and PACI.

Coagulants	Al _T (mol/L)	Al species distribution (%)		
		Al _m	Al ₁₃	Al _{other}
Nano-Al ₁₃	0.089	2.32	93.16	4.52
PACI	1.076	24.34	32.61	43.05

shear rate should be fully considered in the evaluation of second coagulant addition on coagulation.

Besides floc re-growth, fractal structure is another floc property closely related to the final coagulation efficiency and it could also be essentially affected by the additional dose. To make a precise evaluation of the second addition effect on coagulation–flocculation process, it is necessary to systematically investigate its effects on floc size, strength and fractal dimension, which has not been previously reported.

What is also worth noticing is the impact of second coagulant addition on the residual Al in the finished water. It has been well known that Al-based coagulants, particularly alum, may result in elevated concentrations of residual Al in finished water [16,17], which has been considered to be an undesirable aspect of treatment practice. The occurrence of Al in treated water is associated with several problems, including increased turbidity, reduced disinfection efficiency, a loss in hydraulic capacity and potential adverse effects such as Alzheimer's disease [17,18]. In China, the total Al concentration in drinking water should not exceed 0.200 mg/L. However, the two-stage addition of Al coagulant could probably affect the residual Al concentration in the coagulation effluent, which has never been considered in the previous studies. Thus the analysis and determination of residual Al in treated water after the second coagulant dosing is very necessary and meaningful for both the water treatment plants and human health. Additionally, the current studies on Al₁₃ species mainly concern the coagulation efficiency and floc characteristics [4,19,20]. There has not been a special report addressing the effect of Al₁₃ on the residual Al concentration in the finished water.

Consequently, the aim of the present paper is to investigate the influence of second dosing of PACI and Al₁₃ species on the coagulation efficiency, floc properties and the residual Al in effluent. Additionally, a series of shear forces were applied in the floc break-up and re-growth experiments to explore the influence of velocity gradient on the beneficial effect of second addition.

2. Materials and methods

2.1. Preparation and characterization of coagulants

The procedures of preparing PACI and Al₁₃ polymer can be described as follows: PACI with a basicity value (B, OH/Al molar ratio) of 2.0 was synthesized by adding pre-determined amount of Na₂CO₃ and AlCl₃ slowly into deionized water under intense agitation. The temperature was kept at 70.0 ± 0.5 °C by recycling water bath. Al₁₃ species was separated from the PACI by ethanol/acetone separation method and the details can be found in other paper [21]. All the reagents used were of analytical grade and deionized water was used to prepare all solutions.

Total Al concentrations were determined by titrimetric method according to the national standard of China [22]. The Al_m and Al₁₃ species in different Al coagulants were analyzed by ²⁷Al NMR spectroscopy with ²⁷Al NMR spectra obtained from a Varian UNITY INOVA (500 MHz). The undetectable species, denoted as Al_{other}, was Al_T minus Al_m and Al₁₃. The properties of Al₁₃ and PACI coagulants are summarized in Table 1.

2.2. Water samples

Humic acid (HA), a major component of natural organic matter (NOM) [23], was used to prepare the suspension. HA used in this study was commercial reagent grade solid (Shanghai, China). The HA stock solution was prepared as follows: 1.0 g of HA was dissolved in 1 L of deionized water that contained 4.2 g of NaHCO₃ under 3.0 h of continuous stirring, then stored in refrigerator at 4 °C for later use. The synthetic test water was prepared by dissolving 10.0 mL of HA stock solution in deionized water and diluting the solution to 1 L. The test water was pre-filtered through a 0.45 μm glass fibre paper for UV₂₅₄ absorbance and DOC measurements. UV₂₅₄ absorbance was tested by a UV-754 UV/VIS spectrophotometer (Precision Scientific Instrument Co. Ltd., Shanghai, China) at 254 nm using 1 cm quartz cells, and DOC was analyzed with a TOC analyzer (TOC-VCPH, Shimadzu, Japan). Turbidity was directly measured by a 2100P turbidimeter (Hach, USA) without filtration, and pH was measured using a pH analyzer (pHs-3C, Luoqite, Shanghai). The properties of the synthetic test water used were as follows: UV₂₅₄ = 0.299 ± 0.02, turbidity = 4.35 ± 0.20 NTU, DOC = 2.11 ± 0.03 mg/L, pH = 7.97 ± 0.2.

2.3. Jar tests

Initially, coagulation optimization tests were performed using a conventional jar-test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) to ascertain the optimum coagulant dosage for HA removal by Al₁₃ polymer and PACI. The experiments were conducted at a room temperature of 15 ± 1 °C. Predetermined amount of coagulant was added at the start of coagulation; thereafter, 1.5 min rapid mixing at 200 revolutions per minute (rpm) was applied, followed by 15 min of slow stirring at 40 rpm. Then after 30 min of quiescent settling, the sample was collected from 2 cm below the surface for subsequent analyses, including residual turbidity, UV₂₅₄ and final pH. Zeta potentials were measured immediately after the 1.5 min of rapid mixing using a Zetasizer 3000HSa (Malvern Instruments, UK).

Floc breakage tests were programmed similarly in floc growth phases as aforementioned. After the slow stir phase (15 min at 40 rpm), the suspension was exposed to a high shear of 200 rpm (or 75, 100, 150, 300 and 500 rpm) for a further 5 min, and then a slow stirring at 40 rpm was reintroduced for flocs re-form, followed by 30 min of settlement. Yu et al. [7] stated that the second coagulant addition near the end of the breakage period gave better than 100% re-growth of broken flocs. So in the case of coagulation with a second coagulant addition, the additional coagulants were added into the stirred suspension 15 s before the breakage period finished in this study.

A continuous laser diffraction instrument (Mastersizer 2000, Malvern, UK) was used to measure the dynamic floc size as the coagulation proceeded. More details have been reported in other paper [24]. Size measurements were taken every 30 s for the duration of the jar test and the 50 percentile floc size (*d*₅₀) was used to denote flocs size in this study.

2.4. Determination of floc recovery factor and fractal structure

In order to quantitatively investigate the floc re-growth abilities, floc recovery factors were calculated as follows [14]:

$$\text{Recovery factor } (R_f) = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \quad (1)$$

where *d*₁, *d*₂ and *d*₃ are the sizes of flocs in the steady phase before breakage, after the breakage period and after the re-growth to another steady phase, respectively. A higher *R*_f value indicates a better re-growth capacity of flocs.

The complicated structure of floc aggregates is now well described by the application of fractal geometry theory [25–27], where the floc structure is simply described by the mass fractal dimension D_f . Commonly, compact aggregates have higher D_f , while aggregates with loose structures have lower D_f values. Recently, small angle laser light scattering (SALLS) has been successfully used for the determination of D_f of aggregates covering a wide range of particle size, including tiny hematite particles (5–13 μm) [28], medium salt-humic flocs or salt-kaolin flocs (60–650 μm) [29,30] and large ferric precipitate (1000 μm) [31]. Details about SALLS have been well described previously [26,27] and the method is briefly given as follows: the scattered intensity I is a function of the magnitude of the scattering wave vector Q , which is shown as:

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

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, I is related to Q and the fractal dimension D_f [32]:

$$I \propto Q^{-D_f} \quad (3)$$

So, on a log–log scale if there is a straight line, the slope of which is D_f . This relationship is valid only when the length scale of the analysis is much larger than the size of primary particles and much smaller than the size of floc aggregates [27,31].

2.5. Measurement of residual aluminum content

Both the residual Al contents of raw and purified water after coagulation were analyzed by chrome azurol S colorimetric analysis according to the national standard of the People's Republic of China [33]. The residual Al content was obtained through consulting the standard curve of Al content, which was prepared before sample measurement, after measuring the absorbance at 620 nm wavelength with UV-754 spectrophotometer. The residual Al caused by Al-based coagulant was equal to Al content of the finished water minus that of the raw water.

3. Results and discussion

3.1. Effect of initial dose on coagulation efficiency

Coagulation experiments without breakage were performed in the coagulant dose range of 1–10 mg/L to determine the optimum dosages of nano- Al_{13} and PACI for HA removal. Fig. 1 shows the HA removal efficiencies with increasing coagulant doses as well as the zeta potentials and pH values of effluents. It could be observed that at low doses (lower than 3.0 mg/L), both the turbidity and UV_{254} removal efficiencies increased steeply with coagulant concentration regardless of the coagulant used. With coagulants doses further increased, the HA removal efficiencies increased slowly and finally reached the plateaus for both coagulants. The turbidity and UV_{254} removal efficiencies varied slightly in the optimum dosage range. Compared with PACI, Al_{13} polymer gave rise to better UV_{254} removal especially at lower dosages. That could be attributed to the higher positive charge of Al_{13} than PACI as shown in Fig. 1b, which was expected to contribute to better charge neutralization mechanism especially at low coagulant concentrations [3,34]. It could be found from Fig. 1b that the effluents pH decreased after coagulants addition and with the dosages increased from 0.5 to 10.0 mg/L, pH showed a continuous decline from around 8.0 to 7.38 and 7.15 for Al_{13} and PACI coagulations, respectively. At high coagulant concentrations and at neutral pH, $\text{Al}(\text{III})$ species could rapidly transform into voluminous amorphous aluminum hydroxide ($\text{Al}(\text{OH})_{3(\text{am})}$),

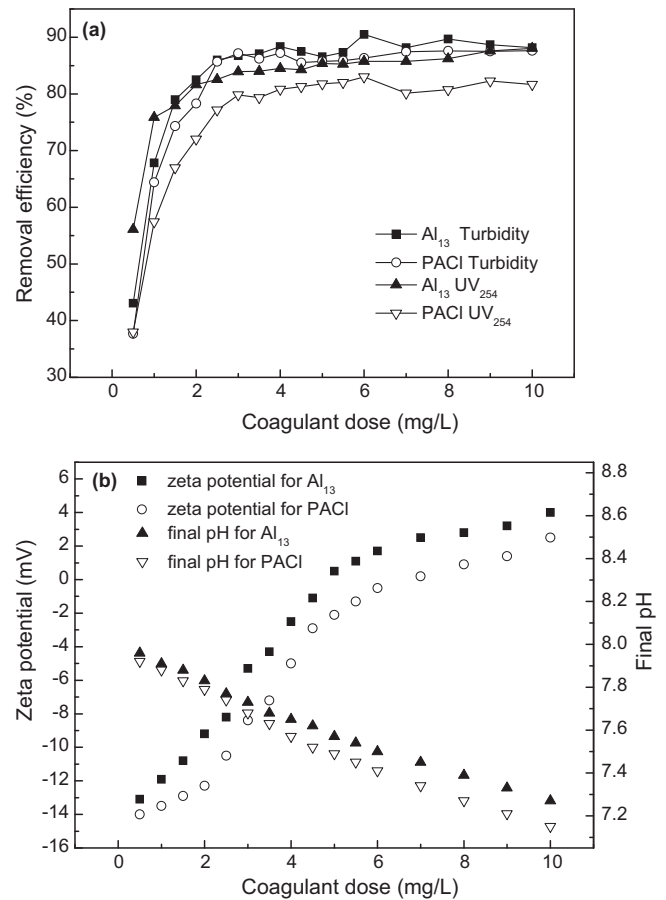


Fig. 1. Effect of coagulants doses on (a) turbidity and UV_{254} removal efficiencies and (b) zeta potentials and effluent pH in HA coagulations by Al_{13} and PACI.

where HA could be mainly removed by surface adsorption for both PACI and Al_{13} coagulations [3,19,35]. Consequently, the differences between coagulation efficiencies of Al_{13} and PACI were lessened despite their different charge neutralization abilities. Considering the cost of coagulants and coagulation efficiency, the initial dosages of Al_{13} and PACI were fixed at 3.0 mg/L for the subsequent experiments in this study.

3.2. Effect of additional dose on coagulation efficiency

Coagulation experiments with 5 min of breakage at 200 rpm along with different additional doses during breakage phases were conducted. The effect of different second dosages on the turbidity and UV_{254} removals are shown in Fig. 2. For comparison, the coagulation efficiencies obtained at single doses of 3.0 and 4.0 mg/L without additional dosing were also provided. It could be observed that for both Al_{13} and PACI, obvious improvement of turbidity and UV_{254} removal efficiencies could be achieved by a small second dosing. However, the coagulation efficiency was not positively correlated with the additional dose. For Al_{13} , the turbidity removal efficiency was around 82% at a single dose of 3.0 mg/L, and a second dose of 0.5 and 1.0 mg/L could obviously improve the efficiency to nearly 90% as shown in Fig. 2a. However, the additional doses at 1.5 and 2.0 mg/L led to an efficiency of about 85%, indicating that a higher additional dose could not further enhance the turbidity removal. Similarly, the best UV_{254} removal efficiency was also obtained at the second dose of 0.5 and 1.0 mg/L, but the enhancement displayed a smaller degree than that of turbidity. By contrast, the improvement contributed by 0.5 mg/L of PACI was much less than that induced by higher additional doses of 1.0, 1.5

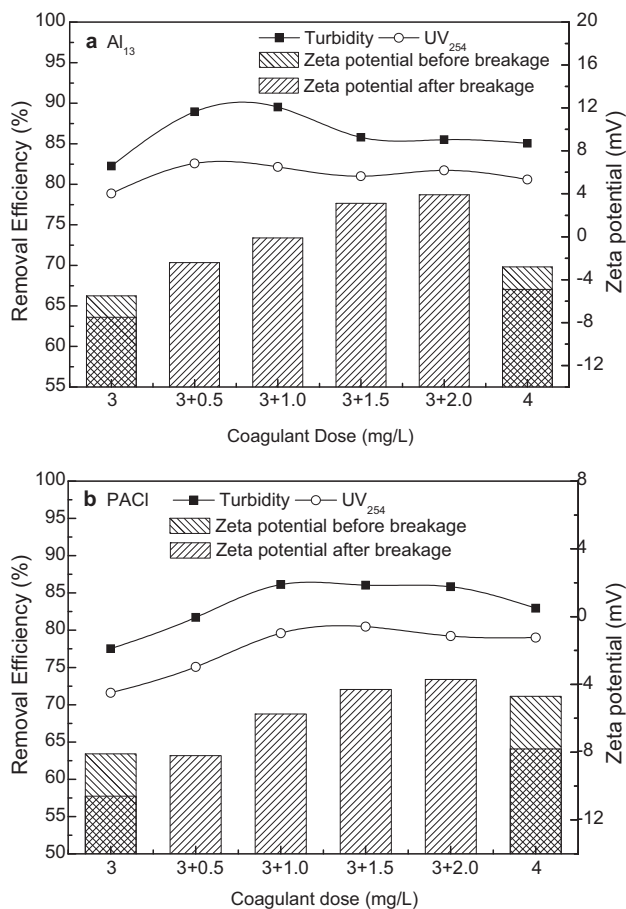


Fig. 2. Turbidity, UV₂₅₄ removal and zeta potentials by various doses of nano-Al₁₃ and PACI after breakage and re-growth.

and 2.0 mg/L, by which the turbidity and UV₂₅₄ removal efficiencies could be increased from the initial 77% and 71% to around 86% and 80%, respectively.

In order to further study the coagulation mechanisms of additional coagulants, samples were taken after dosing and rapid mixing for zeta potential measurement. The measurements were also made on samples at the end of breakage phases and large particles in the samples were removed by sedimentation before the measurements. It is evident from Fig. 2 that zeta potentials decreased conspicuously after breakage for both coagulants without second doses. For Al₁₃, the original zeta potentials at 3 and 4 mg/L were -5.5 and -2.8 mV, and decreased to -7.5 and -4.9 mV after breakage, respectively. A possible reason was that during the break-up process, the flocs were broken into many smaller flocs. The newly exposed surfaces of aggregates might have a net negative charge, which led to decrease in zeta potentials [36]. The study by Yu et al. [7], however, demonstrated that the zeta potentials after breakage were indistinguishable from their original values. This inconsistency might result from the different coagulation conditions, including characteristics of coagulants and water samples, breakage intensity and duration time. The different positive charges and hydroxide reactions of different Al-based coagulants after dosing into the HA suspension could probably be an essential reason. Nevertheless, there has not been a clear understanding of the relationship between zeta potentials and velocity gradient and further work is needed to get a full comprehension.

Second dose during breakage could definitely improve the zeta potentials (Fig. 2), and larger second dose led to higher zeta potentials. It could be observed that at the same total coagulant

concentration, the two-stage addition mode gave rise to higher zeta potentials than one time addition. This indicated that the additional coagulant caused significant charge neutralization in the re-coagulation of broken flocs. Under the same initial and second doses, Al₁₃ tended to produce higher zeta potentials than PACI. It should also be noticed that when the additional doses of Al₁₃ were 1.5 and 2.0 mg/L, charge reversal occurred and the surface charges of aggregates became positive. This might be the reason why the HA removal efficiencies at second doses of 1.5 and 2.0 mg/L were smaller than those at 0.5 and 1.0 mg/L, which proved that charge neutralization played an important role in the second-coagulation. Nevertheless, the coagulation efficiency for two-stage dosing were still higher than that for 1-shot dosing of 3 and 4 mg/L regardless of the charge reversal, implying that besides charge neutralization, other mechanisms such as adsorption and entrapment of the freshly formed hydroxide precipitates, also played crucial parts in coagulation [7].

3.3. Effect of second addition on floc re-growth and fractal structure

Results from continuous monitoring of HA floc formation, breakage by 5 min of high shear at 200 rpm and re-growth with a series of additional Al₁₃ and PACI doses are shown in Fig. 3a and b. In all cases, floc size significantly increased initially and then arrived at a stable phase, implying that an appropriate balance between floc growth and breakage was attained [37,38]. PACI produced larger stable floc size than nano-Al₁₃. Once the high shear rate (200 rpm) was introduced, an immediate and sharp decrease in floc size occurred. When the stirring rate returned to 40 rpm, flocs began to reform rapidly and then grew gradually. To make the results clearer, enlarged views of the floc re-growth curves are provided in Fig. 3c and d. It could be observed that for coagulations with additional coagulants, flocs could re-grow to a larger size after breakage; while smaller re-grown flocs were obtained for the one-time dosing coagulations. The final reformed floc size depended largely on the second dose. For Al₁₃ species, flocs re-grew to a larger size with the additional dose of 0.5 and 1.0 mg/L; while they re-grew to a relatively smaller size when the second dose was 1.5 and 2.0 mg/L, where charge reversal occurred (Fig. 2). This implied that charge neutralization played an important role in floc re-growth after breakage. It should also be noticed that additional Al₁₃ at 1.5 and 2.0 mg/L could also improve the floc re-formation sizes than one-shot dosing even with the charge reversal, which indicated that charge neutralization was not the sole mechanism in floc re-growth. Adsorption of particles on the Al hydroxide precipitates and other mechanisms such as bridging and enmeshment might also contribute to the floc re-aggregation [7]. This seemed to be consistent with the conclusions obtained in Section 3.2. The reformed floc size in PACI coagulation increased with the additional dose as well as zeta potentials (Fig. 2b). It should be noticed that although the second addition coagulant could promote the re-growth of broken flocs, the aggregates could not re-grow to their previous size. This is totally different from the results obtained by Yu et al. [7], which demonstrated that the broken HA flocs could re-grow to higher than 100% of the previous size by the additional alum. That could be ascribed to the different Al_m, Al₁₃ and Al_{other} proportions in alum and the pre-hydrolyzed coagulants (PACI and Al₁₃) used in this study. Compared to alum, Al₁₃ and PACI with more Al₁₃ and Al_{other} species had higher positive charge and were more stable after being dosed into the suspension; while alum mainly composed of Al_m species could immediately hydrolyze and gave rise to amorphous hydroxide precipitates [39]. Coagulants with different Al species distributions resulted in distinct coagulation mechanisms when they were used as the second coagulants, which probably led to different re-grown floc size. Additionally, previous

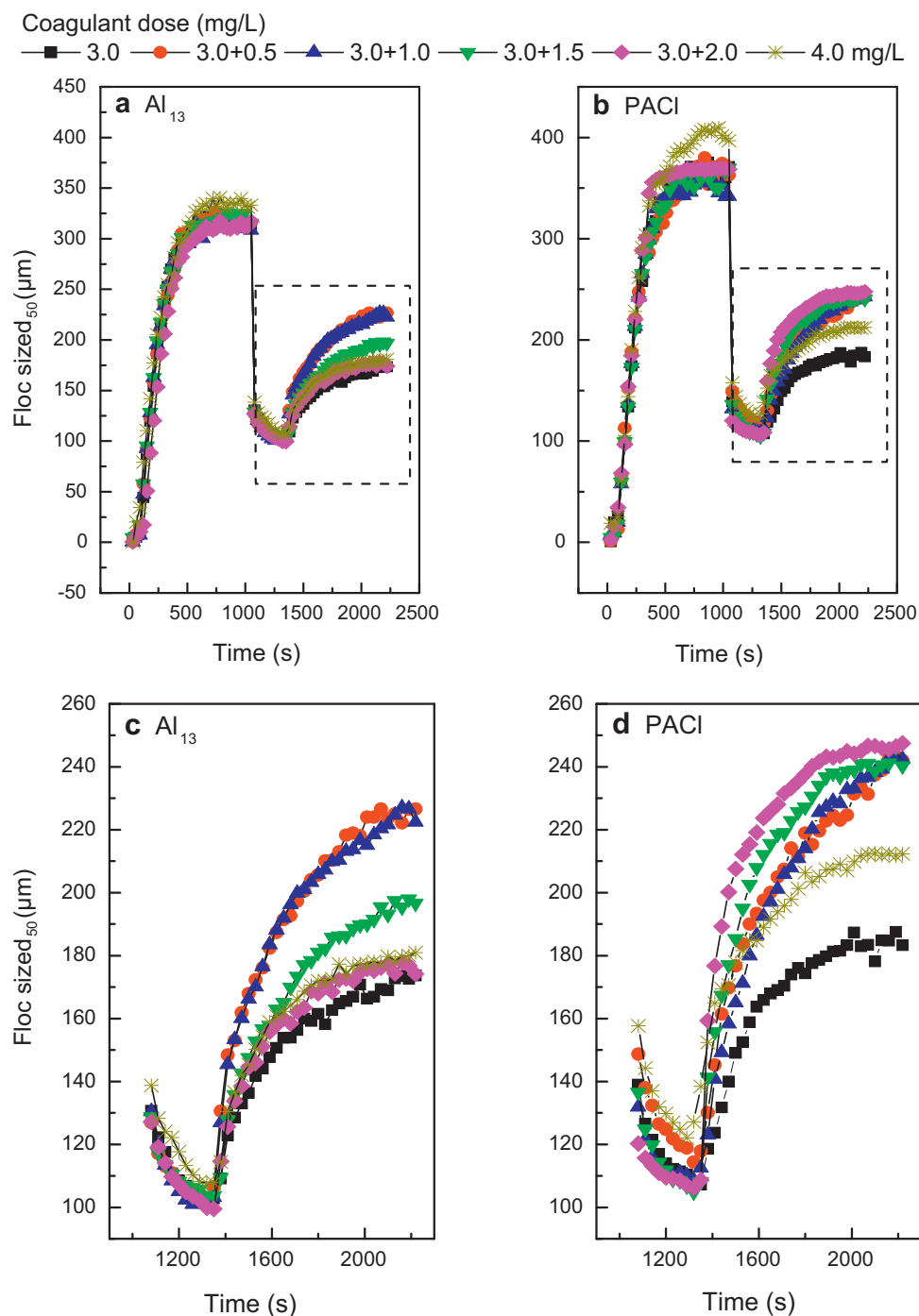


Fig. 3. The floc formation, breakage and re-growth of HA flocs formed by (a) Al_{13} polymer and (b) PACI at various initial and second doses; (c) and (d) the enlarged reviews of floc re-growth phases for Al_{13} and PACI, respectively.

work by Yu et al. [13] showed that the fresh amorphous hydroxide precipitate formed from PACI with more Al_m was highly effective in promoting the re-growth of broken flocs, whereas the PACI with more Al_{13} species was ineffective. This agrees well with the results shown in Fig. 3b. However, the interaction between flocs and freshly dosed coagulant was complicated and it was hard to clearly verify the different coagulation mechanisms of various Al species as the second coagulant. Further work is needed to get a thorough understanding.

The aggregate structures of the re-generated flocs were investigated in terms of fractal dimension (D_f), which was derived from the scattered light intensity (I) as a function of wavenumber (Q).

To keep the power law relationship valid as shown in Eq. (3), the values of $\log Q$ for D_f calculation were maintained in the range of -4.0 to -2.4 as presented in Fig. 4. For the coagulations with one time addition at 3 and 4 mg/L, Al_{13} species produced flocs with larger D_f than PACI. Additional Al_{13} dose at 0.5 and 1.0 mg/L could remarkably improve the floc D_f (Fig. 4a). However, the floc compact degree decreased significantly with further increase of the second dose. Additional dose of Al_{13} at 1.5 and 2.0 mg/L yielded loose aggregates with D_f of 2.42 and 1.82, respectively, which were even much lower than those of flocs formed with one time addition of 3 mg/L (2.52). This could be also attributed to the charge reversal by the overdosed second addition of Al_{13} . According to Fig. 2,

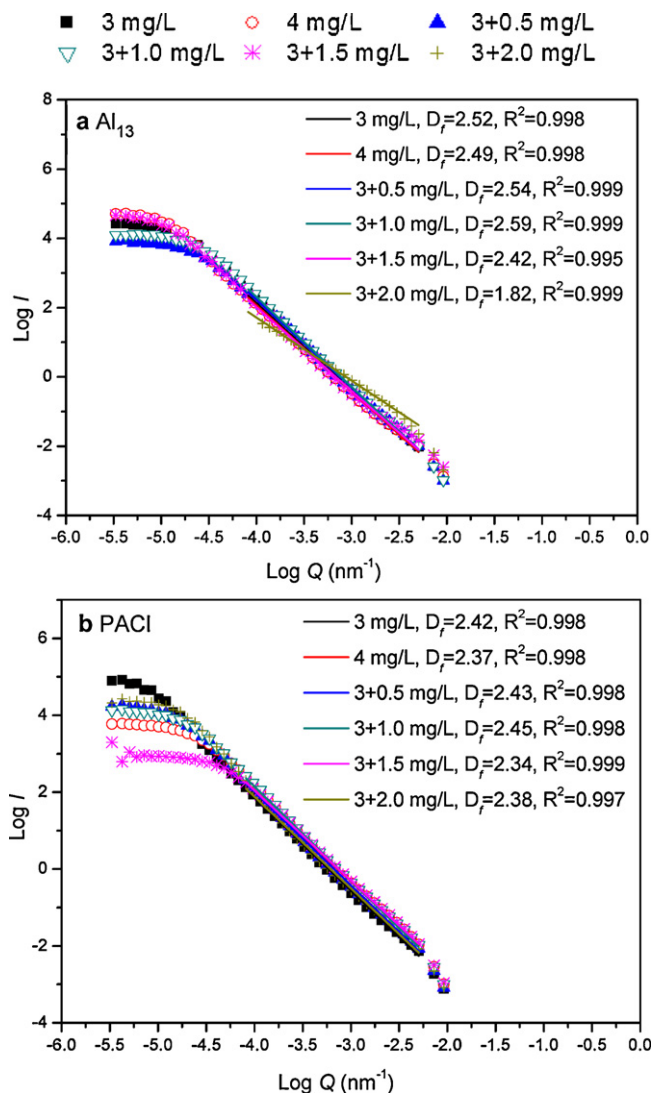


Fig. 4. Determination of the fractal dimension of flocs after breakage and re-growth in coagulation by (a) Al₁₃ without and with additional doses; and (b) PACI without and with additional doses.

zeta potentials were nearly zero in the case of coagulation with additional Al₁₃ of 0.5 and 1.0 mg/L, where the negative charges on broken aggregates and particles were mostly neutralized, accelerating the re-aggregation of broken fragments and particles. With additional dose further increased, charge reversal occurred and the broken flocs became re-stabilized. The re-generation of flocs was dominated by the adsorption and bridging of the newly added Al-based coagulants, which resulted in loosely constructed aggregates [40,41].

The influences of second PACI dose on the fractal dimension of re-formed flocs were not obvious. At additional doses of 0.5 and 1.0 mg/L, the D_f values were slightly improved due to the weaker charge neutralization ability of PACI. Moreover, the monomeric and dimeric Al species in PACI easily hydrolyzed and transformed into aluminum hydroxide precipitates after addition into the suspension, which tended to produce incompact aggregates as aforementioned.

3.4. Effect of breakage shear force on floc properties

The shear rate applied in floc breakage is expected to have a major effect on the floc breakage and re-growth, which has

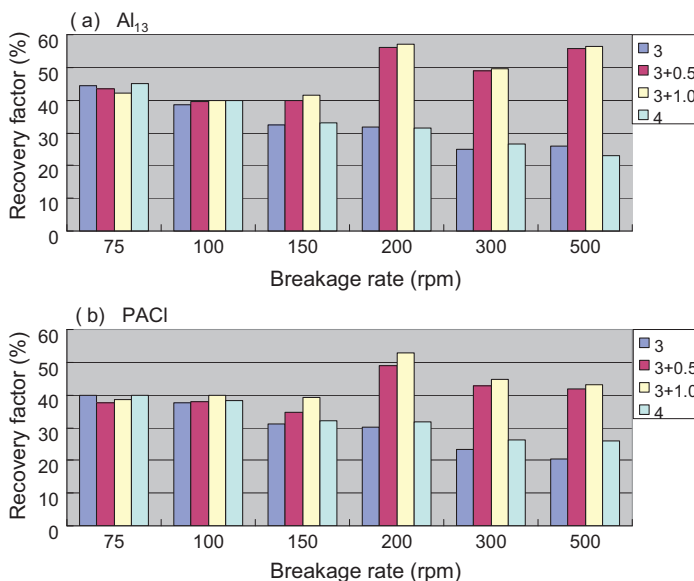


Fig. 5. Effect of shear rate on the recovery factors of HA flocs formed by Al₁₃ and PACI at different initial and additional doses.

been reported in previous studies [4,31]. In order to comparatively investigate the influences of enhanced shear force on the floc properties in two-stage addition coagulation, a further series of tests with various shear rates (75, 100, 150, 200, 300 and 500 rpm) applied in the breakage phases were conducted. Two additional coagulant concentrations, 0.5 and 1.0 mg/L were used in the tests.

The dynamic floc size was continuously monitored by the laser diffraction instrument (Mastersizer 2000) as before and the recovery factors under different coagulant dosing modes were calculated based on Eq. (1). The average floc sizes before breakage, after breakage and after re-growth in all cases are listed in Table 2 and the recovery factors are shown in Fig. 5. It could be observed that for coagulation with 1-shot dose, R_f of flocs steadily decreased with the increasing shear regardless of the initial dose and coagulant applied. However, with a second dose of 0.5 and 1.0 mg/L, the flocs exposed to high shears (200, 300 and 500 rpm) presented even larger R_f than those exposed to low shears (75, 100 and 150 rpm) for both coagulants. It is evident from Fig. 5 that the small second doses during breakage could definitely improve R_f . When the shear rate for breakage was 75 and 100 rpm, the R_f with additional dose was undistinguishable from that without additional dose. However, with the shear force further increased, small additional doses (0.5 and 1.0 mg/L) of Al₁₃ and PACI could markedly improve the R_f . Nevertheless, the floc sizes after re-growth still presented an overall descending trend with the increasing breaking in all the cases as shown in Table 2. Additional dosing during breakage phase could just help alleviate the further decrease of the re-grown floc sizes with the continuously increasing breakage shear.

Zeta potentials under various breakage shears were measured and the results are shown in Fig. 6. It was observed that zeta potentials decreased with increasing shear rate in all cases. The reduction in zeta potentials could be alleviated by the additional dose during breakage for both coagulants. Compared with PACI, additional Al₁₃ at the same dose contributed to obviously larger zeta potentials. Unexpectedly, the re-grown flocs by additional Al₁₃ were not obviously larger than those by PACI, which might be attributed to the better ability of hydroxide precipitates formed from PACI to promote floc re-growth as aforementioned [13].

The fractal dimensions of re-grown flocs under various breakage shear rates were determined by the same method in Fig. 4 and the results are displayed in Fig. 7. It could be found that for one time

Table 2
Mean diameters of flocs before breakage, after breakage and after re-growth under various breaking rates for Al₁₃ and PACI at different initial and additional doses.

Breakage rate (rpm)	Coagulant dose (mg/L)											
	3			3+0.5			3+1.0			4		
	d ₁	d ₂	d ₃	d ₁	d ₂	d ₃	d ₁	d ₂	d ₃	d ₁	d ₂	d ₃
Al₁₃												
75	324.4	268.6	293.4	311.2	247.3	275.0	317.8	258.6	283.5	331.8	240.0	281.4
100	320.2	199.7	246.3	333.7	204.1	255.3	318.3	196.7	245.2	318.1	179.7	234.7
150	315.1	120.7	183.8	311.0	127.4	200.5	310.5	134.6	207.5	330.4	143.4	205.5
200	316.9	100.3	169.5	326.3	102.4	228.3	315.7	100.7	223.1	326.3	106.3	175.7
300	318.6	72.0	133.4	332.7	73.9	200.3	305.0	71.1	187.0	321.6	87.6	149.8
500	314.9	49.7	118.3	332.0	48.3	206.9	326.9	46.7	204.8	335.2	57.7	121.5
PACI												
75	359.0	261.7	300.6	367.1	284.6	315.5	367.0	288.0	318.5	366.9	287.8	319.3
100	366.4	223.7	277.7	374.5	218.9	278.0	381.2	216.3	282.0	362.4	226.3	278.4
150	369.5	135.5	208.5	380.0	144.4	225.8	372.2	155.7	241.0	363.4	162.3	227.1
200	363.5	107.0	184.4	373.2	110.3	238.9	353.3	113.2	239.8	369.7	126.0	203.1
300	375.5	93.8	159.9	370.8	95.5	213.2	362.8	94.4	214.1	358.8	107.2	173.7
500	373.0	61.4	125.0	375.3	62.0	192.9	371.5	61.6	195.7	371.9	70.8	148.5

coagulant addition, the D_f increased first and then decreased with the increasing shear for both coagulants at doses of 3 or 4 mg/L. And small second doses at 0.5 and 1.0 mg/L could always improve the D_f values of the re-formed aggregates for the shear rates investigated in this study. However, the improvement caused by additional PACI was not so obvious as that by additional Al₁₃. More significantly, the D_f for Al₁₃ coagulation with small additional dose increased continuously with the shear rates, which agreed with the point that enhanced shear rate could elevate the compact degrees of flocs by

restructuring and rearrangement [42]. By contrast, the D_f of PACI-HA flocs declined evidently when they were exposed to high shears above 200 rpm even with the additional dose. That was because the rapid velocity gradient caused quite severe damage to the aggregates and the relatively poor charge neutralization of additional PACI could hardly neutralize the negative charges on floc fragments. The re-formation of flocs was mainly dominated by adsorption and entrapment of the freshly formed Al hydrolyzate, which tended to result in incompact aggregates with open-structures [40,41].

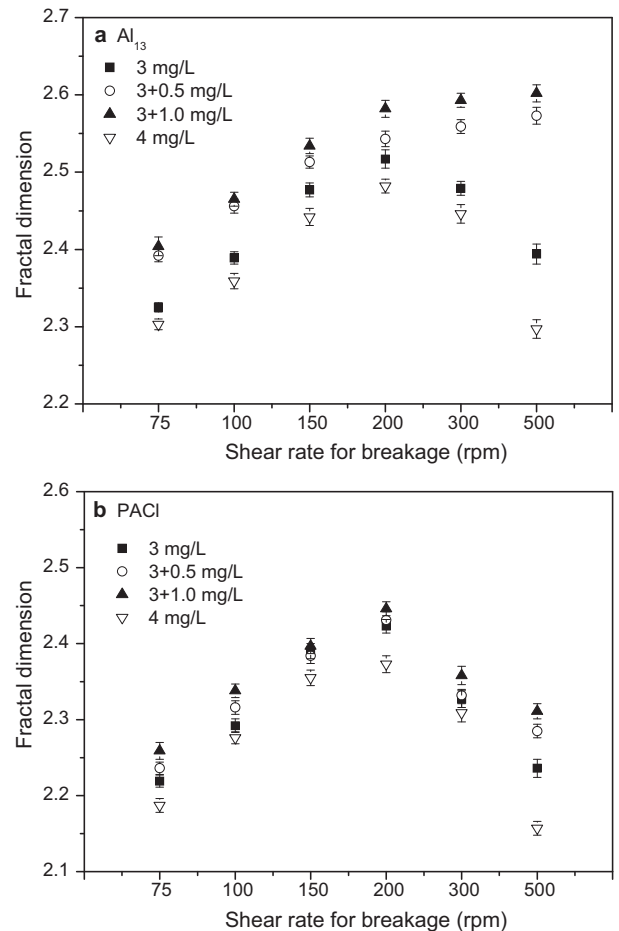
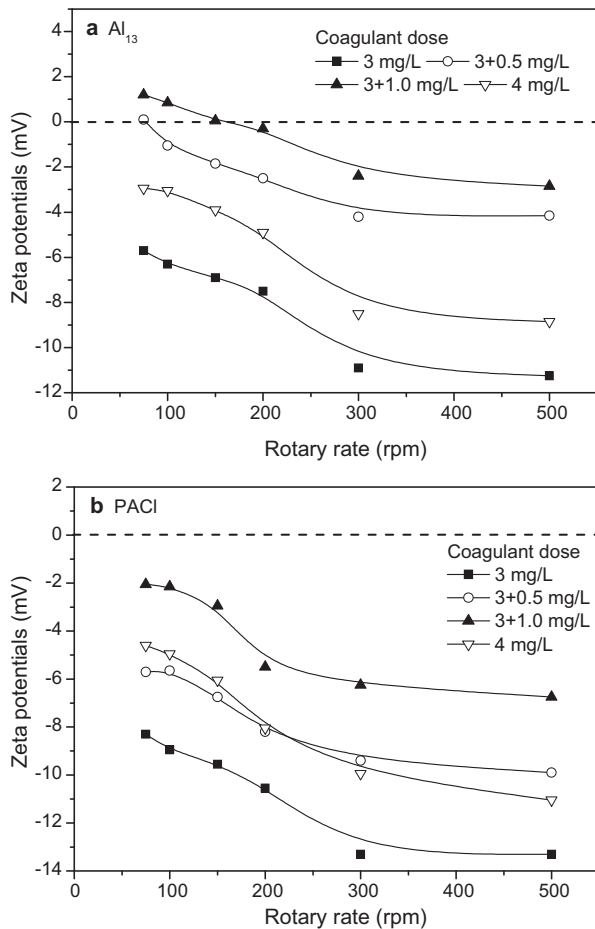


Fig. 6. Effect of shear force on zeta potentials of HA flocs formed by (a) Al₁₃ and (b) PACI at different initial and second doses.

Fig. 7. Effect of breakage shear force on fractal dimension of flocs formed by (a) Al₁₃ and (b) PACI at different initial and second doses.

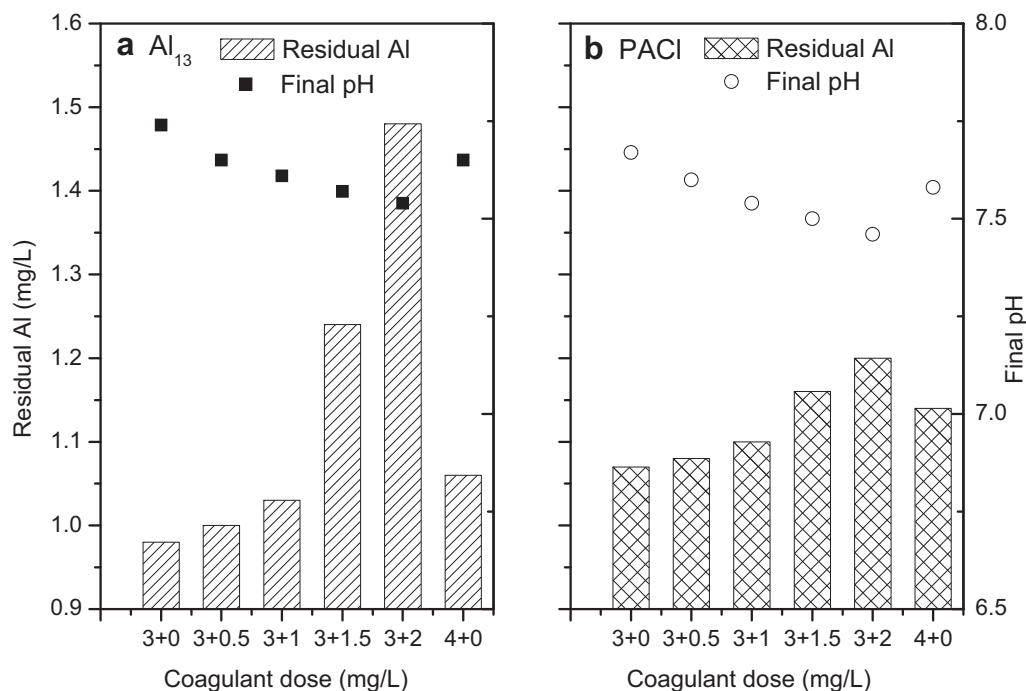


Fig. 8. Residual Al and final pH of the effluent after breakage, re-growth and sedimentation for (a) Al₁₃ and (b) PACI coagulations at different initial and second doses.

3.5. Effect of second addition on residual Al in effluent

The residual Al in effluents after breakage and consequent re-growth with and without additional dose were comparatively measured in this study and the results are displayed in Fig. 8. The higher total residual aluminum concentration than legislation limit could be ascribed to the high Al concentration in the raw water (Al component in HA and some possible impurities in the tap water) together with the fraction caused by Al-based coagulants. For Al₁₃, additional dose at 0.5 and 1.0 mg/L enhanced the residual Al slightly compared to the 1-shot dose of 3 mg/L; while second dose further increased to 1.5 and 2.0 mg/L led to unexpected higher residual Al concentrations, which could be ascribed to the charge reversal as aforementioned. Based on the results shown in Fig. 2a, zeta potentials for Al₁₃ with additional dose of 0.5 and 1.0 mg/L were negative and close to zero, which could facilitate the re-aggregation of floc segments and therefore most of the additional Al could be consumed and then removed together with the aggregates. However, higher additional doses at 1.5 and 2.0 mg/L turned the surface charges into positive, which inhibited the re-aggregation of floc fragments and thus more additional Al remained in the effluent. In the case of PACI, no charge reversal occurred and consequently the residual Al increased steadily and slowly with the increasing additional dose without any abrupt rise. However, Al₁₃ led to lower residual Al concentrations than PACI, except for 1.5 and 2.0 mg/L second doses. That was due to the complexation of monomeric Al species in PACI with HA molecules. The complexes were non-labile, negatively charged and could not be easily removed through conventional coagulation process [17]. Final pHs of the effluents in all cases were measured and the results are also provided in Fig. 8. It could be found that as the total coagulant concentrations increased, pH decreased from around 7.7 to 7.6 and 7.7 to 7.4 for Al₁₃ and PACI, respectively. Previous work by Yang et al. [43,44] indicated that residual Al increased slightly when the pH increased from 7.0 to 8.0. That was due to the formation of soluble Al(OH)₄⁻¹ at higher pH, which was much more difficult to be removed from the water during sedimentation process than the unstable and suspended or particulate aluminum. Thus the decrease of pH by second

coagulant was expected to cause the reduction in residual Al. However, the variation of residual Al with pH change in the range of 7.0–8.0 was slight according to previous work [43,44], and additionally, the variation of pH was minor in this study (Fig. 8). Consequently, it could not prevent the residual Al from increasing as the coagulant dose increased.

It should also be noted that for both Al₁₃ and PACI, the two-stage addition with 3 mg/L initial dose and 1 mg/L second dose resulted in lower residual Al concentration than the one-time dose at 4 mg/L. That is, for the same total coagulant concentration, two-stage addition led to lower residual Al in effluent than one-time addition mode, indicating that the coagulants could fully react with the contaminants and thus were more consumed when they were dosed for several times.

4. Conclusions

The main conclusions of this work are:

- (1) Small additional dose of Al₁₃ could remarkably improve the HA removal efficiency and charge neutralization played an important role; while larger additional dose, which induced charge reversal, could slightly enhance the coagulation efficiency through the newly formed Al hydroxide precipitates.
- (2) The charge neutralization and adsorption of freshly formed hydroxide precipitates formed by additional Al₁₃ and PACI were less effective in promoting floc re-growth than that of aluminum hydroxide precipitates formed by additional alum. Al₁₃ additional dose at the isoelectric point could largely improve the D_f of re-formed flocs, while the additional PACI contributed to inconspicuous influence on floc D_f .
- (3) Additional coagulant dose could alleviate the decrease of re-grown floc size which resulted from the increase of breaking shear. For the coagulation with one-time dose, floc D_f increased initially and then decreased with the increasing shear rates for both coagulants. Small additional Al₁₃ could keep the floc D_f increased continuously with the shear rates, which did not occur in the case of PACI.

- (4) Two-stage addition induced lower residual Al in effluent than one-time addition for a certain total Al coagulant concentration. For the additional doses at isoelectric point, Al₁₃ led to lower residual Al than PACl at the same initial and additional doses. Charge reversal induced by the overdosed second Al₁₃ addition could sharply increase the residual Al in the finished water.

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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 Al₁₃ species and pH control, *Environ. Sci. Technol.* 40 (2006) 325–331.
- [2] J.L. Lin, C.J.M. Chin, C.P. Huang, J.R. Pan, D.S. Wang, Coagulation behavior of Al₁₃ aggregates, *Water Res.* 42 (2008) 4281–4290.
- [3] M.Q. Yan, D.S. Wang, J.R. Ni, J.H. Qu, C.W.K. Chow, H.L. Liu, Mechanism of natural organic matter removal by polyaluminum chloride: effect of coagulant particle size and hydrolysis kinetics, *Water Res.* 42 (2008) 3361–3370.
- [4] W.Y. Xu, B.Y. Gao, Q.Y. Yue, Y. Wang, Effect of shear force and solution Ph on flocs breakage and re-growth formed by nano-Al₁₃ polymer, *Water Res.* 44 (6) (2010) 1893–1899.
- [5] W.Y. Xu, B.Y. Gao, Q.Y. Yue, Q. Wang, Effect of preformed and non-preformed Al₁₃ species on evolution of floc size, strength and fractal nature of humic acid flocs in coagulation process, *Sep. Purif. Technol.* 78 (2011) 83–90.
- [6] C.R. O'Melia, Coagulation and sedimentation in lakes, reservoirs and water treatment plants, *Water Sci. Technol.* 37 (1998) 129–135.
- [7] W.Z. Yu, J. Gregory, L. Campos, Breakage and regrowth of Al-humic flocs – effect of additional coagulant dosage, *Environ. Sci. Technol.* 44 (2010) 6371–6376.
- [8] W.Z. Yu, J. Gregory, L. Campos, The effect of additional coagulant on the re-growth of alum-kaolin flocs, *Sep. Purif. Technol.* 74 (2010) 305–309.
- [9] K. McCurdy, K. Carlson, D. Gregory, Flocs morphology and cyclic shearing recovery: comparison of alumandpolyaluminum chloride coagulants, *Water Res.* 38 (2004) 486–494.
- [10] M.A. Yukselen, J. Gregory, Breakage and reformation of alum flocs, *Environ. Eng. Sci.* 19 (2002) 229–236.
- [11] M. Hermawan, G.C. Bushell, V.S.J. Craig, W.Y. Teoh, R. Amal, Floc strength characterization technique: an insight into silica aggregation, *Langmuir* 20 (2004) 6450–6457.
- [12] P. Jarvis, B. Jefferson, S.A. Parsons, How the natural organic matter to coagulant ratio impacts on floc structural properties, *Environ. Sci. Technol.* 39 (2005) 8919–8924.
- [13] W.Z. Yu, J. Gregory, L.C. Campos, Breakage and re-growth of flocs: effect of additional doses of coagulant species, *Water Res.* 45 (2011) 6718–6724.
- [14] R.J. Francois, Strength of aluminium hydroxide flocs, *Water Res.* 21 (9) (1987) 1023–1030.
- [15] P. Jarvis, B. Jefferson, S.A. Parsons, Floc structural characteristics using conventional coagulation for a high DOC, low alkalinity surface water source, *Water Res.* 40 (2006) 2727–2737.
- [16] J.E. Van Benschoten, J.K. Edzwald, Measuring aluminum during water treatment: methodology and application, *J. Am. Water Works Assoc.* (1990) 71.
- [17] P.T. Srinivasan, T. Viraraghavan, K.S. Surbramanian, Aluminium in drinking water: an overview, *Water SA* 25 (1) (1999) 47–56.
- [18] G. Berthon, Aluminum speciation in relation to aluminum bioavailability, metabolism and toxicity, *Coord. Chem. Rev.* 228 (2) (2002) 319–341.
- [19] J.L. Lin, C.P. Huang, J.R. Pan, D.S. Wang, Effect of Al (III) speciation on coagulation of highly turbid water, *Chemosphere* 72 (2008) 189–196.
- [20] J.L. Lin, C. Huang, C.J.M. Chin, J.R. Pan, The origin of Al(OH)₃-rich and Al₁₃-aggregate flocs composition in PACl coagulation, *Water Res.* 43 (2009) 4285–4295.
- [21] H.Z. Zhao, Z.K. Luan, Y.B. Su, S.G. Wang, Purification and characterization of Al₁₃ species, *Chem. J. Chin. Univ.* 23 (2002) 751–755 (in Chinese).
- [22] GB 15892, Water Treatment Chemicals – Polyaluminum Chloride, National Standards of the People's Republic of China, 1995 (in Chinese).
- [23] J.S. Gaffney, N.A. Marley, S.B. Clark, Humic and Fulvic Acids: Isolation, Structure, and Environmental Role, American Chemical Society, Washington, DC, 1993, pp. 2–16.
- [24] 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 (2009) 354–359.
- [25] J. Gregory, The role of floc density in solid-liquid separation, *Filtr. Separat.* 35 (4) (1998) 367–371.
- [26] S. Tang, A model to describe the settling behavior of fractal aggregates, *Colloids Surf. A* 157 (1999) 185–192.
- [27] T.D. Waite, J.K. Cleaver, J.K. Beattie, Aggregation kinetics and fractal structure of γ -alumina assemblages, *J. Colloid Interface Sci.* 241 (2001) 333–339.
- [28] S.Y. Lee, A. Anthony, G. Fane, T.D. Waite, Impact of natural organic matter on floc size and structure effects in membrane filtration, *Environ. Sci. Technol.* 39 (2005) 6477–6486.
- [29] T. Li, Z. Zhu, D.S. Wang, C.H. Yao, H.X. Tang, Characterization of floc size strength and structure under various coagulation mechanisms, *Powder Technol.* 168 (2006) 104–110.
- [30] J.C. Wei, B.Y. Gao, Q.Y. Yue, Y. Wang, W.W. Li, X.B. Zhu, Comparison of coagulation behavior and floc structure characteristic of different polyferric-cationic polymer dual-coagulants in humic acid solution, *Water Res.* 43 (2009) 724–732.
- [31] P. Jarvis, B. Jefferson, S. Parsons, Breakage regrowth, and fractal nature of natural organic matter flocs, *Environ. Sci. Technol.* 39 (2005) 2307–2314.
- [32] M.Y. Lin, H.M. Lindsay, D.A. Weita, R.C. Ball, R. Klein, P. Meakin, Universality in colloid aggregation, *Nature* 339 (1989) 360–362.
- [33] GB/T 5750, 6-2006, Standard Examination Methods for Drinking Water – Metal Parameters, National Standards of the People's Republic of China (in Chinese).
- [34] R.D. Letterman, S.G. Vanderbrook, P. Sricharoenchaikit, Electrophoretic mobility measurements in coagulation with aluminum salts, *J. Am. Water Works Assoc.* 74 (1982) 44–51.
- [35] J.E. Van Benschoten, J.K. Edzwald, Chemical aspects of coagulation using aluminum slats. 2. Coagulation of fulvic acid using alum and polyaluminum chloride, *Water Res.* 24 (12) (1990) 1519–1526.
- [36] Y.B. Chu, B.Y. Gao, Q.Y. Yue, Y. Wang, The effect of cycle shear and sulfate on dynamic coagulation of alum coagulants, *Sci. China Ser. B: Chem.* 37 (5) (2007) 440–445 (in Chinese).
- [37] 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.
- [38] J.J. Ducoste, M.M. Clark, The influence of tank size and impeller geometry on turbulent flocculation. I. Experimental, *Environ. Eng. Sci.* 15 (3) (1998) 215–224.
- [39] D.S. Wang, W. Sun, Y. Xu, H.X. Tang, J. Gregory, Speciation stability of inorganic polymer flocculant – PACl, *Colloids Surf. A: Physicochem. Eng. Aspects* 243 (2004) 1–10.
- [40] R.M. Wu, D.J. Lee, T.D. Waite, J. Guan, Multilevel structure of sludge flocs, *J. Colloid Interface Sci.* 252 (2002) 383–392.
- [41] B.C. Cao, B.Y. Gao, X.X. Liu, M.M. Wang, Z.L. Yang, Q.Y. Yu, 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.
- [42] 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 (2001) 67–77.
- [43] 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.
- [44] Z.L. Yang, B.Y. Gao, Y. Wang, Q. Wang, Q.Y. Yue, Aluminum fractions in surface water from reservoirs by coagulation treatment with polyaluminum chloride (PAC): influence of initial pH and OH⁻/Al³⁺ ratio, *Chem. Eng. J.* 170 (2011) 107–113.