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The regrowth ability of alum–humic flocs: effect of polyacrylamide

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ABSTRACT

The effect of polyacrylamide (PAM) dosage and mixing time on the formation, breakage, and regrowth of alum flocs was explored by Mastersizer 2000. The result showed that the coagulation efficiency and regrowth ability of broken flocs were determined by the mixing time, PAM dosage, and pH value. When PAM was dosed simultaneously with alum, the broken flocs could not regrow, independent of PAM dosage, while the regrowth ability of broken flocs increased as the dosing time of PAM delayed. Broken flocs could fully regrow when PAM was dosed 5 min after the addition of alum. Both flocs' size and regrowth ability enhanced with the increase in PAM dosage when PAM was dosed 5 min or more later than alum. Although the size of alum-HA flocs could be slightly improved by PAM, the addition of PAM significantly improved both the growth ability of flocs and the regrowth ability of broken flocs at pH 7 and 8. This might be caused by the variation of chemical bonds with pH for PAM and alum precipitate. Scanning electron microscopic images proved that when PAM was dosed simultaneously with alum, PAM would be covered by alum-HA precipitate nanoparticles; but more PAM could be seen on the surface of flocs when PAM was dosed 6 min after the addition of alum. The variation of chemical bonds on the surface of precipitate primary nanoparticles may induce the irreversibility of broken flocs. The hydrogen bonding between PAM and alum-HA flocs may be the main flocculation mechanism for the high growth of flocs and regrowth of broken flocs.

Keywords: Coagulation; PAM; Hydrogen bonding; Breakage and regrowth

1. Introduction

Floc breakage causes low coagulation efficiency, which is inevitable in most water treatment processes. Many drinking water and wastewater treatment plants cannot meet the requirement of standard due to severe floc breakage with low regrowth ability in the coagulation process. Therefore, a lot of work focusing on flocs breakage and regrowth increased in recent years [1–4]. The broken flocs can regrow to the size before breakage when charge neutralization dominates the coagulation mechanism [5–8]. Normally, sweep coagulation is the dominant mechanism at optimal dosage of alum or polyaluminum chloride (PACl), and it is difficult for broken flocs to fully regrow to their initial size before breakage [9]. In addition, flocs formation with natural organic matter (NOM) was difficult to return to their original size [10,11]. There was limited regrowth ability of NOM flocs formed with alum, ferric sulfate, and

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polyDADMAC [12–14], and PACl [15]; regrowth ability reduced in the presence of humic acid [16]. Other researchers also found that only limited regrowth of kaolin flocs occurred, which indicated a significant irreversibility of the floc break-up process [17,18]. It seems that broken flocs have fewer potential connection points for flocs regrowth than the initial growth. Until now, there is little report on the mechanism of floc formation, breakage, and chemical bonds changed or not. When a small additional dosage of alum was added to the suspension during floc breakage, the size of regrown flocs was larger than that before breakage [19]. The result means that there is difference between fresh and aged flocs, especially the chemical bonds on the surface of flocs, but not zeta potential [20].

While for cationic polyelectrolytes, the regrowth of broken flocs occurred to a much greater extent (probably happened) and flocs breakage was almost fully reversible [1]. Therefore, the flocs formed by polyDADMAC is significantly different from the one formed by hydrolyzed coagulant. Yu *et al.* [21,22] found that flocs formed from kaolin by charge neutralization could completely regrow, and the flocs before and after regrowth were very similar with the one formed by polyDADMAC via neutralization.

This work aims to evaluate the regrowth ability of flocs when alum and polyacrylamide (PAM) are applied simultaneously with accentuation on the effect of dosage, PAM dosing time, and pH. The process of flocs formation, breakage, and regrowth was continuously online monitored. Coagulation mechanism was evaluated and investigated in term of the physical bonds and chemical bonds on the surface of flocs.

2. Materials and methods

2.1. Stock suspension and solution

Five gram humic acid, sodium salt (HA, Aldrich, Cat: H1, 675-2), was dissolved in 500-mL deionized (DI) water, adjusting pH to 7. After 24 h mixing by a magnetic stirrer, the solution was diluted to 500 mL and then stored in the shade and cool place. Alum ($Al_2(SO_4)_3 \cdot 18H_2O$, analytical grade) was used as coagulant. Stock alum solutions were prepared at a concentration of 0.1 M in DI water (0.2 M Al). Polyacrylamide (PAM, purchased from Sinopharm Chemical Reagent Co., Ltd, China), having a molecular weight of around 10,000,000, was diluted to concentration of 0.1% or 1 g/L.

2.2. Jar test

The stock humic acid was diluted in 1,000-mL DI water, with 5-mM $NaHCO_3$, giving a test solution with an HA concentration of 10 mg/L. The pH of final solution was maintained at 7.0 after adding a predetermined amount of 0.1 M HCl or NaOH. Initial alum dosage of 0.2 mM was used here since the zeta potential was near 0 mV. The temperature was maintained at 20 ± 1℃.

The tested water was stirred at 50 rpm (23 s^{-1}) for 60 s and then a certain dosage of alum (0.2 mM) was given, with stirring speed to 200 rpm (184 s^{-1}). The stirrer was Flocculator ZR4-2 with setting speeds and time (Shenzhen Zhongrun, China). After maintaining 200 rpm for 1 min, the stirring speed was reduced to 50 rpm and maintained for 15 min to allow flocs to grow. After that the speed was increased to 200 rpm again and maintained for 1 min to break the flocs, and then the speed was reduced to 50 rpm for 10 min for the flocs to regrow. PAM was dosed simultaneously or a couple of minutes later.

2.3. Floc size online monitored by Mastersizer 2000

A laser diffraction instrument (Malvern Mastersizer 2000, Malvern, UK) was used to measure dynamic floc size as the coagulation and flocculation process progressed. The suspension was monitored by drawing water through the optical unit of the Mastersizer and back into the jar by a peristaltic pump. On the backflow, a tube with 5-mm internal diameter peristaltic pump tubing was used. The inlet and outlet tubes were positioned oppositely above the paddle in the holding ports. Samples were taken every 30 s to measure the floc size duration of the jar test. Data were logged onto a PC. Flocs were pumped through the system at a flow rate of 2.0 L/h. Flocs above 2.0 L/h would break the flocs and lower than 2.0 L/h cause flocs to be settled in the tube, which is confirmed by the previous experiment.

2.4. Other analytical methods

Samples were collected and analyzed for zeta potential measurements immediately after 1 min of rapid mixing by a zeta meter (Zetasizer nano ZS90, Malvern, UK). The flocs were collected, air dried, then platinum coated by a sputter, and observed under scanning electron microscope (SEM; JSM7401F, JEDL, Japan).

3. Results

3.1. Zeta potential

Humic acid solutions (10 mg/L) were coagulated over a range of PAM concentrations with 0.2 mM Al, resulting at different final pH, and the zeta potential of flocs was measured. The result is shown in Fig. 1. Zeta potential of alum–humic–PAM flocs did not change too much with the increase in PAM dosage, which present that the dosage was not a critical factor. However, it was clearly shown that pH significantly influenced zeta potential of the flocs.

3.2. Effect of PAM dosage

The processes of coagulation and floc breakage have been studied by adding PAM and alum simultaneously and by adding PAM 6 min later than alum at different doses (0–1 mg/L), respectively. The formation, breakage, and reformation of aggregates at the corresponding dosages and dosing times of PAM with 0.1 mM alum are shown in Fig. 2. When PAM was added with alum simultaneously, the dosage of PAM could not change the growth ability of flocs, and the plateau d_{50} value was almost the same, even though the size of flocs was a little higher by adding 1 mg/L PAM or more (Fig. 2(a)). After the floc was broken, there was significant irreversibility of broken flocs. No difference was found between the regrown flocs with different dosages of PAM.

In the case of PAM being added 6 min after the start of flocculation process (Fig. 2(b)), the steady state, maximum, d_{50} of flocs increased as the dose of PAM increased, especially for the dose range of 0.2–0.5 mg/L. After a sudden floc shearing/breakage (at 15 min of flocculation), the maximum d_{50} of flocs reached the same values as those before breakage (within experimental variation) when the dose of PAM was equal to, or greater than 1 mg/L, while at lower doses of PAM (<0.5 mg/L), the d_{50} values of broken flocs did not return to those before breakage. The results showed that there was significant regrowth ability of broken flocs when the dosage of PAM was higher than 1 mg/L.

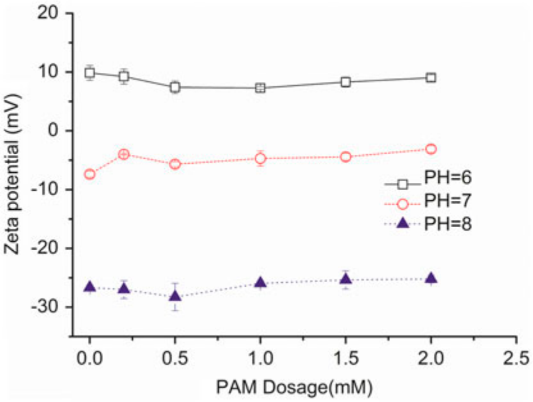

Fig. 1. Effect of PAM dosage on the zeta potential under different pH (0.2 mM Al).

3.3. Effect of PAM addition time

From the above results, it can be concluded that there was significant difference in flocculation performance between adding PAM simultaneously with alum or 6 min later. The effect of dosing PAM at different times during the flocculation period on the growth ability of flocs was explored with a constant PAM dose of 1 mg/L. Fig. 3 shows the results of experiments in which PAM was dosed at different time but with the same initial alum dosage of 0.2 mM, followed by floc breakage at an increased stirring speed, as described in Section 3.2. The effect of PAM addition on the growth of flocs largely was dependent on its adding time. As shown in Fig. 3, the steady state, maximum d_{50} value increased when the addition of PAM was 1 min after flocculation or later, and the maximum d_{50} value of all flocs was not significantly different for dosing times greater than 1 min. However, with an addition of PAM at different times of the flocculation before breakage, the flocculation process and regrowth process significantly changed.

When PAM was dosed simultaneously with alum, flocs did not increase in size. However, the flocs showed larger size when dosing 1 min or more later than alum. This result is same with the expected mechanism where PAM acts principally as a bridge between previously formed flocs, and thus is not effective in the early stages of flocculation when alum-HA precipitates are poorly defined. When PAM was dosed several minutes later, d_{50} of flocs increased immediately and significantly to several times larger than the one without dosing PAM. After breakage, the sizes of regrown flocs were all significantly larger than the one formed by adding PAM and alum simultaneously. The results showed that if PAM was added 6 min after flocculation started, there was significant regrowth of the disrupted flocs and these could grow back to a similar size to the flocs before breakage. The resistance of flocs and regrowth ability of broken flocs increased as the PAM dosing time delayed, and this is probably related to the chemical bonds between PAM and alum precipitate. In these tests with the delayed addition of PAM, the nearly full regrowth of disrupted flocs showed that the broken points were

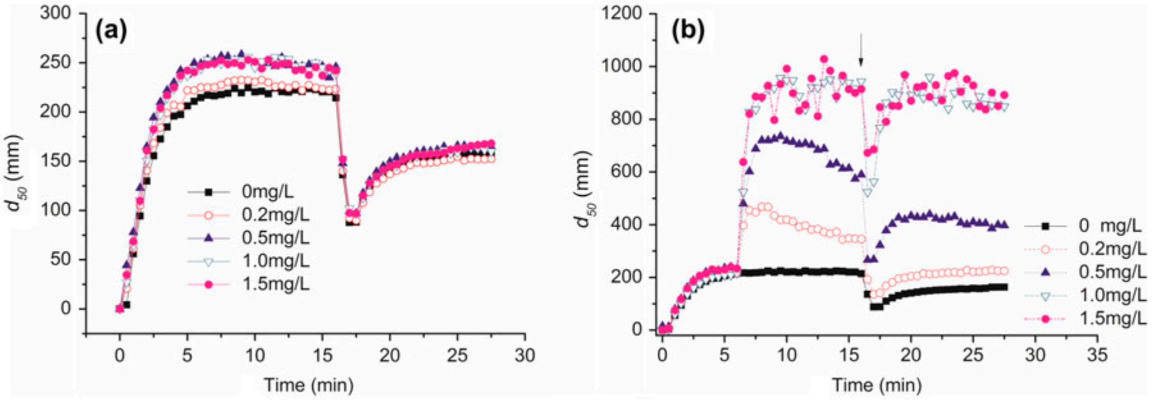

Fig. 2. Effect of PAM dosage on the formation, breakage, and regrowth of flocs: (a) PAM was dosed simultaneously, (b) PAM was dosed 6 min later.

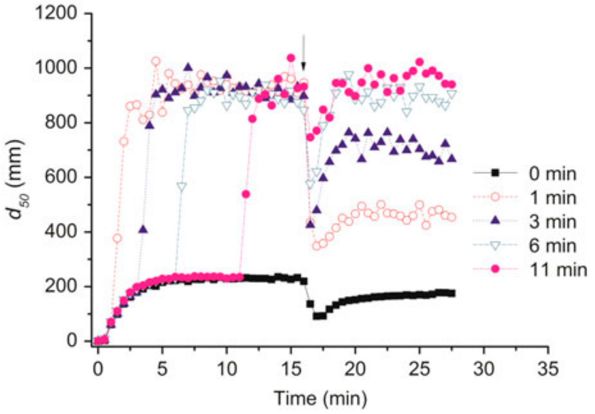

Fig. 3. Effect of PAM adding time on the regrowth of flocs (1 mg/L PAM).

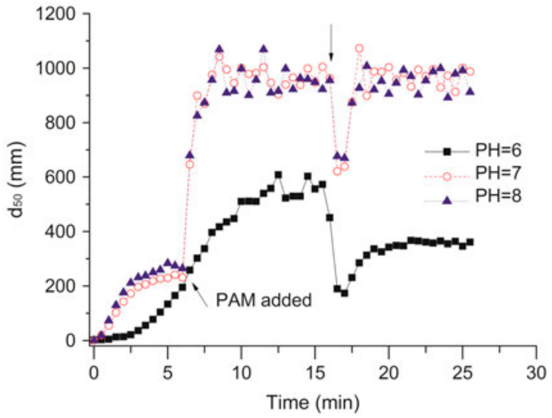

Fig. 4. Effect of pH on formation, breakage, and regrowth of PAM–alum flocs.

still active if the cluster–cluster bond(s) were due to the presence of PAM.

3.4. Effect of pH

The characteristics of PAM floc breakage and regrowth were also influenced by different pH values in the range of 6–8. Sharp contrast in coagulation efficiency at different pH can be seen in Fig. 4, and there was a significant difference when the pH increased from 6 to 7. The initial growth ability of flocs before breakage was lowest at pH 6. Also the addition of PAM caused the lowest plateau d_{50} value of flocs, with significant irreversibility of broken flocs. While at pH 7 and 8, the addition of PAM caused a significant increase in floc size, with the broken flocs restoring to the original size. Therefore, PAM should be used under moderate pH or alkaline pH. Although the zeta potential of flocs was near −20 mV at pH 8 (Fig. 1), the growth/regrowth ability of flocs was nearly the same as the one at pH 7 with zeta potential of around 0 mV. Therefore, zeta potential here was not determining the regrowth ability of broken flocs.

3.5. SEM of flocs

In order to learn the regrowth mechanism of flocs formed by alum and PAM with different experiment conditions, microscopic images of flocs were observed with SEM (Fig. 5). As shown in Fig. 5(a) with small part of a floc, it can be seen that the floc was consist of thousands of nanoscale primary particles (near 30 nm), which were formed by alum precipitate and humic acid. When PAM and alum were dosed simultaneously, PAM was covered by thousands of nanoscale primary particles, and

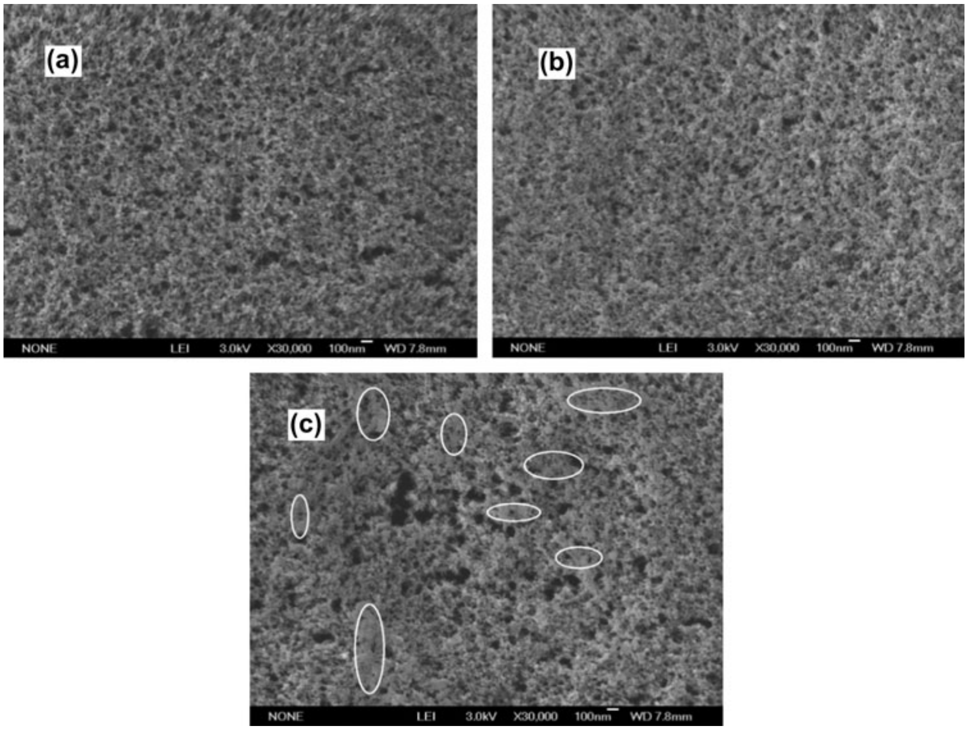

Fig. 5. Image of flocs by different PAM addition modes: (a) without PAM, (b) PAM and alum dosed simultaneously, and (c) PAM dosed 6 min later than alum.

the flocs surface was very similar with the one formed by only alum, little PAM could be seen on the flocs surface. However, when PAM was dosed 6 min later than alum, there was more PAM attached on the surface of flocs (marked in the images). Therefore, when PAM was covered by the nanoscale primary particles, the nature of these flocs was very similar with the one without PAM, which suggests that the size of regrown flocs could not return to the original size; otherwise, the broken flocs can grow again when PAM interacts with alum-HA nanoparticles.

4. Discussion

PAMs have amino group (–NH_2) and most of commercial PAMs contain a proportion of carboxylic groups, which ionize to give anionic sites along the chain at higher pH. PAM can easily form hydrogen bond with –OH_2/–OH on the surface of alum precipitate [23], which is a physical bond. As shown in Fig. 6, –NH_2 changed into –NH_3^+ as the pH decreased, the number of –OH_2 increased and –OH decreased on the surface of nanoscale primary particles of precipitate. It is much more difficult for –COOH to forms hydrogen bond with –OH_2 at pH 6, compared with –COO^- and –OH_2/–OH at pH 7 and 8, which caused lower connection ability of flocs and smaller flocs at pH 6.

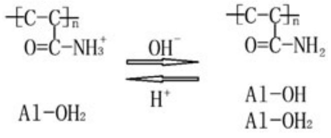

Fig. 6. Variation of chemical bonds of PAM and alum flocs surface with pH.

When PAM is fully covered by thousands of primary nanoparticles, these nanoparticles as replace PAM determine the flocs growth and regrowth property. This fact can explain why the flocs growth didn't change by PAM when alum was dosed simultaneously with PAM, and different adding time of PAM causes different regrowth ability of broken flocs. Optimization of dosage and time interval of dosing PAM and alum would promote the coagulation efficiency.

5. Conclusions

In this paper, flocs formation, breakage, and regrowth have been studied with different PAM dosing method.

When PAM was dosed simultaneously with alum, the dosage of PAM did not change the growth ability of flocs, and plateau d_{50} value of floc size was nearly the same. The broken flocs could not return to their original size, regardless of the PAM dosage.

The size of flocs increased as the dosage of PAM increased when PAM was dosed 6 min after the start of coagulation process; and the regrowth ability of broken flocs increased with the dosage of PAM.

The size of flocs as well as the regrowth ability of broken flocs increased significantly when PAM was dosed 1 min later than alum. Full regrowth of broken flocs was observed when PAM was dosed 6 min after the start of the flocculation of process.

The addition of PAM slightly improved plateau d_{50} value of flocs at pH 6, resulting in reversible broken flocs. While at pH 7 and 8, PAM promoted the flocs to increase in size and broken flocs could also return to the original size.

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