Investigation of the property of kaolin–alum flocs at acidic pH

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HIGHLIGHTS

- There was full re-growth for monomeric Al or *in situ* polymeric Al₁₃.
- The break-up process displayed irreversibility for unstable small polymeric Al.
- There was a significant increase of D_f when the pH changed from 5.2 to 6.0.
- The number of small flocs after breakage and re-growth decreased at acidic pH.
- The strength of flocs is strongly correlated with D_f of flocs.

GRAPHICAL ABSTRACT

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ABSTRACT

The formation, breakage and re-growth of flocs were investigated using aluminium sulfate (alum) at acidic pH to explore the property of flocs and coagulation mechanism by different Al species formed *in situ*. The broken flocs can fully re-grow to the size before breakage, when monomeric Al or polymeric Al₁₃ forms dominate the coagulant species. However, for relatively unstable small polymeric Al (Al₃–Al₈) and alum precipitate, the break-up process displayed a distinct irreversibility.

There was a distinct increase of fractal dimension (D_f) when the pH changed from 5.2 to 6.0, as well as the strength of flocs (the size of broken flocs), which meant that the flocs structure changed significantly. Also the D_f of broken flocs was higher than that of flocs before breakage, and the D_f values of re-grown flocs were not greatly different from the values before breakage. The number of small flocs after breakage and re-growth was much lower than that before breakage at acidic pH (pH 5.2) when the average size of flocs was chosen at the same value before breakage and after re-growth. An important finding is that the strength of flocs is strongly correlated with D_f of flocs.

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1. Introduction

Hydrolyzed coagulants are usually used in the purification of drinking water [1–3], and pH is of great importance for the coagulation process. The effect of pH on the binding between particles and/or precipitate and their surface charge determines the growth of flocs. Some researchers found that adjusting the pH downwards

to acidic pH could improve the coagulation process [4,5]. But other researchers found that the coagulation efficiency was greater at neutral pH as the size flocs formed was much larger than the one at acidic pH [6]. The low growth ability of small flocs at the acidic pH is the main factor causing not too large flocs compared with sweep coagulation at neutral pH. Therefore, the cohesion/re-cohesion ability for the flocs growth should be explored.

Improved knowledge of the factors affecting the re-growth ability of broken flocs, and the effect of floc breakage and re-growth on particle separation processes would give a better understanding of the coagulation mechanism. Many researches [7,8] found that it was difficult for the broken flocs to fully return to their

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size before breakage, and repeated breakage of flocs resulted in lower re-growth ability [9]. The re-growth of flocs after exposure to high shear forces was found limited for waters coagulated with aluminium sulfate (alum), ferric sulfate and cationic polyelectrolyte [10]. When water contains particles such as kaolin, whether the flocs can return to the original size before breakage is dependent on the properties of broken flocs [11–13]. Yukselen and Gregory [11,12] found that only limited re-growth of Al–kaolin flocs occurred indicating a significant irreversibility of the floc break-up process; and residual turbidity increased after floc breakage and re-growth when the coagulant was alum or polyaluminum chloride (PACl). However, for cationic polyelectrolytes, the re-growth of broken flocs occurred to a much greater extent. Li et al. [14] and Yu et al. [15] also showed that broken kaolin flocs were difficult to re-grow when alum was used. Increased humic acid concentration had a slight influence on the cohesion of kaolin flocs and resulted in much worse floc re-growth [16,17]. Complete re-growth of flocs can occur if a small additional coagulant dose is added during breakage, depending on the coagulant type [18,19] and strategy of application [20]. But until now, there is little investigation of flocs breakage and re-growth at acidic pH.

The flocs generated in acidic conditions were stronger and more recoverable than those generated in alkaline conditions independent of coagulant species [21]. Detailed experiments have not been carried out at acidic pH for the flocs re-growth results. Therefore, this work aimed to evaluate the re-growth ability of flocs when the coagulation process was carried out by alum at different acidic pH from 4.4 to 7, which caused different breakage behaviour. Floc properties, including size and fractal dimension before and after breakage, and zeta potential were investigated to explore the coagulation mechanism, and some distinct variations were found in the narrow pH area around 5.

2. Materials and methods

2.1. Suspension and coagulant

Kaolin clay (Shanghai, China) was used as the model suspension [22]. 200 g of kaolin was dispersed in 500 ml of deionized (DI) water in a high-speed blender. To obtain full dispersion it was necessary to raise the pH of the suspension to about 7.5, which was achieved by adding 5 ml of 0.1 M NaOH. After blending at 4000 rpm for 10 min the clay suspension was diluted to 1 L with DI water and allowed to stand overnight in a measuring cylinder. The top 750 ml was decanted and retained. Its solids content was determined gravimetrically and found to be 57.8 g/L.

Aluminium sulfate hydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, >99%) ‘alum’ was used. Stock alum solutions were prepared at a concentration of 0.2 M (calculated as Al).

2.2. Jar test and zeta potential measurement

The test solutions were prepared using DI water with addition of 5 mM NaHCO_3 , and the stock suspension was diluted in the water to give a clay concentration of 50 mg/L. The pH of the solution was adjusted to fixed value by pre-addition of 0.1 M HCl to adjust to the final pH value between 4 and 7. The experiments were conducted at a temperature of $20 \pm 1^\circ\text{C}$. All reagents used were of analytical grade.

A known amount of alum (0.01 mM or 0.02 mM Al) was added into the test suspension (1000 ml) with 50 mg/L kaolin and at the same time the stirring of Flocculator ZR4-2 (Shenzhen Zhongrun, China) begun. The stirring speed was set at 200 rpm (average shear rate 184 s^{-1} , [16]) for 1 min and 50 rpm (23 s^{-1}) for more than 30 min until the size of flocs reached a steady-state, according to

the pre-tests. The speed was then increased to 200 rpm for 1 min to break the flocs and then back to 50 rpm for more than 30 min for flocs to re-grow.

Samples were taken after 1 min rapid mixing of coagulant, and zeta potentials were determined by a laser zeta analyzer (Zetasizer Nano ZS90, Malvern, UK).

2.3. On-line floc size monitoring

A laser diffraction instrument (Mastersizer 2000, Malvern, UK) was used to measure dynamic floc size as the coagulation and flocculation process proceeded, which has been used by many researchers [10,23]. The suspension was monitored by circulating water from the flocculation vessel through the optical unit of the Mastersizer, and then back into the vessel by a peristaltic pump on the return tube with 5 mm inner diameter peristaltic pump tubing. The inflow and outflow tubes were positioned opposite each other at a depth below the water surface of 5 cm. Size measurements were taken every 30 s for the duration of the jar test and logged by computer. Flocs were pumped through the system at an optimal flow rate of 2.0 L/h; preliminary tests showed that flow rates above this value gave rise to floc breakage, while below this rate flocs settled in the tubing.

2.4. Fractal dimension of flocs

The determination of fractal dimension by use of small angle laser light scattering (SALLS, Mastersizer 2000, Malvern, UK) has been previously described [24–26], so only a brief overview is given below.

The total scattered light intensity I is a function of the scattering vector Q , where Q is the difference between the incident and scattered wave vectors of the radiation beam in the medium [26], which is given by Eq. (1)

$$Q = \frac{4\pi n \sin(\delta/2)}{\lambda} \quad (1)$$

where n is the refractive index of the suspending medium, δ is the scattering angle, and λ is the wavelength of the radiation in a vacuum.

For independently scattering aggregates, I is related to Q and the fractal dimension D_f can be calculated by Eq (2):

$$I \propto Q^{D_f} \quad (2)$$

A confirmation of the power relationship (e.g. Spicer et al. [23]) is to plot I against Q on a log–log scale. A power law relationship exists if this plot yields a straight line, the slope of which is used to give D_f .

3. Results

3.1. Change of zeta potential

The changes of zeta potential of alum–kaolin flocs as pH increased from 4 to 7 are presented in Fig. 1, together with values for kaolin particles alone. The doses of alum were 0.01 mM and 0.02 mM. Zeta potential for kaolin particles decreases as the pH increased, and changed from positive to negative at pH around 5, which was similar with the finding of Kretzschmar et al. [27]. In the presence of alum, zeta potentials was about constant between pH 4 and pH 5 and then increased until about pH 5.5, after which there was a steady decrease, with surface charge reversal occurring above pH 6.5. The zeta potential–pH behaviour was almost similar for the two alum concentrations and was consistent with the formation and adsorption of cationic hydrolysis products of Al, as the OH/Al ratio increased.

Fig. 1. Zeta potentials of alum-kaolin flocs as a function of pH.

3.2. Effect of pH on floc growth, breakage and re-growth

The formation, breakage and re-formation of aggregates by different doses of alum at pH between 4.4 and 7 are shown in Fig. 2. The size of flocs before breakage increased as the pH increased, and the complete lack of flocculation at pH 5.5 is because of its high zeta potential (Fig. 1). Also, slow growth, before significant growth of flocs, was longer at lower pH. At pH 7, where rapid hydroxide precipitation would be expected, there is rapid floc growth, especially for the higher dose of alum. At both doses flocs that formed at lower pH values showed more reversible breakage, although at pH values around 5 with narrow pH range floc breakage was not fully reversible. However, the flocs showed significantly

Fig. 3. Influence of pH and alum doses on the size of broken flocs (strength factor) (a) and re-growth factor and (b) of flocs.

irreversible breakage at pH 7. But at pH 6, the re-grown flocs were almost the same size as those before breakage. The result meant that the surface of flocs by low dose of alum was greatly different at pH 6 and pH 7. Comparing Fig. 2a and b, 0.02 mM alum caused larger average size of flocs (d_{50}) than that by 0.01 mM alum. The results meant that the strength of flocs increased as the dosage of alum increased from 0.01 mM to 0.02 mM.

3.3. Floc strength and re-growth ability

In order to characterize the efficiency in formation of flocs before breakage and after re-growth, and to compare the shear properties of flocs in different conditions, re-growth factors were calculated, as well as the size of broken flocs, which depends on the floc strength. The formula for the floc re-growth factor is as follows [10].

$$F_1 = \frac{d_3 - d_2}{d_1 - d_2} \times 100\% \text{ (re-growth factor)} \quad (3)$$

where d_1 is the maximum plateau value of floc size before floc breakage; d_2 is the minimum floc size when flocs are broken, and d_3 is the maximum plateau value of floc size after re-growth of broken flocs.

The size of broken flocs and re-growth factor of flocs were analyzed for different pH and doses of coagulant (Fig. 3). On the whole, the size of broken flocs increased as the pH increased from 4 to 7, especially for the pH between 5.2 and 6.0 (Fig. 3a). The size of broken flocs formed with 0.02 mM Al was much greater than that with 0.01 mM Al at pH higher than 6. But there was little difference between these two doses at pH lower than 5.2. No floc formed at pH between 5.2 and 6.0. As only Al^{3+} and its lower polymers existed at pH lower than 5.2, charge neutralization at this condition caused lower strength of flocs (smaller size of broken flocs). According to the result by Van Benschoten and Edzwald [28], for pH 7, the solubility of Al is near $1 \mu\text{mol/L}$. Therefore, the larger size of broken flocs should be existence of hydroxide precipitate. Thus,

Fig. 2. Formation, breakage and re-formation of aggregates by alum between pH 4 and pH 7, (a) 0.01 mM and (b) 0.02 mM.

Fig. 4. Variation of fractal dimension of flocs at acidic pH after formation (a), breakage (b), and re-growth (c).

the strength of flocs increased as the increase of connection points between micro-flocs and the formation of amorphous aluminium hydroxide.

On the contrary, the re-growth factor of broken flocs was much different at different pH values (Fig. 3b). It should be noted that the re-growth factor was about 100% when monomeric Al or Keggin Al_{13} was the coagulant species at acidic pH. While at pH 7, the re-growth factor decreased significantly. Also there was a very interesting result that the re-growth factor of flocs formed at pH near 5 with narrow pH range was lower than the one formed at lower or higher pH. According to the variation of zeta potential at the pH around 5, the unstable small polymeric Al may not be the case.

Fig. 5. The size distribution of flocs before breakage and after re-growth with same d_{50} value ($125 \mu\text{m}$) at pH 5.2, (a) 0.01 mM and (b) 0.02 mM.

3.4. Fractal dimension of flocs before breakage and after re-growth

Variation of fractal dimension of flocs at acidic pH after formation, breakage, and re-growth are shown in Fig. 4. There was significant difference of D_f before breakage between the one formed at low pH (lower than 5.2) and that at relative high pH (higher than 6), as shown in Fig. 4a. At pH values of 6 or higher flocs formed with 0.01 mM Al had much lower D_f than those formed with 0.02 mM Al, whereas there was no significant difference when pH was lower than 5.2. Comparing Fig. 3a with Fig. 4a, it is very interesting that the D_f of flocs formed at different pH was very similar with the variation of size of broken flocs at different pH values. The results meant that there is a strong relationship between the strength of flocs and D_f of flocs.

Broken flocs (Fig. 4b) showed D_f values higher than those of flocs before breakage over the entire pH range. Again there was a noticeable difference between the two alum concentrations at the highest pH values for all flocs before and after breakage. After re-growth (Fig. 4c), D_f values of flocs were comparable to those before breakage pH (6.0–7.0).

3.5. Particle size distribution (PSD) of flocs before breakage and after re-growth

The samples were taken before breakage and after re-growth at a time when the d_{50} values were the same, but analysis of the floc PSD in Fig. 5 shows that the size distributions of flocs before breakage and after re-growth at pH 5.2 were distinctly different. After the re-growth phase at 0.01 mM Al, the proportion of small flocs ($1\text{--}50 \mu\text{m}$) decreased compared with the values before breakage. With 0.02 mM alum, the PSD data again showed a reduction in the flocs around $1\text{--}50 \mu\text{m}$ after floc re-growth (Fig. 5b). The number of flocs with medium size increased after breakage may cause

greater cohesion frequency of small particles to be adsorbed onto these flocs.

3.6. Discussion

There are different species of Al produced during Al hydrolysis, such as smaller polymeric Al ($\text{Al}_3\text{--Al}_8$), Al_{13} and even amorphous hydroxide precipitate [29–31]. The dissolved Al changed from larger polymeric Al into amorphous aluminium hydroxide when the pH increased from 5 to 7, and there may be significant change of Al species in this pH area. As shown in our previous work [31], larger polymeric Al, such as Al_{13} , was formed and it was relatively stable compared with other polymeric Al. Also Furrer et al. [32] found that the flocs formed from aggregation of the relative stable Keggin Al_{13} even existed in many streams. The higher re-growth ability of broken flocs for Al_{13} may be because the highly charged outer-sphere sorption complexes dominated the cohesion ability of the flocs. The distinct increase of fractal dimension of flocs with the pH increased from 5 to 6 confirmed the results. According to the aluminium solubility diagram by many researchers [33–35], amorphous aluminium hydroxide is the only main hydrolyzed product of Al^{3+} for 0.01–0.02 mM Al^{3+} at pH 7, which was due to oversaturation, and there was no full re-growth ability of broken flocs. Also the low re-growth ability of flocs formed at pH around 5 should be researched further, to investigate the properties of the unstable small polymeric Al species.

4. Conclusions

The main conclusions of this work are:

1. The broken flocs can fully re-grow to the size before breakage, when monomeric Al or polymeric Al_{13} forms dominate the coagulant species. However, for relatively unstable small polymeric Al ($\text{Al}_3\text{--Al}_8$) and alum precipitate, broken flocs showed very limited re-growth.
2. There was significant difference of fractal dimension (D_f) when the pH increased from 5.2 to 6.0. D_f of flocs increased if the flocs were exposed to high shear, and after re-growth D_f decreased.
3. The number of small flocs after breakage and re-growth was much less than before breakage at pH 5.2 when d_{50} value was chosen the same before breakage and after re-growth.
4. There is positive correlation between the strength of flocs and D_f of flocs, and both of them increased greatly at pH between 5.2 and 6.0.

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