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ENVIRONMENTAL
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Hydrolysis of polyaluminum chloride prior to coagulation: Effects on coagulation behavior and implications for improving coagulation performance

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ARTICLE INFO

Article history:

Received 30 January 2016

Revised 25 October 2016

Accepted 31 October 2016

Available online 29 November 2016

Keywords:

Polyaluminum chloride (PACl)

Precipitate

Hydrolysis

Charge neutralization

Sweep coagulation

ABSTRACT

The effects of polyaluminum chloride (PACl) hydrolysis prior to coagulation on both the coagulation zone and coagulation performance of a kaolin suspension were investigated by a novel jar test named the “reversed coagulation test”. The tests showed that PACl hydrolysis prior to coagulation decreased the performance of charge neutralization coagulation in the case of short-time slow mixing (10 min; $G = 15 \text{ sec}^{-1}$) and increased the optimal dosage for charge neutralization and sweep coagulation. Moreover, the hydrolysis time had insignificant effects on the size and zeta potential of PACl precipitates and the residual turbidity of the raw water. However, PACl hydrolysis prior to coagulation and the size of PACl precipitates had a negligible effect on the performance of sweep coagulation. The results imply that, in practice, preparing a PACl solution with deionized water, rather than tap water or the outlet water from a wastewater treatment unit, can significantly save PACl consumption and improve the performance of charge neutralization coagulation, while preparing the PACl solution with tap or outlet water would not affect the performance of sweep coagulation. In addition, the optimal rapid mixing intensity appears to be determined by a balance between the degree of coagulant hydrolysis before contacting the primary particles and the average size of flocs in the rapid mixing period. These results provide new insights into the role of PACl hydrolysis and will be useful for improving coagulation efficiency.

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Introduction

Coagulation is an important process in the pretreatment of water and wastewater. Charge neutralization (Yu et al., 2010; Zhao et al., 2011b) and sweep coagulation (Zhao et al., 2011b) are the most important coagulation mechanisms in coagulation processes using metal salt coagulants. Charge neutralization coagulation occurs through mutual aggregation between destabilized particles when coagulants reduce or eliminate the electrostatic repulsion between particles (Ghermaout and Ghermaout, 2012). In sweep coagulation, the particles in solution are removed by entrapment within a suspended coagulant precipitate (Ghermaout and Ghermaout, 2012). The dominant mechanism depends on solution pH (Vepsäläinen et al., 2012) and coagulant dosage (Yu et al., 2010), and appears to be determined by the diphasic equilibrium state between soluble metal species and hydroxide precipitation (Duan and Gregory, 2003).

The charge neutralization mechanisms of conventional hydrolyzing salt coagulants primarily include adsorption of soluble, polymeric metal-hydroxide species (namely, adsorption-charge neutralization) (O'Melia and Stumm, 1967), surface precipitation (Farley et al., 1985), and precipitation-charge neutralization (Dentel, 1988; Dentel and Gossett, 1988). Adsorption-charge neutralization usually takes place under acidic conditions at very low coagulant concentrations (White, 1980). In most cases, surface precipitation or precipitation-charge neutralization play a more important role (Benjamin, 1983; Farley et al., 1985). According to the precipitation-charge neutralization mechanism proposed by Dentel and Gossett (1988), the zeta potential (ZP) of aggregate, $\zeta_{1,2}$, can be given as

$$\zeta_{1,2} = \frac{\zeta_1 A_1 + \zeta_2 A_2}{A_1 + A_2}, \quad (1)$$

where, ζ is ZP, A is the surface area at the shear plane, and 1 and 2 are precipitated aluminum or ferric hydroxide and original particles, respectively. The results predicted by Eq. (1) agreed with the data from closely controlled jar-test experiments involving the addition of aluminum salts (aluminum sulfate) to synthetic suspensions, over a wide range of pH, coagulant dosage, and particle concentrations (Dentel and Gossett, 1988). This implies that the precipitated hydroxide on particles plays a dominant role in charge neutralization.

Based on the above, it can be concluded that the precipitates formed by coagulant hydrolysis are of great importance in both charge neutralization coagulation and sweep coagulation for hydrolyzing coagulants such as aluminum sulfate and ferric chloride.

The most common pre-hydrolyzed coagulant, polyaluminum chloride (PACl), is being used widely in coagulation-flocculation processes because it has benefits over conventional hydrolyzing aluminum or iron salts, including better performance at low temperature (Van Benschoten and Edzwald, 1990; Yu et al., 2007), lower aluminum residuals (Yang et al., 2011), lower sludge volume (Aguilar et al., 2002), a smaller effect on the pH of raw water (Duan and Gregory, 2003; Gregory and Dupont, 2001), and more rapid flocculation (Gregory and Dupont, 2001). However, the effects of PACl hydrolysis on coagulation behaviors, especially the hydrolysis occurring before it is mixed with raw water

and the precipitates of PACl, are still not very clear, although we do know that there are significant differences between alum and PACl in morphology, precipitates and coagulation mechanisms (Hu et al., 2006; Van Benschoten and Edzwald, 1990; Wu et al., 2007). In practice, hydrolysis prior to coagulation usually occurs in water and wastewater treatment engineering, such as during the process of preparing a PACl stock solution before coagulation or in the case of an insufficient dispersion of PACl during the rapid mixing period.

To explore the effects of PACl hydrolysis prior to coagulation, especially the formation of PACl precipitates, on coagulation zones (i.e., stabilization, charge neutralization coagulation, restabilization and sweep coagulation zones) and coagulation performance, a series of jar tests, in particular a novel “reversed coagulation test”, were conducted using a kaolin suspension as a model raw water. The implications of the experimental results for the improvement of coagulation performance are discussed. This work will be helpful for improving our understanding of the role of PACl hydrolysis and optimizing coagulation performance.

1. Materials and methods

1.1. Preparation of PACl stock solution

A commercial powder PACl (Nanning Chem. Eng. Co. Ltd., Nanning, China), with a basicity (OH/Al) of 1.35 and an Al_2O_3 content of 30% (wt), was dispersed into deionized water to prepare a concentrated stock solution of 2 mol/L Al. A fresh coagulant solution of 0.1 mol/L Al was prepared from the stock solution one day before each set of experiments, to avoid aging phenomena and improve reproducibility. Deionized water was used to prepare the PACl solution.

1.2. Synthetic kaolin suspension

Kaolin was used as a model suspension. A stock suspension of kaolin was prepared by dispersing 10 g of kaolin in powder form (Xudong Chemical Plant, Beijing, China; chemical grade) into 5 L of tap water to a concentration of 2 g/L, followed by rapid mixing for 24 hr. The experimental suspensions were prepared by diluting the stock suspension to 100 mg/L, with a corresponding turbidity of 68 NTU (Nephelometric Turbidity Unit). Tap water was used for diluting the stock kaolin suspension. The size distribution of the kaolin suspension, measured by a Mastersizer 2000 (Malvern Instruments Ltd., Worcestershire, UK), was in the range of 1.18 to 28.3 μm , with a mean volume diameter of 7.28 μm , as reported in a previous study (Zhang et al., 2013). The characteristics of the tap water are as following: SO_4^{2-} 36.5 mg/L, Cl^- 13.4 mg/L, NO_3^- 9.83 mg/L, total hardness as CaCO_3 224 mg/L, alkalinity as CaCO_3 145 mg/L, COD_{Mn} 1.3 mg/L, pH 7.2, Fe < 0.05 mg/L, and electrical conductivity 370 $\mu\text{S}/\text{cm}$ (Zhang et al., 2013). It should be noted that under alkaline conditions, the hardness of the tap water can cause the destabilization of kaolin particles to a certain extent during preparation of a kaolin suspension (Liu and Wei, 2012). The ability of Ca^{2+} and Mg^{2+} to destabilize kaolin particles, however, is far lower than that of Al^{3+} (Liu and Wei, 2012). Moreover, the kaolin suspensions used in all the

experiments had the same concentration (100 mg/L). Therefore, we can neglect the effect of the hardness of the tap water in the work. Using tap water rather than deionized water, we could prepare a simulated water closer to a real surface water.

1.3. Jar test

1.3.1. Conventional coagulation test

In this study all coagulation experiments were conducted with the same coagulation mixer (Model JTY, Daiyuan Comp. Ltd., Beijing, China). The experimental procedures were described in our previous work (Zhang et al., 2013). The coagulation vessel was a 1-L cylindrical container with an inner diameter of 105 mm, and mixing was provided by a 50 × 40 (H × W) mm flat rectangular blade, centrally located 15 mm above the base of the container. The amount of the kaolin suspension in the coagulation vessel was 1 L for each test. The rotation speed of the blade was adjustable. The final pH of the kaolin suspension was adjusted by hydrochloric acid and sodium hydroxide, which were added before coagulant dosing. The quantity of hydrochloric acid or sodium hydroxide required was predetermined by titration before each set of experiments. In our previous study (Wei et al., 2015), the typical four coagulation zones, i.e., stabilization, charge neutralization destabilization, restabilization, and sweep zones, were observed at the final pH of 8.0, where the optimal coagulation performance was also obtained in both charge neutralization and sweep coagulation for the kaolin suspension. Therefore, all the tests in the study were conducted at the final pH of 8.0. It should be noted that the final pH was the pH value of the kaolin suspension after rapid mixing with coagulant.

After a kaolin suspension at 100 mg/L was prepared and mixed for 1 min at $G = 245 \text{ sec}^{-1}$, predetermined amounts of hydrochloric acid or sodium hydroxide were added to the suspension and mixed for an additional 1 min. The coagulant was then directly injected above the surface of suspension, followed by rapid mixing for 3 min at $G = 245 \text{ sec}^{-1}$, slow mixing for 10 min at $G = 15 \text{ sec}^{-1}$, and then settling for 10 min. After settling, a 25-mL sample was taken from 10 mm below the water level for residual turbidity (RT) measurement (Turbidimeter 2100 N, Hach Chemical Comp., Loveland, Colorado, USA). At the end of rapid mixing, a 5-mL sample was taken for ZP measurement (Zetasizer 2000, Malvern Instruments Ltd.).

1.3.2. Reversed coagulation test

A novel “reversed coagulation test” was proposed to investigate the effects of PACl hydrolysis on coagulation. The main experimental processes were as follows: First, a predetermined amount of hydrochloric acid or sodium hydroxide was added to a jar containing 950 mL of tap water and mixed for 1 min. PACl coagulant was then injected into the jar and simultaneously mixed at $G = 245 \text{ sec}^{-1}$ for a desired time (defined as the hydrolysis time), followed by introducing 50 mL of kaolin stock suspension to give a kaolin content of 100 mg/L. Finally, rapid and slow mixing, settling and several measurements were carried out sequentially. The difference between the conventional and the reversed coagulation tests is that in the former method, coagulant is added to the jar

after the wastewater or model suspension, but in the latter case, coagulant is added to the jar first to hydrolyze and even finally form precipitates before mixing with the wastewater or model suspension (Fig. 1). It should be noted that the reversed coagulation test is not a practicable water treatment process and only an experimental method used to investigate the effect of coagulant hydrolysis on the coagulation process.

The reversed coagulation tests were conducted at a final pH of 8.0 with a PACl dosage of 1.35 mg/L as Al. The ZP and size of PACl precipitates were measured at a mixing rate of $G = 245 \text{ sec}^{-1}$. An on-line size monitoring system with a Mastersizer 2000 laser diffraction particle size analyzer, a diagram of which can be found in our previous work (Zhang et al., 2013), was used to measure the dynamic size of PACl precipitates during hydrolysis. The suspension in the jar was drawn up by a peristaltic pump into the sample cell, and then returned to the jar through a 4.8 mm internal-diameter tube. The inflow and outflow tubes were situated opposite each other at a depth just above the paddle in the holding ports. The flow rate of suspension through the pump was 34 mL/min. Flow rates higher than this would cause significant precipitate breakup, whereas lower flow rates allowed the precipitate to settle and flocculate in the tube, and consequently, the precipitate size shown by the instrument was unstable.

2. Results and discussion

2.1. Effects of PACl hydrolysis on coagulation zones

At a fixed final pH, four zones including stabilization, charge neutralization coagulation, restabilization and sweep coagulation zones, usually occur sequentially with increasing coagulant dosages (Duan and Gregory, 2003). The effects of PACl hydrolysis before rapid mixing on these coagulation zones were investigated using the reversed coagulation test, at final pH 8.0 and hydrolysis time of 3 min. The experimental results were compared with those obtained from the conventional

Fig. 1 – Procedures for the reverse and conventional coagulation tests.

coagulation test conducted under the same conditions (Fig. 2). As shown in Fig. 2a the charge neutralization and restabilization zones were shifted towards higher dosages in the reversed coagulation process. For example, the optimal dosages for charge neutralization in the conventional and reversed coagulation processes were 2.16 and 5.40 mg/L as Al, respectively, and the dosages at which the RT was the highest in the restabilization zone for both coagulation zones were 5.40 and 8.10 mg/L as Al, respectively. The reason for this shift is that a higher dosage is needed to reach the same ZP in reversed coagulation than in conventional coagulation, as shown in Fig. 2b. In other words, the ability of PACl to neutralize charges decreased when it was hydrolyzed before mixing with the suspension. For example, the ZP corresponding to the optimal dosage (2.16 mg/L as Al) in the charge neutralization zone by conventional coagulation was +3.4 mV, but the ZP at the same dosage for reversed coagulation was

Fig. 2 – Effects of polyaluminum chloride (PACl) dosage on residual turbidity (a), and zeta potential (b) for both conventional and reverse coagulation tests. Initial kaolin concentration 100 mg/L; final pH 8.0; $21 \pm 1^\circ\text{C}$; premixing of PACl solution: $G = 245 \text{ sec}^{-1}$, 3 min; rapid mixing: $G = 245 \text{ sec}^{-1}$, 3 min; slow mixing: $G = 15 \text{ sec}^{-1}$, 10 min; settling: 10 min. Each residual turbidity point shown in this figure is the average of two tests. Coagulation zones: (I) stabilization zone, (II) charge neutralization coagulation zone, (III) restabilization zone, (IV) sweep coagulation zone.

only -8.5 mV (Fig. 2b). It indicates that a higher dosage was required for charge neutralization coagulation to obtain the optimal coagulation performance in the case of PACl hydrolysis before rapid mixing.

Moreover, PACl hydrolysis led to a decrease in coagulation performance during charge neutralization coagulation, as shown in Fig. 2a. The RT corresponding to the optimal dosage during charge neutralization in reversed coagulation, 5.12 NTU, was significantly higher than that in conventional coagulation, 0.496 NTU. The ZPs corresponding to the optimal dosage were closely similar, at 3.6 and 3.4 mV for reversed and conventional coagulation, respectively. This indicates that in addition to the charges on the surface of the particles, other factors also affect charge neutralization coagulation. Electrostatic patches are also involved in the charge neutralization coagulation process for PACl (Wang et al., 2002; Wu et al., 2007; Ye et al., 2007a).

In the sweep coagulation zone, however, the difference in the RT values between the two coagulation processes was negligible (Fig. 2a), meaning that PACl hydrolysis prior to coagulation had a negligible effect on coagulation performance.

Fig. 2b shows that at PACl dosages higher than 5.40 mg/L as Al, the ZP of the flocs in reversed coagulation was much closer to that of a PACl precipitate in the absence of kaolin clay. This occurs because the surface of the clay would be fully covered by the precipitate when in the presence of sufficient PACl. Because of the incomplete coverage, the ZP of the flocs was lower than that of the precipitate at dosages below 5.40 mg/L as Al. At PACl dosages higher than 2.16 mg/L as Al, the ZP of the flocs in conventional coagulation was higher than that of the precipitate formed by PACl. This result possibly arises because in addition to the precipitate formed by PACl, some highly charged polynuclear hydrolysis products of PACl, including $\text{Al}_{13} [\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}]$ (Bi et al., 2012; Choi et al., 2013; Gregory and Dupont, 2001; Hu et al., 2006; Johansson et al., 1960; Zhao et al., 2011a) and $\text{Al}_{30} [\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{24}^{18+}]$ (Chen et al., 2006, 2007; Mertens et al., 2011; Yang et al., 2010), also adsorb to the surface of kaolin particles, neutralizing the charges. Furthermore, Fig. 2b shows that the ZP of the precipitates increases with PACl dosage. This occurs because more highly (positively) charged polyions of aluminum are formed with increasing PACl dosage and are then adsorbed on the surface of PACl precipitates and clay.

2.2. Effects of PACl hydrolysis time on coagulation performance

The effects of PACl hydrolysis time on residual turbidity are shown in Fig. 3, where the solid lines are the regression lines for observed values. The RT during charge neutralization coagulation, which was conducted respectively at dosages of 1.35 and 2.70 mg/L as Al, increased with hydrolysis time, and the extent of increase was more marked at lower dosages (Fig. 3a). For example, when the hydrolysis time increased from 0 to 5 min, the corresponding RT increased from 0.934 to 17.5 NTU (an increase of 18.7 times) for a dosage of 1.35 mg/L as Al, but only from 0.694 to 4.53 NTU (an increase of 6.52 times) for a dosage of 2.70 mg/L as Al. During sweep coagulation, on the other side, the RTs at different hydrolysis times were much more similar. For example, the RTs at 0 and

Fig. 3 – Effects of PACl solution hydrolysis time prior to coagulation on residual turbidity (a), and zeta potential (b). Initial kaolin concentration 100 mg/L; final pH 8.0; water temperature $21 \pm 1^\circ\text{C}$; premixing of PACl solution: $G = 245 \text{ sec}^{-1}$; rapid mixing: $G = 245 \text{ sec}^{-1}$, 3 min; slow mixing: $G = 15 \text{ sec}^{-1}$, 10 min; settling: 10 min.

5 min were 0.829 and 1.65 NTU, respectively. These indicate that charge neutralization coagulation is observably affected by the hydrolysis time of the PACl solution, but sweep coagulation is virtually unaffected.

Yu et al. (2015) also found that for charge neutralization coagulation with PACl, delaying addition of kaolin to NaHCO_3 solutions with PACl had a significant impact on the floc size represented by the flocculation index in the case of short-time slow mixing such as less than 10 min, which is consistent with results found in our work. However, the highest flocculation indexes for different delay times were nearly the same, but a longer slow-mixing time was needed to reach the highest flocculation index with a longer delay time, corresponding to a longer hydrolysis time for PACl (Yu et al., 2015). This implies that a long slow-mixing time, such as 20 min in the work of Yu et al. (2015), can offset the adverse effect of PACl hydrolysis prior to coagulation on the performance of charge neutralization coagulation.

The ZP of flocs decreased generally with hydrolysis time, whether during charge neutralization coagulation or sweep coagulation, as shown in Fig. 3b. This indicates that PACl hydrolysis leads to a decrease in its charge neutralization capability. At a dosage of 1.35 mg/L as Al, the increase in RT with hydrolysis time can be explained by a decrease in the ZP of the flocs. At a dosage of 2.70 mg/L as Al, it is difficult to explain the increase in RT during the initial hydrolysis of 2 min, because the ZP of the flocs was eventually close to the zero ZP. Furthermore, there was a discrepancy between the optimal charge neutralization coagulation and the zero ZP of the flocs in our previous work (Wei et al., 2015), which was also found during coagulation with alum by Letterman et al. (1982). These results imply that there are other factors that affect charge neutralization coagulation, although the extent of destabilization of particles controls the coagulation process. These phenomena are perhaps related to the role played by electrostatic patches (Wang et al., 2002; Ye et al., 2007b).

During sweep coagulation, the RT was essentially constant over the range of hydrolysis times conducted in this study, although the ZP of flocs decreased slightly with hydrolysis time (Fig. 3). This indicates that the ZP of flocs has little effect on sweep coagulation. However, it should be noted that the occurrence of sweep coagulation is possibly controlled by a correlation between the volume of coagulant precipitates and the ZP of the flocs. Sweep coagulation will not occur before sufficient precipitates are formed if the ZP is too high. When sufficient precipitates are available, however, sweep coagulation will occur even if the ZP of the flocs is as high as +15 to +38 mV (Wei et al., 2015). Of course, other factors such as the configuration of flocs also affect sweep coagulation. Fig. 4 shows that the size of PACl precipitates changes with hydrolysis time, especially during the initial 3 min, but the RT in sweep coagulation did not vary, as shown in Fig. 3a. This implies that the size of PACl precipitates has no effect on sweep coagulation.

The decrease in floc ZP with PACl hydrolysis time can be explained by three effects. The first is a decrease in the number of highly charged hydrolysis products of PACl, such

Fig. 4 – Effects of hydrolysis time prior to coagulation on the precipitates formed by PACl. Final pH 8.0; water temperature $21 \pm 1^\circ\text{C}$; $G = 245 \text{ sec}^{-1}$; PACl dosage: 1.35 mg/L as Al.

as Al_{13} , caused by their gradual conversion into precipitates with hydrolysis time (Chen et al., 2009). The other effects are a decrease in the ZP of PACl precipitates and an increase in the size of PACl precipitates (Fig. 4). The decrease in the ZP of PACl precipitates was possibly induced by a decrease in the number of highly charged hydrolysis products that can be adsorbed on the surface of the PACl precipitates, because some highly charged hydrolysis products were converted into precipitate. When the volume of the precipitates remained constant, their surface area, A_1 , would decrease with an increase in the size. Consequently, a decrease in the ZP of PACl precipitates, ζ_1 , and an increase in the size of PACl precipitates would lead to a decrease in the ZP of flocs, $\zeta_{1,2}$, based on Eq. (1).

It should be noted that the experimental results do not indicate that the hydrolysis of PACl had a negative effect on its coagulation, but showed that hydrolysis before the coagulant was mixed with raw water was unfavorable for charge neutralization coagulation. PACl hydrolysis and the resulting precipitates formed during the coagulation process can play an important role in improving its coagulation performance (Liu et al., 2009, 2011; Wang et al., 2002; Yan et al., 2008), and the optimal conditions for PACl coagulation is related to the formation of PACl precipitates with maximum volume (Wei et al., 2015).

2.3. Implications for preparing PACl solution in practice

Preparation of a coagulant solution is an essential part of the coagulant/flocculation process in water and wastewater treatment. In most cases, tap water is used to dissolve a solid coagulant or dilute a liquid coagulant to a certain concentration to prepare the solution. In some cases, even the outlet water from a wastewater treatment unit is used to prepare a PACl solution. The alkalinity in tap water or outlet water can promote the hydrolysis of PACl and promote the formation of PACl precipitates to a certain extent during the preparation and storage of the stock solution. Based on the above results, it can be concluded that preparing a coagulant solution using tap water or outlet water will increase the optimal PACl dosage and decrease the performance of charge neutralization coagulation due to PACl hydrolysis and the formation of PACl precipitates before PACl is mixed with raw water. However, it would not affect the performance of sweep coagulation, but would lead to an increase in PACl dosage.

Based on the work done by Wang et al. (2004), solution pH has a significant effect on the hydrolysis of PACl, especially for PACl with a low basicity ($[\text{OH}]/[\text{Al}]$). It was found that a large amount of Al_b can form for PACl within weak acidic condition, but it transforms quickly into Al_c after aging. Al_b has a close relationship with Al_{13} (Parker and Bertsch, 2002) and so a high concentration of Al_b is favorable for charge neutralization coagulation. Furthermore, the polymer species of PACl become aggregated and precipitate out above pH 7.5 (Benschoten and Edzwald, 1990). The maximum amount of Al_b occurs at the near neutral pH condition close to the pH value of deionized water (Wang et al., 2004). Moreover, some ions present in tap water or outlet water will facilitate the hydrolysis of PACl and the formation of PACl precipitates. For example, sulfate will react with Al^{3+} and form the precipitate

$\text{Al}(\text{OH})_{3-2x}(\text{SO}_4)_x$ (Wang et al., 2004). Therefore, preparing a PACl solution with deionized water is beneficial for reducing PACl dosage and improving the performance of charge neutralization coagulation because deionized water does not promote the formation of PACl precipitates.

Of course, a cost accounting exercise is necessary to make the decision regarding whether or not to use deionized water. In addition, further study is necessary to determine the impact of using tap water and outlet water for preparing PACl solution on coagulant consumption and coagulation performance in water and wastewater treatment engineering. The impact is expected to be related to the degree of PACl hydrolysis before coagulation.

2.4. Implications for determining rapid mixing intensity of PACl coagulation

Rapid mixing and slow mixing are generally both necessary procedures in coagulation processes (Sun et al., 2012; Yu et al., 2011; Zhang et al., 2013). Rapid mixing is more complicated and important than slow mixing for coagulation efficiency (Dharmappa et al., 1993; Rossini et al., 1999). During the rapid mixing period, an inorganic metal coagulant is usually rapidly dispersed into raw water by intense agitation, and this then induces the destabilization of the primary particles in raw water by charge neutralization or double-layer compression, amongst other effects. The hydrolysis of inorganic coagulants such as aluminum sulfate and PACl is inevitable and beneficial to the coagulation process. Al_{13} (Bi et al., 2012; Choi et al., 2013; Gregory and Dupont, 2001; Hu et al., 2006; Johansson et al., 1960; Zhao et al., 2011a) and Al_{30} (Chen et al., 2006, 2007; Mertens et al., 2011; Yang et al., 2010), which play vital roles in charge neutralization coagulation of PACl, will be formed during PACl hydrolysis. However, a low rapid-mixing intensity will cause the formation of PACl precipitates through poor dispersion of PACl, and consequently lead to a decrease in the performance of charge neutralization coagulation, based on the above results. Therefore, a sufficient rapid-mixing intensity is necessary for charge neutralization coagulation to avoid excessive hydrolysis of PACl before it comes in contact with primary particles in raw water. On the contrary, a low rapid-mixing intensity probably has a negligible effect on sweep coagulation according to the above results. Indeed, it was found that rapid-mixing intensity had a more significant effect on charge neutralization coagulation than on sweep coagulation for aluminum sulfate (Amirtharajah and Mills, 1982). However, excessive rapid mixing is unfavorable for coagulation processes, according to the literature (Rossini et al., 1999; Zhang et al., 2013). Therefore, a suitable rapid-mixing intensity is highly important for achieving optimal performance with PACl.

The monitoring results from a photometric dispersion analyzer revealed that the size of flocs formed during the rapid mixing process is closely related to the coagulation performance for alum and PACl, and the largest average size of flocs corresponds to the optimal coagulant performance (Kan et al., 2002; Ramphal and Sibiya, 2014). In addition, the average size of flocs is greatly affected by mixing intensity and decreases with increasing mixing intensity (Wang et al., 2011). However, a high rapid-mixing intensity can facilitate

the dispersion of coagulant (hindering the formation of coagulant precipitates during hydrolysis) in the raw water and the destabilization of primary particles by charge neutralization. Therefore, the optimal rapid-mixing intensity appears to be determined by a balance between the degree of coagulant hydrolysis before contacting the primary particles and the average size of flocs during the rapid mixing period.

3. Conclusions

PACl hydrolysis prior to coagulation caused an increase in the optimal dosage for charge neutralization coagulation and sweep coagulation, and also induced an increase in the residual turbidity of a kaolin suspension during charge neutralization coagulation.

For charge neutralization coagulation, the hydrolysis time of PACl had insignificant effects on the residual turbidity of the kaolin suspension in the case of short-time slow mixing (10 min), and simultaneously on the size and zeta potential of PACl precipitates formed during hydrolysis.

For sweep coagulation, the hydrolysis of PACl and its duration prior to coagulation had a negligible effect on coagulation performance. Furthermore, the size of PACl precipitates seemed to have no effect on sweep coagulation.

The experimental results can provide guidance for preparing PACl solution and be beneficial for better understanding the mechanism of the influence of rapid-mixing intensity on coagulation performance for different coagulation mechanisms, including charge neutralization coagulation and sweep coagulation.

Acknowledgments

The authors would like to thank the Special Fund for the Technical Development of Scientific Research Institutions, financed by the Ministry of Science and Technology of the People's Republic of China (Nos. 2011EG111307 and 2012EG111122), and the Program for Overseas Talents of the Beijing Academy of Science and Technology (No. OTP-2013-015).

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