Evaluation of Al$_{30}$ polynuclear species in polyaluminum solutions as coagulant for water treatment

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Abstract

Polyaluminum coagulant with a content of 76.8% of Al$_{30}$ (PAC$_{Al30}$) was prepared. Its coagulation behaviors were compared with high Al$_{13}$ content polyaluminum coagulant (PAC$_{Al13}$) and AlCl$_3$. The species stability was studied using Al-Ferron method and $^{27}$Al NMR. The coagulation performances were investigated by studying the rate of flocs development, the turbidity removal efficiency and charge neutralization capacity under fixed pH conditions and uncontrolled pH conditions. The effect of pH on coagulation was also studied. The results show that PAC$_{Al30}$ are stable for using as coagulant. PAC$_{Al30}$ causes less pH depression than PAC$_{Al13}$. The charge neutralization capacity of PAC$_{Al30}$ is slightly lower than that of PAC$_{Al13}$ at pH $\geq$ 6.8 and higher at pH $\leq$ 6.5. PAC$_{Al30}$ achieves the most effective turbidity removal in these three coagulants. And it acts effectively within a much broader dosage range and a wider pH range when compared with PAC$_{Al13}$. PAC$_{Al30}$ achieves the highest turbidity removal due to its strong flocs formation capacity. The results verify that Al$_{30}$ is another highly active coagulation/flocculation species for turbidity removal.

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Keywords: Al$_{13}$ species; Al$_{30}$ species; Charge neutralization; Coagulation; Polyaluminum chloride; Turbidity removal

1. Introduction

Coagulation/flocculation is a common process in water and wastewater treatment, which destabilizes the suspended and dissolved materials, followed by aggregation into large flocs that are easily separated from the water by subsequent sedimentation/ flotation and filtration processes. Coagulant plays a key role during the process of coagulation. The pre-hydrolyzed polyaluminum coagulants are the most widely used coagulants and receive extensive research (Duan and Gregory, 2003). Compared with the conventional Al salts such as AlCl$_3$ and alum, polyaluminum coagulants have the advantage of being more effective within a broader pH range and more rapid aggregation velocity (Gao et al., 2002). Additionally, the high charge neutralization capacity of polyaluminum species often results in a decrease in dosage and the associated waste sediment production. Polyaluminum coagulants can achieve higher turbidity removal efficiency than traditional Al salts because the hydrolysis degree of polyaluminum can be controlled during manufacturing, and the hydrolytic Al species in polyaluminum coagulant can be tailor made. The polynuclear Al species in polyaluminum coagulant remains relatively stable for a long-term after dosing. However, the traditional Al salts hydrolyze and precipitate rapidly after dosing into water (Luan, 1997). The formation of Al species during this process is uncontrollable, and varies with the change of raw water nature.

Various meta-stable or transient state species such as monomers, oligomers, Al$_{13}$ ([AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$) polymer, other high polymers and Al sols coexist in
polyaluminum coagulant (Tang, 1998). It is generally believed that Al13 species is the optimal species for coagulation in polyaluminum coagulant due to its high charge neutralization capability, strong structure stability and nanometer molecular diameter (1.0 nm). Thus, the high content of Al13 is one of the goals in the production of polyaluminum coagulants. However, the commercial polyaluminum coagulant only contains small amount of Al13 due to the aggregation of Al13 (Wang and Hsu, 1994), which is an insurmountable problem in the production of polyaluminum coagulant.

Al30 ([Al30O5(OH)56(H2O)24]18+) polymer is another polycation with Keggin structure in hydrolytic polyaluminum solutions, which was characterized by 27Al nuclear magnetic resonance (NMR) and single-crystal X-ray diffraction. Al30 species is composed of two δ-Al13 connected by four Al monomers. The two tetrahedral coordinated Al in Al30 species produce a broad 27Al NMR signal at δ = 70 ppm (Allouche et al., 2000; Rowsell and Nazar, 2000). Al30 is more temperature resistant and less sensitive to pH variations than ε-Al13 (Allouche et al., 2000). Al30 possesses eighteen positive charges and unique nanometer molecule dimension (2.0 nm in length) (Allouche et al., 2000). It may be another promising active species in polyaluminum coagulant responsible for coagulation/flocculation besides Al13 species. But there is still no report on the coagulation/flocculation performance of Al30 species.

Our previous research investigated the formation conditions of Al30 species, and the results show that Al30 species can become the dominant species in polyaluminum solution when the freshly prepared polyaluminum solution is heated for 12 h at 95 °C. And the formation of Al30 is accelerated by the increase of total Al concentration (Chen et al., 2005). The formation conditions of Al30 coincide with the production conditions of commercial polyaluminum coagulant, in which polyaluminum coagulant has a high total Al concentration and is prepared at high temperature for a long time.

In the present research, polyaluminum coagulant with 76.8% Al30 content (PACAl30) was prepared. Its stability, floc formation rate and coagulation performance were evaluated by comparison with Al13 species and AlCl3.

2. Materials and methods

2.1. Materials

The reagents used in the current research are all of analytical grade. All solutions were prepared by deionised water. The coagulant that contains high content of Al13 (abr. PACAl13) was prepared by slowly neutralizing 1.0 M AlCl3 aqueous solution with 0.6 M NaOH solution at 80 °C under vigorous stirring until the Al hydrolysis ratio (B = [OH]/[Al]) reached 2.4. The final Al concentration (AlT) was 0.2 M. The coagulant that contains high content of Al30 (abr. PACAl30) was prepared by heating PACAl13 at 95 °C for 12 h under stirring and refluxing. Both samples were rested at room temperature for 5 d before analysis, characterization and coagulation experiments. AlT was measured by inductively coupled plasma-atomic emission spectroscopy (Vista-MPX ICP-AES, Varian). B value was measured by chemical analysis according to the Chinese standard method (GB 15892-1995). The pH values were measured on a pH meter (Orion 710A).

The Al species distribution in these two coagulants as well as 0.2 M AlCl3 aqueous solution (abr. AlCl3) were measured by the time-developed Al-Ferron complex colorimetry on UV–Vis spectrophotometer (DR/4000U, Hach) and high-field 27Al NMR method on Fast Fourier Transformation spectrometer (JNM-EC2400P, JOEL).

Based on the difference of the dissociation and complex reaction kinetic rate between Ferron and hydrolyzed Al species, Al species in coagulants were divided into three types: monomeric species (Alm) (reacting with Ferron within 1 min), planar oligomeric and medium polymeric species (Alb) (reacting with Ferron from one to 120 min), and three-dimensional species or sol–gels (Alc) (reacting with Ferron after 120 min and non-reacting with Ferron). Alm was obtained by AlT minus Ala and Alb (Parker and Bertsch, 1992). In 27Al NMR analysis, the aluminum at 0 ppm was assigned to Al monomer (Alm). The concentration for 62.5 ppm and 70 ppm signals were multiplied by 13 and 15, respectively, to obtain the concentration of Al13 and Al30, respectively. The concentration of Al species that cannot be clearly measured (Alu) was calculated by AlT minus Alm, Al13 and Al30 (Chen et al., 2006). The detailed specifications of these coagulants are listed in Table 1. All coagulants were used directly, without prior dilution to avoid the change of Al species arose from dilution.

A stock suspension of kaolin clay was prepared by dispersing a measured amount of reagent-grade kaolin in deionised water by high shear mixing. The suspension was settled overnight, and the upper half of solution was collected and diluted to a concentration of 20 g l⁻¹. The particle size distribution of the kaolin suspension was measured on laser particle size analyzer (Mastersizer 2000, Malvern). The mean particulate size was 1.5 μm, and with 87.4% of particle size was below 2.0 μm. The working solution was prepared by diluting a calculated amount of stock suspension with deionised water. The concentration of alkalinity and electrolyte of working solutions were adjusted using 0.5 M NaHCO3 and 0.5 M NaNO3, respectively.

2.2. Methods

The development of flocs size during coagulation period was measured on a modified Laser Particle Size Analyzer (Mastersizer 2000, Malvern). The input and output tubes of the particle size analyzer were connected to a jar test flocculator with a single-paddle stirrer. The suspension in the beaker of flocculator was sucked into the particle size analyzer by a peristaltic pump continuously for online measurement of particle size during coagulation. The
turbidity, pH, and NaHCO₃ and NaNO₃ concentration of working solution were 80 NTU, 7.5, 5.0 mM, and 5.0 mM, respectively. The 1000 ml working solution was added into the beaker. A measured amount of coagulant was pipetted into the working solution to give a dosage of 50 µM as Al under rapid stirring. The solution was stirred rapidly at 200 rpm for 2 min after coagulant dosing, and followed by slow stirring at 30 rpm for 15 min. The mean diameter of flocs was measured once every 60 s after the addition of coagulant.

Coagulation experiments were carried out at 25 °C using jar test on a six-paddle gang stirrer. The pH of the working solutions was adjusted to certain values with 0.1 M HCl solution or 0.1 M NaOH solution before the addition of coagulants. The pH value of working solution was depressed by the acidity and hydrolysis of coagulants after dosing. Coagulation experiments under fixed pH conditions and uncontrolled pH conditions were carried out. Experiments under fixed pH conditions were conducted by compensating the pH decrease with 0.1 M NaOH solution using an automatic titrator. Experiments under uncontrolled pH conditions were carried out without alkalinity compensation. A measured amount of coagulant was pipetted into the working solution to give a certain Al concentration under rapid stirring. The solution was stirred rapidly at 200 rpm for 2 min after coagulant dosing, followed by slow stirring at 30 rpm for 15 min. A supernatant sample was withdrawn for residual turbidity (RT) measurement (2100N Turbidimeter, Hach) after sedimentation. A sample was taken using a syringe immediately after the 1 min rapid mix period for the measurement of Zeta potential (Zetasizer 2000, Malvern). All experiments were repeated at least three times to assure the reproducibility of experimental results.

3. Results and discussion

3.1. Stability of PAC₃₀ and PAC₃₁₃

In water treatment practices, it is not practical to prepare fresh coagulant. For a commercial coagulant, stability is needed for storage purposes. After aging for 60 d at room temperature, PAC₃₁₃ and PAC₃₀ solutions are both transparent, and there exists no visible deposition. The Al species distribution of samples aged at room temperature for 30 and 60 d are listed in Table 1. The Al species distribution in PAC₃₁₃ and PAC₃₀ change slightly after aged for 60 d. Al₆₆ content decreases, Al₃₀ content increases. Al species in PAC₃₁₃ and PAC₃₀ tend to further polymerize and aggregate slowly upon aging. Al₃₀ content in PAC₃₁₃ and Al₃₀ content in PAC₃₀ decrease slightly. In general, the two coagulants have adequate stability for acting as a coagulant.

3.2. Study of flocs development

The development of flocs mean size after the coagulant addition is shown in Fig. 1. It can be seen that PAC₃₀ exhibits the strongest aggregation and flocs formation capacity. After coagulating for 17 min, PAC₃₀ achieves larger flocs than PAC₃₁₃ and AlCl₃. The average diameters of flocs formed by PAC₃₀, PAC₃₁₃ and AlCl₃ are about 549 µm, 482 µm, and 413 µm, respectively. Within 60 s after coagulant addition, PAC₃₁₃ displays more quick aggregation rate than PAC₃₀ and AlCl₃ due to its strong charge neutralization capacity. But the sizes of flocs for all coagulants are small at this time. The flocs mean sizes increase rapidly after a short lag time (1–3 min), and reach

<table>
<thead>
<tr>
<th>Samples</th>
<th>Al₃₀ (M)</th>
<th>B</th>
<th>Al species distribution (%)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC₃₀</td>
<td>5 d</td>
<td>0.2</td>
<td>2.4</td>
<td>74.3</td>
</tr>
<tr>
<td>30 d</td>
<td>0.2</td>
<td>2.4</td>
<td>2.6</td>
<td>22.8</td>
</tr>
<tr>
<td>60 d</td>
<td>0.2</td>
<td>2.4</td>
<td>2.5</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Table 1
The Al species distribution and pH values of freshly prepared and aged samples
a plateau. The rapid increase in flocs size is caused by the hydrolysis of coagulants and the formation of amorphous hydroxide precipitation (Wang et al., 2002). When the precipitated hydroxide precipitation reaches a certain size and number, rapid aggregation of particles achieves due to the surface interaction between the impure particles and the hydroxide precipitation with high specific surfaces. AlCl₃ displays the shortest lag time (60 s) due to its rapid hydrolysis and precipitation after dosing into water. However, PACₐ₁₃ displays the longest lag time (200 s). The stability of colloidal particles is possibly enhanced by the formation of highly charged Al oxyhydroxide sol–gels when Al₁₃ hydrolyzes on surfaces of the colloidal particles (Waite et al., 2001). The rapid increase in flocs size can only be reached after further hydrolysis of these sol–gels.

3.3. Coagulation under pH uncontrolled

It is well known that the results of coagulation are related to raw water conditions (e.g. pH, alkalinity, ionic strength, co-existing anion, and particles concentration, distribution and charge density), coagulant and coagulation assistant employed, dosage, and coagulation parameters (temperature and mixing conditions). In order to compare the coagulation performance of different coagulants, the same raw water conditions and coagulation parameters were adopted during jar test. And the pH value of working solution was depressed without pH adjustment after the addition of coagulant. The turbidity, pH value, and NaHCO₃ and NaNO₃ concentration of raw water as a function of dosage are shown in Fig. 2. As can be seen from Fig. 2b, with the increase of dosage, the Zeta potential of particles increase rapidly firstly and reverse for PACₐ₁₃ and PACₐ₃₀, then increase slowly and monotonically. The particulate Zeta potential for coagulating with AlCl₃ is much lower than that for coagulating with PACₐ₁₃ and PACₐ₃₀ within low dosage range. However, the particulate Zeta potential for AlCl₃ presents a second rapid increase within high dosage range, and it exceeds the particulate Zeta potential for PACₐ₁₃ and PACₐ₃₀, because AlCl₃ causes much more pH decrease than PACₐ₁₃ and PACₐ₃₀ at a high dosage range. The dosages required to reach zero point of Zeta potential for PACₐ₃₀, PACₐ₁₃ and AlCl₃ are 6.25 μM, 3.55 μM, and 154 μM, respectively. This indicates that the charge neutralization capacity of PACₐ₁₃ is slightly higher than that of PACₐ₃₀, and that of AlCl₃ is markedly lower than that of polymeric coagulants (PACₐ₁₃ and PACₐ₃₀).

As can be seen from Fig. 2a, the RT curves decrease sharply within low dosage range for all three coagulants with the increase of dosage, and maintain a very low turbidity level within a certain dosage range, then increase rapidly to a high turbidity and level off when the dosage increases further. PACₐ₃₀ is more effective than PACₐ₁₃ and AlCl₃ for turbidity removal. The minimum dosages needed to achieve effective turbidity removal (RT ≤ 2 NTU) for PACₐ₃₀, PACₐ₁₃ and AlCl₃ are 94 μM, 153 μM, and 122 μM, respectively. The discrepancy between turbidity removal efficiency and charge neutralization capacity indicates that there exist other coagulation mechanisms besides the charge neutralization mechanism. PACₐ₃₀ achieves effective turbidity removal within a much wider dosage range than PACₐ₁₃ and AlCl₃. AlCl₃ can only give effective turbidity removal within a very narrow dosage range. The broad dosage range for PACₐ₃₀ to achieve effective turbidity removal is benefit to avoid the fluctuation of treated water quality in practical water treatment plant, especially for coagulation of raw water with its nature changing frequently.

As can be seen from Fig. 2a and c, the pH of solutions treated by PACₐ₃₀ is only slightly higher than that treated by PACₐ₁₃, but PACₐ₃₀ achieves effective turbidity removal within a much broader dosage range. The broad dosage range for PACₐ₃₀ is not only related to the less pH depression of PACₐ₃₀ than that of PACₐ₁₃ and AlCl₃, but also related to the difference of Al speciation in coagulants. Restabilization occurrence under uncontrolled pH condition is due to the pH decrease caused by Lewis acidity needed to achieve effective turbidity removal (RT ≤ 2 NTU) for PACₐ₃₀, PACₐ₁₃ and AlCl₃ are 94 μM, 153 μM, and 122 μM, respectively. The discrepancy between turbidity removal efficiency and charge neutralization capacity indicates that there exist other coagulation mechanisms besides the charge neutralization mechanism. PACₐ₃₀ achieves effective turbidity removal within a much wider dosage range than PACₐ₁₃ and AlCl₃. AlCl₃ can only give effective turbidity removal within a very narrow dosage range. The broad dosage range for PACₐ₃₀ to achieve effective turbidity removal is benefit to avoid the fluctuation of treated water quality in practical water treatment plant, especially for coagulation of raw water with its nature changing frequently.

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of coagulants, and the restabilization happens at high dosage regions. With the increase of dosage, as the pH value of PACAl30 treated water decrease below 6.5–6.6, restabilization ($RT \geq 10 \text{ NTU}$) occurs due to particle charge reverse, at the same time, the depression of pH prevents the hydrolysis of coagulant and the formation of Al hydroxide precipitation that needed for sweeping coagulation. The threshold pH values of restabilization for PACAl13 and AlCl3 are 6.7–6.8 and 5.7–5.8, respectively. The different Al species distribution in these coagulants result in Al hydroxide precipitation form at different minimum pH value after dosing, and which lead to restabilization occur at different pH value.

### 3.4. Coagulation under fixed pH condition

Fig. 3 shows the RT and Zeta potential as a function of dosage when coagulating at fixed pH 7.5. The raw water employed is the same as that during coagulation under uncontrolled pH condition above. PACAl30 achieves the lowest residual turbidity than PACAl13 at the same dosage though the charge neutralization ability of PACAl30 is slightly lower than that of PACAl13. Corresponding with the rapid increase of Zeta potential, the significant turbidity removal can be observed for three coagulants with the increase in dosage. And the RT reaches a low value and levels off. There exists no restabilization at high dosage region because the addition of NaOH supplied the alkalinity required for the hydrolysis of Al species. The conventional restabilization under fixed pH condition takes place at a low dosage region, and it is mainly related to particle charge reverse (Duan and Gregory, 2003). The hydrolysis of Al species results in the formation of amorphous Al(OH)$_3$ precipitations, which assures the function of flocs patch, adsorption, bridging, enmeshment and sweeping (Duan and Gregory, 2003). Although PACAl13 has the strongest charge neutralization ability at all dosage range, it does not achieve the optimal turbidity removal. The optimum dosages for turbidity removal for both PACAl30 and PACAl13 do not coincide with the zero points of Zeta potential. Due to the high positive charge of Al$_{13}$ and Al$_{30}$ species, the dosage needed to neutralize the negative charge of colloidal particles is very low, and the aggregate rate of the destabilised colloidal particles is very slow within this low dosage range. So it is difficult to form large particles for turbidity removal during the subsequent settlement. The effective turbidity removal occurs at a higher dosage, and the particulate Zeta potential reach positive values within this dosage range. These results further indicate that besides charge neutralization, there exist other flocculation mechanisms such as flocs patch, sweeping, bridging, enmeshment and adsorption, which may governs or jointly governs the turbidity removal (Wang et al., 2002). Additionally, the amount of NaOH needed to neutralize the pH depression caused by AlCl$_3$ addition is much more than that needed for coagulation with PACAl13 and PACAl30. PACAl30 causes the least NaOH consumption to maintain constant pH of working solution.

### 3.5. Effect of pH

The effect of pH on the coagulation efficiency and charge neutralization capacity of coagulants are shown in Fig. 4. The turbidity of raw water is 80 NTU. The respective concentration of NaHCO$_3$ and NaNO$_3$ in raw water are 5 mM. The dosage is 100 $\mu$M as Al, and the coagulation was conducted at fixed pH condition. It can be seen that the pH has an important effect on the coagulation behavior of coagulants. The Zeta potential of colloids decreases monotonically with the increase of pH value. As can be seen from Fig. 4b, PACAl13 and PACAl30 display much higher charge neutralization capacity than AlCl$_3$. The isoelectric pH for PACAl30, PACAl13 and AlCl$_3$ are about 8.9, 9.1, and 7.2, respectively. The charge neutralization capacity of coagulants is not only related to Al speciation in coagulants, but also related to the hydrolysis rate of Al species after dosing into water. Al$^{3+}$ in AlCl$_3$ undergoes rapid hydrolysis, polymerization and precipitation after dosing, and ultimately forms low charged amorphous Al(OH)$_3$ sols and precipitations (Dental, 1988). However, the pre-polymerized Al$_{13}$ and Al$_{30}$ in PACAl13 and PACAl30 are rather stable and have a better opportunity to adsorb...
on negative colloidal particles and to neutralize the negative charges (Luan, 1997). The higher the pH of working solution is, the faster the coagulants hydrolyze. At the same time, the increase in particulate negative charges caused by the increase of pH also results in the decrease of the apparent charge neutralization capacity of coagulants. At higher pH region (pH \( \geq 6.8 \)), PAC \(_{Al13}\) behaves slightly higher charge neutralization capacity than PAC \(_{Al30}\). But PAC \(_{Al30}\) exhibits slightly higher charge neutralization capacity than PAC \(_{Al13}\) at lower pH region (pH \( \leq 6.5 \)). This is because \( Al_{30} \) is more labile to hydrolysis and polymerisation than \( Al_{13} \) in medium and high pH solutions due to the relative high acidity of the four connected Al atoms in \( Al_{30} \) (Rustad, 2005). This may be why PAC \(_{Al30}\) exhibits a stronger flocs formation capacity than PAC \(_{Al13}\).

As can be seen from Fig. 4a, PAC \(_{Al13}\) and PAC \(_{Al30}\) achieve effective turbidity removal at a much broader pH range than AlCl\(_3\). The optimal pH range for AlCl\(_3\) is 6.5–7.5, and it is more adjacent to the low pH side than that of PAC \(_{Al13}\) and PAC \(_{Al30}\), which is broadly consistent with the data of Zeta potential of AlCl\(_3\) (Fig. 4b). PAC \(_{Al30}\) is more effective than PAC \(_{Al13}\) at weak acid side (e.g. pH 6.8–7.0) because it is easier to produce flocs than PAC \(_{Al13}\). Outside the optimum coagulation pH range, the turbidity removal is rather poor. At the high acid side, flocs are difficult to form due to the increase in equilibrium solubility of amorphous Al(OH)\(_3\) precipitation. At the high alkaline side, due to the increase of particulate negative charges and the formation of Al(OH)\(_4\) and low charged non-settling Al colloids (Pernitsky and Edzwald, 2003), the particulate negative charges are insufficiently neutralized. The optimal pH value for turbidity removal of AlCl\(_3\) is lower than that of PAC \(_{Al13}\) and PAC \(_{Al13}\), which is consistent with the minimum solubility of Al salts and polyaluminum coagulants. Coagulation at the optimal pH value for different coagulants should be effectively minimize dissolved residual Al in treated water (Pernitsky and Edzwald, 2003). The detail about residual Al is subjected to further investigation.

4. Conclusions

The experimental results indicate that the coagulation performance of polyaluminum coagulants is improved by transforming \( Al_{13} \) species into \( Al_{30} \) species. Although the charge neutralization capacity of \( Al_{30} \) species is slightly lower than that of \( Al_{13} \) species under medium and high pH conditions, \( Al_{30} \) achieves better turbidity removal than \( Al_{13} \) due to its higher flocs formation capacity. Compared with \( Al_{13} \) species, \( Al_{30} \) species causes less pH depression, and it achieves more effective turbidity removal within a broader dosage range and within a wider pH range. These advantages of \( Al_{30} \) species are benefit to practical application, especially for coagulation of raw water with water nature changing frequently. The results verified that \( Al_{30} \) species is a high active species for coagulation. The research results will shed new light on the development and investigation of highly effective polyaluminum coagulants.

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