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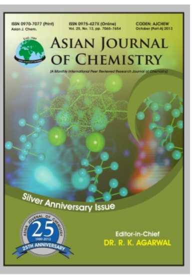

Flocculation Performance and Shearing Capacity Study on Al_{30} Morphology in Polyhydroxy Aluminium

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As a newly discovered polyaluminum morphology after Al_{13}, Al_{30} is the highest charge cation of polyhydroxy aluminum so far. By comparative analyzing synthetic Al_{30}, Al_{13} and commercial polyaluminum chloride, test results show that Al_{30} has optimal coagulation effect by contrasting turbidity, UV_{254} removal efficiencies and electric neutralization capacity. The particle size analysis of flocculated kaolin micro particles shows that the three flocculants can combine with kaolin particles below 10 μm. The floc size in Al_{30} is the largest, followed by Al_{13} and then polyaluminum chloride, which further proved the advantage of Al_{30} in flocculation process. The conventional jar test and the monitoring technique of floc size online are employed to investigate the shearing capacity of the flocs formed by Al_{30}. It is found that remixing can make the broken flocs fully recovered and the particle size of recovered flocs are greatly increased, especially in Al_{30}.

Key Words: Polyaluminum chloride, Flocculation performance, Particle size analysis, Breakage, Recovery.

INTRODUCTION

Polyaluminum chloride (PAC) is a main stream flocculant in water and wastewater treatment industry. It has characteristics of low dosage, strong charge neutralization capacity[1], forming dense flocs[2], producing less sludge[3], *etc.*, which are closely related to the highly charged polyhydroxy aluminum cation in polyaluminum chloride. For a long time, researchers believed that $[AlO_4Al1_2(OH)_{24}(H_2O)_{12}]^{7+}$ (abbreviated as Al_{13}) as the representative aggregation form plays a critical role in flocculation performance. Studies on the generation, morphological identification[4] and flocculation performance[5] of Al_{13} are numerous and long-lasting.

In recent years, with the improvement of analysis technologies, a new polyaluminum morphology larger than Al_{13} was found. This was Al_{30}. In 2000, based on the study of AlP_1, AlP_2 and AlP_3, Rowsell and Nazar[6] proposed that the structure of AlP_2 was Al_{30} ($[Al_{30}O_8(OH)_{56}(H_2O)_{24}]^{18+}$). In the same year, Allouche *et al.*[7] also proposed the same structure of Al_{30}. The structure consists of two δ-Al_{13} through four hexacoordinated aluminum octahedral coupled together, with 18 positive electric charges. Al_{30} is the new largest polyhydroxy aluminum cation so far. Study on the flocculation performance and mechanism of Al_{30} is important to the development of its series efficient flocculants.

Generally speaking, coagulation process consists of two phases: rapid mixing stage after coagulant dosage and slow flocculation stage that flocs gradually shaped. Since to velocity gradient is maldistributed in coagulation structures, flocs fractured easily and broken flocs can also occur flocculation. In addition, in some stirring intensity, the breakage and recovery processes are concurrence, eventually reaching to a stable dynamic balance. After flocs are broken, if an appropriate slow stirring velocity is imposed, there will be varying degrees of recovery. Researches on aluminum sulfate salts as flocculant had shown that recovery degree of flocs is related to coagulation mechanism. The flocs in charge neutralization flocculation can be fully recovered, however in sweep flocculation process, the flocs are difficult to recover[8].

Now, researches on floc breakage and recovery situation are mainly for single-molecule traditional flocculants. Polyaluminum chloride as the mainstream flocculant has not been systematically studied. Researches on Al_{13} and Al_{30} series flocculants are empty. Such flocculants are different with traditional one-component flocculant in the molecular structure, hydrolysis precipitation, floc morphology and characteristics[9,10]. For this reason, results from traditional flocculants can not be used into composite macromolecular flocculants. System studies on floc breakage and recovery processes are necessary. This paper used kaolin suspension as simulated wastewater and comparative analyzed floc breakage and recovery capacity of commercial polyaluminum chloride, synthetic Al_{13} and Al_{30} through investigating residual turbidity and floc particle size in jar test.

EXPERIMENTAL

The Al_{30} sample with total Al concentration of 0.2 mol L^{-1} were prepared by the following method: 20 mL AlC_{l3} aqueous solution with Al concentration of 1.0 mol L^{-1} was added into 250 mL glass reactor equipped with a Teflon anchor stirrer and a reflux condenser. The solution was heated to a predetermined temperature (80 °C) using a thermostatic apparatus, then 80 mL of aqueous solution of NaOH with a calculated concentration (0.6 mol L^{-1} for B = 2.4) was pumped into the reactor through peristaltic pump at a speed of 0.5 ml min^{-1} under rapid stirring until the hydrolysis ratio ($B = [OH^-]/[Al^{3+}]$) reached a prearranged value. After the addition of NaOH solution finished, the reactants were continuously stirred and heated at a predetermined temperature. This sample was PAC with high content of Al_{13} (PAC-Al_{13}). PAC-Al_{30} were prepared by heating PAC-Al_{13} solution at 95 °C for 36 h. under stirring and refluxing.

Detection method: Coagulation experiments were carried out at room temperature using jar test on a six-paddle gang stirrer (ZR4-6, Zhongrun Co., China). A measured amount of flocculant was added into the water sample under rapid stirring. The characteristics of the water sample are given in Table-1. The water solution was stirred rapidly at 200 rpm for 3 min after coagulant dosing, followed by slow stirring at 50 rpm for 13 min and then settled for 40 min. While in floc breakage and recovery experiment, after slow stirred in normal coagulation procedures above, continue to stir rapidly at 200 rpm for 2 min, followed by slow stirring at 50 rpm for 10 min and then settled for 10 min. Monitor the change of floc particle size online in the entire process and residual turbidity after settlement.

TABLE-1
CHARACTERISTICS OF RAW WATER

Indexes	Kaolin (mg L^{-1})	Humic acid (mg L^{-1})	UV_{254}	Turbidity (NTU)	Zeta (mV)	pH
	100	10	0.38	49.6	-25	7.5

The development of floc size during the flocculation period was measured on a Laser Particle Size and Shape Analyzer (Winner 2000, Winner Co., China). The sample was taken using a syringe immediately after coagulant addition and rapid mixing to measure the Zeta potential in Zetasizer Nano ZS90 (Malvern Co., UK). Supernatant sample was withdrawn and filtered through the common qualitative filter paper for UV_{254}. UV_{254} representing humic acid concentration was measured at 254 nm through a DR5000 UV spectrophotometer (HACH Co., USA). After settlement, take the sample to measure residual turbidity in a 2100P turbidimeter (HACH Co., USA) and pH through a PHs-3c (Dapu Co., China).

RESULTS AND DISCUSSION

The mechanisms to explain the coagulation of humic substances include charge neutralization, precipitation, bridge-aggregation, adsorption and sweep-flocculation[11,12]. Under different conditions, the different mechanisms or their combination may be dominant. Because of the high positive charge and big molecular Al_{30}, charge neutralization and bridge-aggregation may play a more important role.

Distribution of Al species: The prepared samples were analyzed by ^{27}Al nuclear magnetic resonance technology. Al_{13} species are 80.3 % in unmatured product[13], while Al_{30} species are 76.8 % in aging product[14]. So we called the unmatured product Al_{13} and aging product Al_{30}. Al_a, Al_b and Al_c were measured in commercial PAC, Al_{13} and Al_{30} through Al-Ferron timed complex colorimetric method[15]. In commercial PAC, the proportion of Al_a, Al_b and Al_c are 23.97, 64.78 and 11.25 %, while in Al_{13}, Alb is the main form, taking over 88.4 %. In synthetic Al_{30}, Al_c is 73.6 % and Al_b takes 24.3 %. So aluminum monomer is precious little in Al_{30}.

Comparison of charge neutralization capacity: Coagulation experiments were carried out using synthetic PAC-Al_{13}, PAC-Al_{30} and commercial PAC. As shown in Fig. 1, the dosages of PAC, Al_{13} and Al_{30} are 8, 6.8 and 5.72 mg/L respectively when they reach to zero electric potential point. The charge neutralization capacity of Al_{30} performs complexly. When in low dosage, the charge neutralization capacity is lower than Al_{13}. While the system electric potential is close to neutralization (*i.e.*, when the system electric potential is close to -5 to +5 mV), the charge neutralization capacity of Al_{30} is stronger than Al_{13}. According to the dosage in zero electric potential point, the order of the three flocculants charge neutralization capacity is $Al_{30} > Al_{13} > PAC$, which is related to Al_{30} with high charge.

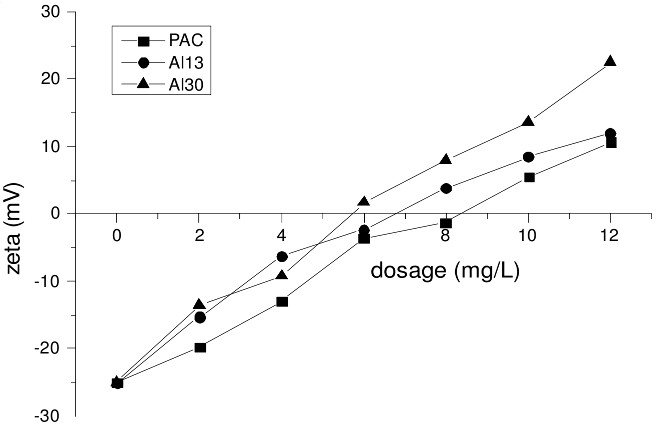

Fig. 1. Comparison of charge neutralization capacity of PAC, Al_{13} and Al_{30}

Comparison of removal efficiency of turbidity: As shown in Fig. 2, turbidity removal efficiency of all the three kinds of flocculants can reach to more than 97 % in kaolin simulated water sample. When the dosage is in 4 mg/L or above, PAC and Al_{13}, RT curves coincide. Residual turbidity curves tend to be gentle after the dosage reaching to 10 mg/L. The removal efficiency of turbidity of Al_{30} is higher than another two flocculants. When the dosage is close to 8 mg/L, the system reaches to the best turbidity removal, which is essentially coincident with its zero electric potential point. Fig. 2 showed that the main coagulation mechanisms of the three flocculants are charge neutralization.

Change of pH: Addition of flocculants caused the pH reduction of coagulation system as shown in Fig. 3, of which the reduction amplitude in descending order is PAC, Al_{13} and then Al_{30}. This is because that the PAC contains more Al^{3+} monomers which cause hydrolysis after being added into water. Hydrolysis causes pH reduction of the coagulation system. However, after high-temperature aging, Al_{30} contains Alb and Al_c as its main forms. There is less pH reduction in Al_{30}.

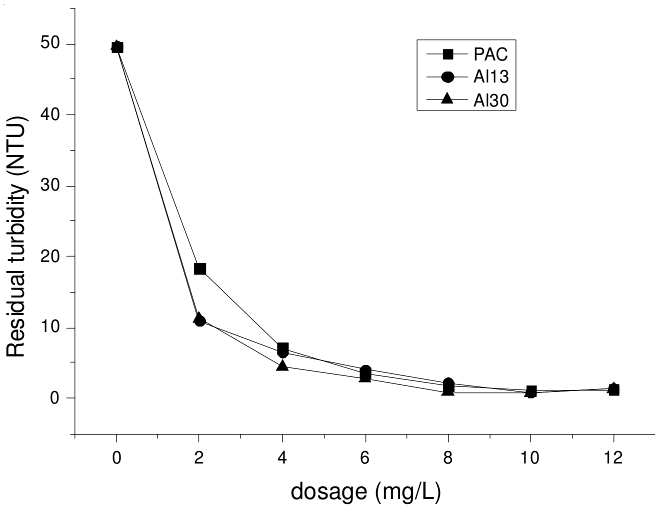

Fig. 2. Comparison of removal efficiency of turbidity of PAC, Al_{13} and Al_{30}

Comparison of UV_{254} removal capacity: UV_{254} has good relation with organic matter in water[16]. As shown in Fig. 4, the UV_{254} removal curves of PAC, Al_{13} and Al_{30} showed a ladder-type downward trend. When dosages are over 10 mg/L, UV_{254} removal efficiencies of all coagulants can reach to 40 %. According to Fig. 4, UV_{254} removal efficiencies of the three coagulants are not high, because their coagulation mechanisms are mainly charge neutralization rather than adsorption bridging.

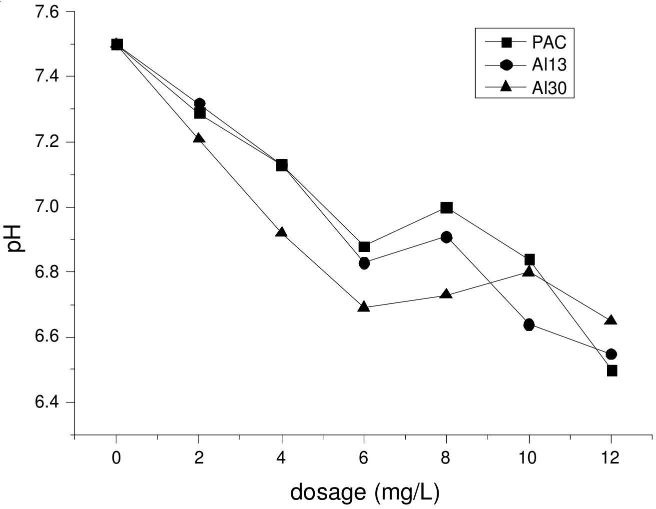

Fig. 3. Change of pH in coagulation performances of PAC, Al_{13} and Al_{30}

Analysis of kaolin microparticle flocculation characteristics: As shown in Fig. 5, three kinds of flocculants have good flocculation abilities on the kaolin simulated water sample with average particle size of 4.08 μm. Distribution of kaolin particles less than 10 μm is 0 after flocculation. Viewing from the floc particle sizes, PAC forms floc size between 10 μm and 30 μm, while Al_{13} forms particle size between 40 μm and 50 μm. The size of floc formed in Al_{30} is bigger, more in 50 μm and 80 μm. This is because that due to charge neutralization and double electric layers compression, diffusion layers of particles are compressed to reduce the zeta electric potential and to form larger particles under the action of van der Waals force. Al_{30} has higher electric charge, higher relative molecular mass and stronger charge neutralization capacity than another two flocculants, therefore, the size of floc formed in Al_{30} is bigger.

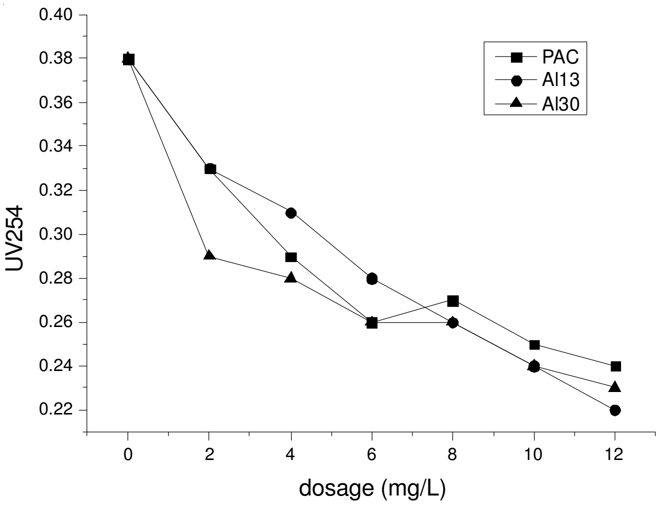

Fig. 4. Comparison of UV_{254} removal efficiency of PAC, Al_{13} and Al_{30}

Change of floc size and residual turbidity in floc breakage and recovery process: Floc particle size can directly reflect the floc breakage and recovery condition after remixing. Yukselen and Gregory[17] believed that the grown of flocs is mainly a physical process in charge neutralization flocculation, unrelated to the destruction of chemical bond, as a result, the broken flocs can recover. While in sweep flocculation, the grown of flocs is mainly a chemical process, the broken flocs can lead to destruction of chemical bonds, as a result, the broken flocs are difficult to recover. Some researchers[14,18,19] have suggested breakage factor (B_f) (Eq. 1) and recovery factor (R_f) (Eq. 2) represent floc broken and recovery degree respectively and strength factor (S_f) (Eq. 3) represents the floc strength.

$$B_f = \frac{d_a - d_b}{d_a} \times 100\% \tag{1}$$

$$R_f = \frac{d_c - d_b}{d_a - d_b} \times 100\% \tag{2}$$

$$S_f = \frac{d_b}{d_a} \times 100\% \tag{3}$$

In these equations, d_a represents the floc size before broken; d_b represents the minimum particle size after broken, while d_c represents the floc size after recovery.

As shown in Fig. 6, for the same dosage (6 mg/L) in PAC, Al_{13} and Al_{30} flocculation processes, remixing leads to floc broken, and hence, floc particle size declines. In the slow stirred process, floc particle sizes of the three flocculants get fully recovery and the recovered particle sizes are bigger than that before broken. In this condition, the B_f of PAC, Al_{13} and Al_{30}

are 49.3, 34.3 and 31.1 %, respectively. The R_f are 112.4, 159 and 155 % respectively, while the S_f are 68.7, 58.9 and 81.7 %, respectively. Relatively speaking, flocs of Al_{30} are stronger than another two flocculants and more difficult to be broken, processing strong recovery function.

Final residual turbidity after settlement in the system showed different floc breakage and recovery degrees. This experiment investigated remixing influence on residual turbidity and compared with the situation of that was not remixed. Experimental result shows that for the same dosage (6 mg/L), residual turbidity of PAC, Al_{13} and Al_{30} are 3.6 NTU, 4.05 NTU and 2.77 NTU when the system was not remixed.

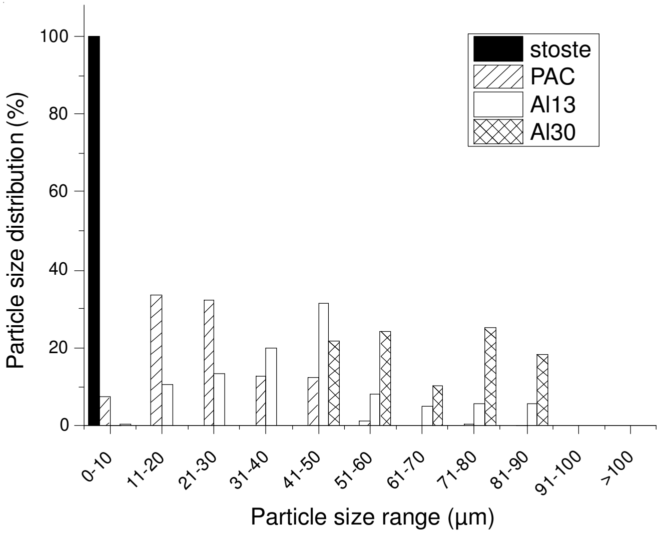

Fig. 5. Kaolin particle size analysis of PAC, Al_{13} and Al_{30}

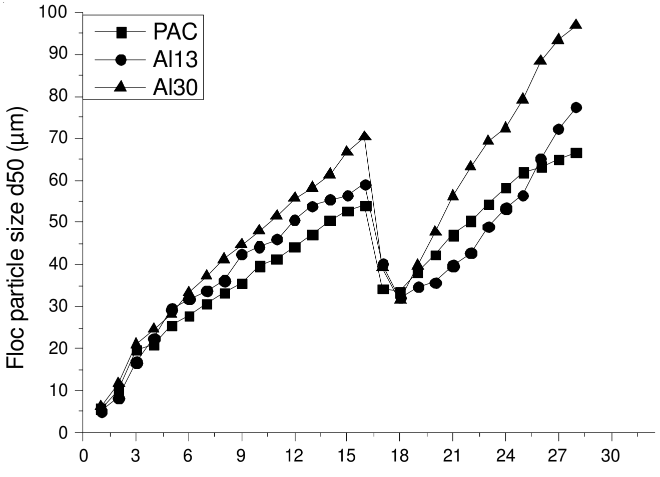

Fig. 6. Change of particle size in floc breakage and recovery process in PAC, Al_{13} and Al_{30}

However, when the system was remixed at 200 rpm, residual turbidity of PAC, Al_{13} and Al_{30} are 3.23 NTU, 2.79 NTU and 2.02 NTU respectively. In all the three coagulation systems, broken flocs after remixing can be fully recovered in charge neutralization flocculation zone and residual turbidity of the systems are significantly lower after remixing. This experiment further proves the stability of Al_{30} in flocculation process.

Conclusion

By contrasting turbidity and UV_{254} removal efficiencies, charge neutralization capacity and change of pH in commercial PAC, synthetic Al_{13} and Al_{30}, analysis result showed that charge neutralization is the main mechanism of the three flocculants, ofwhich the charge neutralization capacity in Al_{30} is better than another two flocculants with minimum pH variation. Flocculation effect of Al_{30} is the best flocculants. By contrasting particle size of kaolin flocculation microparticles in commercial PAC, synthetic Al_{13} and Al_{30}, the three flocculants can be combined with kaolin particles less than 10 μm. The order of floc particle size is $Al_{30} > Al_{13} >$ PAC, which further demonstrates the superiority of Al_{30} in flocculation process.

In floc breakage and recovery experiment, remixing can make the broken flocs fully recovered and the particle size of recovered flocs are greatly increased. At the same time, residual turbidity has also been reduced. All of this further proves the stability of Al_{30} in flocculation process.

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