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Coagulation behavior of polyaluminum chloride: Effects of pH and coagulant dosage[☆]

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ABSTRACT

Coagulation mechanisms of polyaluminum chloride (PACl) at various dosages were studied using a conventional jar test at different final and initial pH values during treating kaolin suspension. The optimal final pH and dosages for PACl were obtained based on residual turbidity and zeta potential of flocs. The coagulation zones at various PACl dosages and solution pH values were developed and compared with those of alum. It is found that the optimal mechanism under acidic condition is charge neutralization, while alkaline condition will facilitate the coagulation of PACl. Both charge neutralization coagulation and sweep coagulation can achieve high coagulation efficiency under the alkaline condition ranging from final pH 7.0 to 10.0. Stabilization, charge neutralization destabilization, restabilization and sweep zones occur successively with increasing PACl dosages with the final pH values fixed at 7.0 and 8.0, but restabilization zone disappears at final pH 10.0. When the final pH is not controlled and consequently decreases with increasing PACl dosage, no typical sweep zone can be observed and the coagulant efficiency decreases at high PACl dosage. It seems that the final pH is more meaningful than the initial pH for coagulation. Charge neutralization coagulation efficiency is dominated by zeta potential of flocs and PACl precipitates. The charge neutralization and sweep coagulation zones of PACl are broader in the ranges of coagulant dosage and pH than those of alum. The results are helpful for us to treat water and wastewater using PACl and to understand the coagulation process of PACl.

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1. Introduction

Coagulation mechanisms may be different under different coagulation conditions for metal salt coagulants, such as double-layer compression [1], charge neutralization [2,3], and sweep coagulation [3,4]. Charge neutralization and sweep coagulation are the most important coagulation processes. Double-layer compression is not a feasible method for wastewater treatment [5] and is only important at low pH [6]. The dominant mechanism depends on solution pH [6,7] and coagulant dosage [2], and is apparently determined by the diphasic equilibrium state between soluble metal species and hydroxide precipitation [8]. At a fixed final pH in the coagulation process with conventional hydrolyzing salt as coagulant, four zones, namely stabilization, charge neutralization, restabilization and sweep coagulation zones, usually occur sequentially with the increase of coagulant dosage [8].

Charge neutralization is the most complicated coagulation mechanism. For conventional hydrolyzing salt coagulants such as aluminum sulfate, charge neutralization primarily includes adsorption of soluble, polymeric metal-hydroxide species (*i.e.* adsorption–charge neutralization) [9], surface precipitation [10], and precipitation–charge neutralization [11,12]. In most cases, surface precipitation or precipitation–charge neutralization are more important than adsorption–charge neutralization [10,13]. Adsorption–charge neutralization usually occurs under acidic conditions at very low coagulant concentrations [14].

Coagulation with hydrolyzing coagulants has been studied thoroughly, but the coagulation behavior of pre-hydrolyzed coagulants such as polyaluminum chloride (PACl), especially the coagulation mechanisms at various coagulant dosages and pH values of raw water, has not been systematically investigated and not been well understood [8,15]. Different coagulation mechanisms occur for aluminum sulfate (alum) and PACl [16]. As a pre-hydrolyzed coagulant, PACl is becoming increasingly popular in the coagulation–flocculation process. PACl has many benefits over conventional hydrolyzing aluminum or iron salts, such as better performance at low temperature [17,18], less aluminum residuals [19], less sludge volume [20], less effect on the pH value of raw water [8,21], and more rapid flocculation [21]. Furthermore, there are large differences between alum and PACl in morphology and precipitates in water [17,22]. At present, most discussion about coagulation mechanisms of PACl is confined to adsorption–

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charge neutralization because of the high positive charges of $\text{Al}_{13} [\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}]$ [21–27] and $\text{Al}_{30} [\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{24}^{18+}]$ [28–31]. Electrostatic patch [32], sweep coagulation and bridge-aggregation are also involved in the PACl coagulation process [15,16,33]. In essence, electrostatic patch coagulation is one of the charge neutralization coagulation mechanisms because it is very difficult to differentiate between electrostatic patch coagulation and precipitation–charge neutralization coagulation.

In this study, coagulation mechanisms of kaolin suspension with PACl as coagulant at various final and initial pH values are investigated, the relationship between the optimal PACl dosages and final pH values in charge neutralization coagulation is explored, and the coagulation zones of PACl are also developed and compared with those of alum at different coagulant dosages and final pH values.

2. Materials and Methods

2.1. Preparation of PACl solution

Commercial PACl powder (Nanning Chemical Engineering Co. Ltd., Nanning, China), with a basicity (OH/Al) of 1.35 and Al_2O_3 content of 30% (mass fraction), was dispersed into deionized water to prepare a concentrated stock solution ($2 \text{ mol} \cdot \text{L}^{-1} \text{ Al}$). To improve the reproducibility and avoid the degradation of solution, a fresh coagulant solution ($0.1 \text{ mol} \cdot \text{L}^{-1} \text{ Al}$) was prepared from the stock solution the day before each set of experiments.

2.2. Synthetic kaolin suspension

Kaolin was used as a model suspension in this study. A stock suspension ($2 \text{ g} \cdot \text{L}^{-1}$) of kaolin was prepared by dispersing 10 g kaolin powder (chemical grade, Xudong Chemical Plant, Beijing, China) into 5 L of tap water with rapid mixing for about 24 h. Suspensions for the experiments were prepared by diluting the stock suspension to a concentration of $100 \text{ mg} \cdot \text{L}^{-1}$. The turbidity was 68 NTU. The size distribution of the kaolin suspension was measured by a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, U.K.) as $1.18\text{--}28.3 \mu\text{m}$ (mean volume diameter $7.28 \mu\text{m}$).

The basic characteristics of the tap water were as follows [34]: $[\text{SO}_4^{2-}] = 36.5 \text{ mg} \cdot \text{L}^{-1}$, $[\text{Cl}^-] = 13.4 \text{ mg} \cdot \text{L}^{-1}$, $[\text{NO}_3^-] = 9.83 \text{ mg} \cdot \text{L}^{-1}$, total hardness = $224 \text{ mg} \cdot \text{L}^{-1}$ as CaCO_3 , alkalinity = $145 \text{ mg} \cdot \text{L}^{-1}$ as CaCO_3 , $\text{COD}_{\text{Mn}} = 1.3 \text{ mg} \cdot \text{L}^{-1}$, $\text{pH} = 7.2$, $[\text{Fe}] < 0.05 \text{ mg} \cdot \text{L}^{-1}$, electrical conductivity = $370 \mu\text{S} \cdot \text{cm}^{-1}$.

2.3. Jar test

In this study, the jar test was used to evaluate the predominant coagulation mechanism with various dosages of PACl. Dosages were given as the concentration of aluminum from PACl in milligrams per liter ($\text{mg} \cdot \text{L}^{-1} \text{ Al}$). All coagulation experiments were conducted with the same coagulation mixer (Model JTY, Daiyuan Company Ltd., Beijing, China) as that in our previous work [35]. The coagulation vessel was a 1 L cylindrical container with an inner diameter of 105 mm. The mixing was provided by a $50 \text{ mm} \times 40 \text{ mm}$ (H $\times$ W) flat rectangular blade centrally located 15 mm above the base of the container. The rotation speed of the blade was adjustable. The final pH values of all suspensions were adjusted using hydrochloric acid and sodium hydroxide, which were added before the coagulants. The quantity of hydrochloric acid or sodium hydroxide required was predetermined by titration before every set of experiments.

After the kaolin suspension of $100 \text{ mg} \cdot \text{L}^{-1}$ was prepared and mixed for 1 min at a velocity gradient (G value) of 245 s^{-1} , a predetermined volume of hydrochloric acid or sodium hydroxide was added into the suspension and mixed for 1 min. Then the coagulant was injected above the surface of suspension, followed by rapid mixing at 245 s^{-1} for 3 min and slow mixing at 15 s^{-1} for 10 min, and settling for 10 min. After rapid mixing, a 5 ml sample was taken for zeta potential (ZP) measurement (Zetasizer 2000, Malvern Instruments Ltd.).

Following settling, a 25 ml sample was taken from 10 mm below the water level for residual turbidity (RT) measurement (Turbidimeter 2100N, Hach Chemical Company, Loveland, CO).

3. Results and Discussion

3.1. Effect of PACl dosage at various final pH values

Coagulation mechanisms with PACl were investigated by measuring the RT and ZP at various dosages at a constant final pH. Fig. 1 shows the effects of PACl dosages on the RT and ZP at different final pH values. With final pH values of 6.0, 7.0, and 8.0 [Fig. 1(a–c)] the typical four coagulation zones (i.e. stabilization, charge neutralization destabilization, restabilization and sweep) are observed with increasing coagulant dosages, while at the final pH of 10.0, there is no restabilization zone [Fig. 1(d)]. A similar result has been obtained in coagulation with PACl at pH 10 [36] and for coagulation with aluminum salts at high pH or in the presence of high concentrations of SO_4^{2-} [37]. This is related to the increase in PACl precipitates [Fig. 2(a)], the decrease in ZPs of PACl precipitates [Fig. 2(b)] and kaolin particles [38] with increasing final pH, and consequently the decrease in ZP of flocs [Fig. 1(d)]. The highest ZP of the flocs ($+3.5 \text{ mV}$) at the final pH 10.0 is within the range of $\pm 5 \text{ mV}$ for strong coagulation–flocculation as recommended by ASTM [5]. Furthermore, Letterman *et al.* [37] have found that the restabilization zone will disappear when the electrophoretic mobility of flocs is less than approximately $+2.5$ to $+3.5 \mu\text{m} \cdot \text{s}^{-1} \cdot \text{V}^{-1} \cdot \text{cm}^{-1}$ when the corresponding ZP is between $+3.1$ and $+4.4 \text{ mV}$ at 20°C . The effect of pH on ZP can be explained by the surface ionization reaction proposed by Hohl *et al.* [39]. For example, the following reactions occur for hydrous aluminum oxide:

where Al represents an ionizable site on the solid surface.

At pH 6.0, the RT during sweep coagulation is obviously higher than that during charge neutralization, and the latter is higher than that at pH 7.0–10.0. This indicates that the optimal mechanism at pH 6.0 for PACl is charge neutralization and the optimal pH for coagulation with PACl is above 7.0. These results could be related to the formation of PACl hydrolysis precipitates under alkaline conditions [40]. At pH 7.0–10.0, sweep coagulation and charge neutralization have similar RT, but the former occurs over a wider range of dosages than the latter.

3.2. Effect of PACl dosage at various initial pH values

In the treatment process of wastewater by coagulation, the optimal coagulant dosage is usually determined according to the coagulation performance of various coagulant dosages at a fixed initial pH value. Therefore, the coagulation mechanisms with various PACl dosages were also investigated at the initial pH values of 7.6 and 9.3. At both pH values, the typical four coagulation zones were not observed and there was no obvious sweep coagulation zone, as shown in Fig. 3(a1) and (b1), which are similar to those in earlier work [15,22]. Moreover, the RT at both pH values decreased with increasing PACl dosage, and reached minima at the dosages of 1.9 (pH 7.6) and 2.7 (pH 9.3) $\text{mg} \cdot \text{L}^{-1} \text{ Al}$. The corresponding ZP around 0 mV indicated that the predominant mechanism was charge neutralization. After the optimal dosages were reached for both pH values, the RT increased with increasing PACl dosage up to $81 \text{ mg} \cdot \text{L}^{-1} \text{ Al}$ and then decreased slightly. The ZP at both pH values increased with increasing PACl dosage up to $135 \text{ mg} \cdot \text{L}^{-1} \text{ Al}$. Besides dosage, Ye *et al.* [15] found that with highly basic PACl the ZP increase will be

Fig. 1. Effect of PACl dosage (as Al) on residual turbidity (■) and zeta potential (○) for kaolin suspensions at final pH values of 6.0 (a), 7.0 (b), 8.0 (c) [34] and 10.0 (d). Initial kaolin concentration: 100 mg·L⁻¹; water temperature: (15 ± 1) °C; rapid mixing: 245 s⁻¹, 3 min; slow mixing: 15 s⁻¹, 10 min; settling: 10 min.

quicker than that with less basic PACl. Because of PACl hydrolysis, the pH value of the solution decreased with the addition of PACl [Fig. 3(a2) and (b2)], which is similar to the results in earlier studies [15,22]. However, highly basic PACl solutions can reduce the extent of the decrease in pH [15]. At both pH values, at PACl dosages > 135 mg·L⁻¹ Al, the pH equilibrated at around 4.5. This indicates that PACl hydrolysis stops at around pH 4.5. At the dosages of > 81 mg·L⁻¹ Al, a slight decrease in RT with increasing dosage could be attributed to the increase in PACl precipitates trapping original particles suspended in the model water solution.

3.3. Optimal PACl dosages at different final pH in charge neutralization coagulation

Coagulant dosage is one of the most important factors in determining coagulation performance. With the best coagulation performance, the coagulation at the optimal coagulant dosage reduces the amount of coagulant used in wastewater treatment. The optimization of coagulant dosage is particularly important for charge neutralization coagulation process because the dosage range in this process is narrow.

Fig. 2. Effect of final pH on the formation and zeta potential of PACl precipitates in tap water without kaolin. (PACl: 54.0 mg·L⁻¹ as Al; water temperature: 12.5 °C).

Fig. 3. Effect of PACI dosage (as Al) on the residual turbidity (○) and zeta potential (■) of kaolin suspensions at the initial pH values of 7.6 (a) and 9.3 (b). Initial kaolin concentration: 100 mg·L⁻¹; water temperature: (15 ± 1) °C; rapid mixing: 245 s⁻¹, 3 min; slow mixing: 15 s⁻¹, 10 min; settling: 10 min.

The optimal dosages of PACI at different final pH values in charge neutralization coagulation are shown in Fig. 4, which are based on Figs. 1 and 3. Fig. 4 also shows the concentration of PACI precipitates forming in the solution without kaolin at the optimal PACI dosages. With increasing final pH, the optimal PACI dosage decreased at pH values < 8.0 and increased at pH values > 8.0 [Fig. 4(a)]. This is similar to the production of PACI precipitates [Fig. 2(a)], indicating that the production of PACI precipitates affects charge neutralization coagulation. It also appears that the optimal pH for PACI coagulation relates to the pH value at which PACI precipitate formation is maximized. Based on flocculation theory, PACI precipitates have three functions in the coagulation process. Firstly, the precipitate surface with positive charges as shown in Fig. 2(b) can neutralize the charges on the surfaces of primary particles suspended in the water (i.e. precipitation-charge neutralization) [12]. Secondly, the precipitates increase the number and size of particles during flocculation process and then improve the flocculation efficiency based on ortho-kinetic flocculation theory [41]. Lastly, the precipitates are involved in electrostatic patch [15,33] and enmeshment [4], and facilitate charge neutralization coagulation process.

Fig. 4. Effect of final pH on optimal PACI dosage (as Al), zeta potential, and PACI precipitation at the optimal dosage during charge neutralization coagulation. Initial kaolin concentration 100 mg·L⁻¹; water temperature (15 ± 1) °C; rapid mixing: 245 s⁻¹, 3 min; slow mixing: 15 s⁻¹, 10 min; settling: 10 min. ○ optimal PACI dosage; ● PACI precipitates at the optimal dosage; × zeta potential at the optimal dosage.

The ZP at the optimal PACI dosage during charge neutralization coagulation process decreased with increasing final pH as shown in Fig. 4, similar to the change in the ZP of PACI precipitates as shown in Fig. 2(b). The ZP at the optimal PACI dosage was 0 mV at a final pH around 8.4, above 0 mV at final pH values < 8.4, and below 0 mV at final pH values > 8.4. In the standpoint of conventional charge neutralization coagulation, the optimal ZP should be 0 mV because no electrostatic repulsion between two different particles is optimal for particle aggregation driven by van der Waals forces. However, the ZPs at the optimal PACI dosages of different final pH values are from +2.1 mV (final pH 7.0) to -3.4 mV (final pH 10.0), which further demonstrates the vital importance of PACI precipitates in controlling charge neutralization coagulation. For the final pH 6.0, the ZP at the optimal PACI dosage is 6.2 mV although the coagulation efficiency at the optimal dosage is not satisfactory. Furthermore, it can be seen in Fig. 4 that more PACI precipitates form as PACI dosage increases under the conditions for optimal coagulation performance. It seems that the ZP of particles and PACI precipitates dominate charge neutralization coagulation efficiency. When the ZP of particles is close to 0 such as at final pH 8.0 with the ZP of 0.9 mV, less PACI precipitates are needed and so less PACI is required for the optimal coagulation efficiency. When the ZP of particles is far from 0 such as at final pH 6.0 (with ZP of 2.1 mV) or 10.0 (with ZP of -3.4 mV), more PACI precipitates are needed and so more PACI is required for the optimal coagulation efficiency.

3.4. Coagulation zones at various PACI dosages and final pH values

Based on the results presented in Figs. 1 and 3, the changes in the coagulation zones are presented schematically in Fig. 5 with increasing PACI dosage in the range of pH 6 to 10. The charge neutralization coagulation of PACI will begin at the dosage of 2.2 mg·L⁻¹ Al at pH 6.0 and 0.8 mg·L⁻¹ Al at pH values between 7.0 and 10.0. At the same time, the ZP changes from positive (1.0 mV at pH 6.0) to negative (-5.6 mV at pH 10.0) as shown in Fig. 1.

The dosage range of the restabilization zone for PACI widens with decreasing pH at pH < 10.0. For example, the dosage range for the restabilization zone at pH 7.0 was 5.4–21.6 mg·L⁻¹ Al, while at pH 6.0 it was 8.1–81.0 mg·L⁻¹ Al. At pH 10.0, the restabilization zone of PACI was not present at the final pH of 12.0. It should be noted that the restabilization zone did not occur at pH 7.0 or 8.0 in the same

Fig. 5. Coagulation zones for PACl and alum [43] at various final pH values. Initial kaolin concentration: $100 \text{ mg} \cdot \text{L}^{-1}$; water temperature: $(15 \pm 1)^\circ \text{C}$; rapid mixing: 245 s^{-1} , 3 min; slow mixing: 15 s^{-1} , 10 min; settling: 10 min. sweep coagulation zone of PACl; restabilization zone of PACl; charge neutralization zone of PACl; stabilization zone of PACl.

experiments conducted at 25.0°C . Kan *et al.* [42] also found that the restabilization zone disappeared during PACl coagulation at a final pH of 7.5.

The alum coagulation zones from Amirtharajah and Mills [43] are also plotted in Fig. 5 for comparison with those of PACl. Both the adsorption destabilization and combined (adsorption and sweep) destabilization for alum in Fig. 4 can be considered as charge neutralization destabilization based on the precipitation–charge neutralization mechanism [12]. Stabilization, charge neutralization, restabilization, and sweep coagulation zones occur during the coagulation with both PACl and alum. However, there are several remarkable differences between the zones for the two coagulants. Firstly, a higher dosage of PACl than alum (in $\text{mg} \cdot \text{L}^{-1} \text{Al}$) is required for both the charge neutralization and sweep coagulations. A similar result was obtained by Hu *et al.* [22] for treatment of a water sample from the Guanting reservoir in Beijing. They found that the optimal dosages for turbidity removal were around 16 and $32 \text{ mg} \cdot \text{L}^{-1} \text{Al}$ for aluminum chloride and PACl, respectively, forming less precipitates with PACl at the same dosage. For example, for PACl in deionized water at 25°C , the highest turbidity of precipitates was 1.2 NTU for $5.04 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{Al}$, while for alum under the same conditions it was 7.5 NTU for $5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{Al}$ [17]. Secondly, efficient coagulation occurs at a higher final pH for PACl than for alum at the same dosage, because of the differences between PACl and alum for the lowest and optimal pH values for precipitate formation. Benschoten and Edzwald [17] found that the lowest and optimal pH values for precipitate formation were around pH 7.0 and around pH 8.3, respectively, for PACl in deionized water at 25°C . By contrast, the lowest and optimal pH values for alum under the same conditions were around pH 4.5 and pH 5.5, respectively. Thirdly, the restabilization zone disappears at a higher pH for PACl than alum, because the lowest pH for precipitate formation with PACl is higher than that for alum [17], as discussed above. Finally, both the charge neutralization and sweep coagulation zones for PACl are larger than those for alum, so there is a wider dosage range for PACl than for alum for charge neutralization coagulation and sweep coagulation. Furthermore, PACl performs well for coagulation in zones where alum cannot induce coagulation, such as the charge neutralization coagulation zone and sweep coagulation zone below the line for $\text{Al}(\text{OH})_4^-$ in Fig. 5. These results are relevant

to the difference between PACl and alum for the highest pH where the precipitate of coagulant hydrolysis disappears. Benschoten and Edzwald [17] found that the highest pH values were around 6.0 and 9.5 for PACl and alum, respectively, in deionized water at 25°C .

4. Conclusions

In the conventional jar tests for the coagulation of kaolin suspension with PACl as coagulant, the pH value of the treated suspension and PACl dosages have significant effects on the coagulant mechanism of PACl. Four coagulation zones, namely stabilization, charge neutralization destabilization, restabilization, and sweep zones, occur successively with increasing PACl dosage with the final pH fixed at 7.0 and 8.0, while the restabilization zone does not occur at the final pH of 10.0. When the final pH is not controlled and consequently decreases with increasing PACl dosage, no typical sweep zone can be observed. The optimal mechanism at final pH < 7.0 is charge neutralization. Satisfactory coagulation efficiency could be obtained with either charge neutralization coagulation or sweep coagulation at the final pH values from 7.0 to 10.0. The coagulation process of PACl and the formation of PACl precipitates have the same optimal pH value.

There are some differences in coagulation behavior between PACl and alum. More PACl (as Al) is required for charge neutralization and sweep coagulations than alum (as Al). The restabilization zone of PACl coagulation disappears at a higher final pH value than that of alum coagulation. Moreover, the charge neutralization and sweep coagulation zones of PACl are broader in the ranges of coagulant dosage (as Al) and pH value than those of alum.

The destabilization extent of primary particles and PACl precipitates seems to control charge neutralization coagulation process. Sufficient PACl precipitates could reduce the adverse effect of insufficient destabilization in charge neutralization coagulation process to some extent.

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