Coagulation Behavior of Aluminum Salts in Eutrophic Water: Significance of Al_{13} Species and pH Control

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The coagulation behavior of aluminum salts in a eutrophic source water was investigated from the viewpoint of Al-(III) hydrolysis species transformation. Particular emphasis was paid to the coagulation effect of Al_{13} species on removing particles and organic matter. The coagulation behavior of Al coagulants with different basicities was examined through jar tests and hydrolyzed Al(III) speciation distribution characterization in the coagulation process. The results showed that the coagulation efficiency of Al coagulants positively correlated with the content of Al_{13} in the coagulation process rather than in the initial coagulants. Aluminum chloride ($AlCl_3$) was more effective than polyaluminum chloride (PACl) in removing turbidity and dissolved organic matter in eutrophic water because $AlCl_3$ could not only generate Al_{13} species but also function as a pH control agent in the coagulation process. The solid-state ^{27}Al NMR spectra revealed that the precipitates formed from $AlCl_3$ and PACl were significantly different and proved that the preformed Al_{13} polymer was more stable than the in situ formed one during the coagulation process. Through regulating Al speciation, pH control could improve the coagulation process especially in DOC removal, and $AlCl_3$ benefited most from pH control.

Introduction

The eutrophication of surface water is a threat to the safety of the drinking water supply in China and many other countries. Eutrophication is caused by excessive inputs of nutrients, especially phosphorus and nitrogen, which stimulate algal blooms. Massive growth of algae may cause many problems in the production of drinking water, such as unpleasant taste and odors, filter clogging, and filter penetrating (1, 2), and may also function as trihalomethane precursors (3), which may lead to the deterioration of drinking water quality. In addition, the change of dissolved organic carbon (DOC) composition, i.e., the ratio of large molecules to small molecules declined as eutrophication continued, has made DOC removal difficult in the traditional treatment processes of drinking water (4, 5). At present, enhanced

coagulation has gained much attention to increase the removal efficiency of algae and DOC in raw waters (5–7).

In drinking water treatment, coagulation is an essential process for the removal of various particulates and organic matters. Aluminum salts, e.g., polyaluminum chloride (PACl), aluminum chloride ($AlCl_3$), and alum, are commonly used to coagulate small particles into larger flocs that can be effectively removed in subsequent separation processes such as sedimentation and/or filtration (8). PACl has been claimed to be superior to traditional Al coagulants (e.g., $AlCl_3$ and alum) in particulate and/or organic removal with inherent advantages of less alkalinity consumption (9), reduction in cost, less sludge production (10), less temperature dependence, (11, 12), and less pH dependence (13). It is known that PACl products contain cationic species, of which the most important is the Al_{13} ($[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) species (14–16). Al_{13} is composed of 1 tetrahedral center surrounded by 12 octahedral Al units (17–20). Besides the characteristics of high positive charge and strong binding ability to aggregates, it is temporarily refractory to hydrolysis before adsorption onto particle surfaces. These special properties contribute to the superior behaviors of PACl in coagulation. Many researchers believed that Al_{13} was the most active species in PACl composition responsible for coagulation or precipitation (15, 21–23). Thus, they claimed that a high content of Al_{13} was the main aim of the research and production industry of PACl. However, there also were some conflicting views. Previous study (11) indicated that PACl showed no significant improvement over alum on natural organic matter (NOM) removal. Lu et al. (24) found that Al_{13} polymer was not an important cation in the removal of humic substances, and Exall's (25) results indicated a negative correlation between the amount of Al_{13} and a coagulant's ability to remove organic matter. Whether the Al_{13} content positively correlates with coagulation efficiency or not is a controversial question to date.

The selection of an appropriate coagulant for a given raw water was found to depend most strongly on certain raw water quality parameters and the chemical characteristics of the coagulants (26, 27). On one hand, although eutrophication is menacing the safety of drinking water supply, the coagulation behavior of Al coagulants in eutrophic water has not been systemically studied. On the other hand, although the influence of Al speciation on coagulation behavior has received a lot of attention (11, 24, 28, 29), few investigators focused on the effect of Al_{13} species on the coagulation efficiency in raw water. Furthermore, the relationship between Al speciation and coagulation behavior needs clarification from the viewpoint of the transformation of Al hydrolysis products during the coagulation process.

The purpose of this study was to examine the coagulation behavior of three Al salts in eutrophic water. Particular emphasis was paid to understanding the effect of Al_{13} species on the coagulation behavior for removal of particulates and/or organic substances. The effect of water pH on Al speciation and thus on coagulation efficiency was clarified. The present study also provided insight into the mechanism of Al coagulants for the treatment of eutrophic water.

Materials and Methods

Raw Water. The water sample was collected from the Guanting reservoir when eutrophication occurred in July, 2004. Table 1 summarizes its major characteristics. The reservoir once served as the drinking water source for Beijing. Owing to the deterioration of water quality, it had been

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TABLE 1. Characteristics of the Water Sample from Guanting Reservoir

total nitrogen (mg/L)	4.10
total phosphorus (mg/L)	0.36
pH (20 °C)	8.60
alkalinity (mg CaCO ₃ /L)	226
turbidity (NTU)	14.50
DOC (mg/L)	16.62
UV absorbance 254 nm (cm ⁻¹)	0.1244
SUVA (m ⁻¹ /mg/L)	0.75

abandoned since 1997. Presently, the Beijing government has proposed to improve its water quality and reuse it before 2010.

Coagulants Characterization. Three coagulants with different Al speciation distributions were selected to make a comparison on their coagulation behaviors in eutrophic water. AlCl₃·6H₂O and a commercial PACl (PACl₁, Nanning Chemical Industry Co. Ltd., China) were used. Besides, another PACl (PACl₂) was prepared with the method of an electrolysis process (30, 31). Total Al concentrations (Al_T) were determined using ICP-AES (Perkin Elmer, Optima 2000, U.K.). Basicity values (B, OH/Al molar ratios) were determined by titrimetric methods (standard method of the chemical industry of China).

²⁷Al nuclear magnetic resonance (NMR) spectroscopy was used to characterize the Al species with ²⁷Al NMR spectra obtained on a Varian UNITY INOVA (500 MHz) spectrometer. Details of the operating approaches and parameters of the apparatus can be found in the literature (31). The ²⁷Al NMR spectroscopy of PACls is shown in Figure 1. The intensities of the ²⁷Al signals relative to the aluminate reference were used for calculating the Al concentrations. The intensities at the 0 and 4.3 ppm resonances represented the quantitative determinations of the monomeric and dimeric Al, respectively. The monomeric and dimeric Al species were named together as Al_m. The intensity at the 63 ppm resonance represented the quantitative determination of the Al₁₃ polymer in an Al solution. The 80 ppm resonance represented sodium aluminate. The concentration for the 63 ppm signal was multiplied by 13 to obtain the concentration of Al₁₃ (32). The difference between Al_T and [Al_m + Al₁₃] was an undetected part (Al_u, i.e., larger polymer species and/or solid-phase Al(OH)₃) by ²⁷Al NMR. The ferron colorimetric method was also used to analyze initial Al species distributions of the three coagulants (33). The absorbance increase was monitored for 120 min such that three fractions could be operationally defined which included Al_a, Al_b, and Al_c, corresponding to monomeric, medium polymer, and larger polymer species and/or solid-phase Al(OH)₃, respectively. The reaction time of Al_a-ferron was 1 min, and the Al species reacting with the ferron reagent before 120 min represented [Al_a + Al_b], then Al_c was obtained by Al_T minus Al_a and Al_b. Many investigations (21, 33) proved that the Al_b species could be regarded as the Al₁₃ species. Furthermore, the Al_a and Al_c species were approximately equal to the Al_m and Al_u species, respectively.

The properties of coagulants used are summarized in Table 2. The Al₁₃ contents of the three coagulants followed an increasing order of AlCl₃ < PACl₁ < PACl₂.

Analytical Method of Al Species Distributions in the Coagulation Process. Synthetic water containing 5 × 10⁻⁴ mol/L NaHCO₃ and NaNO₃ in deionized water was prepared for control experiments. The solution was analyzed subsequently by ferron assay after coagulants (i.e., AlCl₃ and PACls) were added under rapid stirring at 200 rpm for 2 min. The final solution contained 2 × 10⁻⁴ mol Al/L, and a predetermined amount of 0.2 or 0.05 mol/L NaOH or HCl solution was added first into the synthetic water to control pH.

Although natural water contains many dissolved chemical species that may significantly affect Al species distributions, deionized water was used first to provide baseline species distributions data during the coagulation process and highlight differences in Al species distributions among the three different coagulants.

Solid-state ²⁷Al NMR was performed on freeze-dried floc samples obtained from the precipitates of the three coagulants at a dose of 18 mg Al/L. The precipitates were separated from water samples with a refrigerating centrifuge (J2-HS, Beckman, U.S.A.) as soon as the jar tests finished. ²⁷Al MAS NMR spectra were recorded on a Varian INOVA300 spectrometer at 78.2 MHz with a 6 mm chemagnetics double-resonance solid-state probe. The main experimental parameters included a pulse width of 0.3 μs, recycle delay of 1 s, line broadening of 60 Hz, and spinning speed of 7 kHz. The reference chemical shift (0 ppm) was adjusted with 1 mol/L AlCl₃ solution.

Jar Tests. Jar tests were performed using a Phipps and Bird six-paddle stirrer. The procedures consisted of a 1 min rapid mix (200 rpm), 15 min slow mix (30 rpm), and a 30 min settling period. A small amount of sample was taken immediately to measure the zeta potential (Malvern, Zetasizer 2000, U.K.) after the 1 min rapid mix. After settling for 30 min, supernatants were collected to measure residual turbidity (RT) using a HACH 2100N turbidimeter and finished pH values with a pH meter (Orion 720A, U.S.A.). The filtrates were tested for DOC (Tekmar-Dohrman Co., Phoenix, AZ) and the UV₂₅₄ (Hitachi, U-3010 spectrophotometer, Japan). A predetermined amount of 0.2 or 0.05 mol/L NaOH or HCl solution was added first into water samples to examine the influence of pH on particles and DOC removal. All reagents used were of analytical grade.

Results

Removal of Particles and DOC. As shown in Figures 2 and 3, the turbidity removal increased with the increase of coagulant dosages before reaching the optimal dosages, and the zeta potentials remained negative but gradually approached zero. When the zeta potentials were reversed, the turbidity removal decreased due to the restabilization of particles. It was noted that turbidity removal efficiencies reached the optimal values when zeta potentials were close to the isoelectric point. The coagulation efficiency and zeta potential increased with the increase of Al₁₃ content in coagulants at low dosages (0.5 to ~2 mg/L). Whereafter, at medium dosages (4 to ~18 mg/L), the coagulation efficiency and zeta potential decreased with the increasing Al₁₃ content. For the three coagulants, the trend of DOC removal as a function of coagulant dose resembled that of turbidity removal. Moreover, the optimum dosages for DOC removal were approximately consistent with those of turbidity removal. The optimum dosage of AlCl₃ (18 mg/L) was only one-third of that of PACl₂ (54 mg/L). As far as the optimum dosage is concerned, the ability of the coagulants for removing particles and DOC followed the following order: AlCl₃ > PACl₁ > PACl₂.

Figure 4 shows that water pH was depressed by coagulant additions. The order of pH depression was AlCl₃ > PACl₁ > PACl₂. From the lowest dosage to the highest dosage, the pH value decreased from 8.5 to 3.8 with AlCl₃ addition. It is noted that all the finished pH values at the optimal dosages were near 7 (from 6.81 for AlCl₃ to 7.16 for PACl₂). This indicates that the neutral pH situation favors the coagulation process with Al coagulants in eutrophic water. A similar result was also attained by Vilg-Ritter et al. (34) who treated the raw water of the Seine River with alum and aluminum polychlorosulfate.

Effect of pH on Removing Particles and DOC. The effect of pH on removing particles and DOC was examined in the

FIGURE 1. ^{27}Al NMR spectra characterization of PACl samples.

TABLE 2. Characterization of Coagulants by ^{27}Al NMR and Ferron Assay

coagulant	Al_T (mol/L)	B	pH	Al _i (%)					
				Al_m	Al_{13}	Al_u	Al_a	Al_b	Al_c
AlCl_3	0.50	0	2.21	100	0	0	96.2	3.8	0
PACl_1	0.64	1.51	2.78	48.8	34.8	16.4	43	37.4	19.6
PACl_2	0.58	2.35	4.65	0	72.3	27.7	4.2	74.1	21.7

FIGURE 2. Zeta potentials of coagulated material as a function of coagulant dose.

range of pH 4 to ~9 at two dosages of 2 and 8 mg Al/L. As shown in Figure 5, the coagulation efficiency of the 8 mg Al/L dosage was larger than that of the 2 mg Al/L dosage, but the growing trends of their curves were similar. Figure 5 shows that the curves of coagulation efficiency as a function of pH (8 mg Al/L dosage) could be classified as two phases according to the relationship between the Al_{13} content of the coagulant and the turbidity removal efficiency. One was the optimal range of pH 5 to ~7, where the ability of removing particles was $\text{AlCl}_3 > \text{PACl}_1 > \text{PACl}_2$, and the coagulation efficiency negatively correlated with the Al_{13} content of the coagulants. For the DOC removal, the optimal pH range was 5 to ~6.5. The other phase was the acidic and alkaline range (i.e., 4 and 8 to ~9) where the ability of removing particles and DOC was $\text{AlCl}_3 < \text{PACl}_1 < \text{PACl}_2$, and the coagulation efficiency positively correlated with the Al_{13} content. Overall, Al coagulants performed better in acidic conditions than in alkaline conditions because of lower negative charge on the particles and NOM. With a higher content of Al_{13} species, PACl_2 was less dependent on pH to remove particles and DOC.

FIGURE 3. Removal of turbidity and DOC by coagulation as a function of coagulant dose.

Al Species Distributions in the Coagulation Process. The Al species distributions of the three coagulants during coagulation were also studied in the range of pH 4 to ~9. The results indicated that pH significantly affected the Al species distributions. Figure 6 shows that the Al species distributions of AlCl_3 during coagulation process were greatly changed compared with the initial species distributions. In the acidic region, Al_a decreased rapidly with the increase of pH and reached a minimum in the near neutral pH region. If the pH continued to increase to the basic region, the Al_a species increased sharply again. In contrast, a rapid increase of the Al_b species was observed in the acidic pH region. The maximum of Al_b occurred in the near-neutral pH conditions (pH 5 to ~7.5). In the basic region, a rapid decrease of Al_b occurred when the pH was further raised. The distribution

FIGURE 4. Finished pH of water samples as a function of coagulant dose.

FIGURE 5. Effect of pH on the Al coagulants to remove turbidity and DOC at two constant dosages of 2 and 8 mg Al/L.

of Al_c was similar to that of Al_b but at a reduced scale. Similar trends of the change in Al_a , Al_b , and Al_c species were also observable for $PACl_1$. However, the scale of change was considerably decreased. For $PACl_1$, the decrease of Al_a with the large yield of Al_b also occurred obviously in the neutral conditions. The Al species distributions of $PACl_2$ were quite stable and tended to maintain the original condition in the coagulation process. The content of Al_b was almost unchanged throughout the pH range investigated.

The solid-state ^{27}Al NMR spectra of the freeze-dried coagulation precipitates are shown in Figure 7. A peak observed at around 0 ppm, which corresponded to octahedrally coordinated Al (35), was detected in the precipitates of all coagulants. A characteristic peak for Al_{13} was also observed at around 63 ppm for two PACls (Figure 7). It is

FIGURE 6. Speciation characterization after dosing the Al coagulants at a dosage of 2×10^{-4} mol Al/L: (■) $AlCl_3$; (●) $PACl_1$; (▲) $PACl_2$.

assigned to the tetrahedral Al situated at the center of the Al_{13} molecule (36). Although a high content of in situ formed Al_{13} species was found in the treated water during coagulation with $AlCl_3$ (Figure 6b), it was not detected in the precipitate (Figure 7). Particularly, besides the peak assigned to the Al_{13} polymer, monomer was also detected in the precipitate of $PACl_2$ (Figure 7). This showed that the relative intensity ratio of tetrahedral Al positively correlated with the initial content of Al_{13} in coagulants.

Obviously, further transformation of Al species after dosing occurred and depended largely on the original composition of the coagulants and the water pH. The Al_a fraction in the primary coagulants was the most labile species. After dosing, the species would quickly transform into Al_b , and finally Al_c under appropriate conditions. The polymer species and colloidal species, once preformed, were quite stable. For instance, at pH 6 in $PACl_2$, the Al_b fraction still accounted for 68.7%, which was almost equal to the Al_{13} fraction in the initial $PACl_2$ (72.3%). However, at pH 6 in $AlCl_3$, at least 80%

FIGURE 7. Solid-state ^{27}Al NMR spectra of the precipitates from the Al coagulants.

of the Al_3 species in the initial AlCl_3 transformed into the Al_b species (Figure 6b), and 15% further into the Al_c (Figure 6c). After dosing in eutrophic water, the Al speciation of AlCl_3 greatly changed while the Al speciation of PACl_2 was relative constant, which made their coagulation efficiency different.

Discussion

As noted by Duan and Gregory (37), coagulation is generally explained in terms of two distinct mechanisms: charge neutralization and sweep flocculation. Generally, charge neutralization occurs at low coagulant concentrations when only soluble species are present, while sweep flocculation means the appearance of bulk hydroxide precipitation at high coagulant doses. At low dosages (0.5 to ~ 2 mg Al/L) in the present study, coagulation pH values were in the alkaline region (Figure 4), which is not favorable for precipitate formation. Moreover, the difference of coagulation pH values for the three coagulants was not so great that it affected the zeta potentials of the coagulated materials. Under this condition, the difference of the zeta potentials at low coagulant dosages could reflect the neutralization ability of the coagulants. It is worthwhile to note that the relative coagulation efficiency at low dosages corresponded well with the neutralization ability of the three coagulants. With the highest content of Al_{13} species, PACl_2 showed a stronger charge neutralization ability and thus more effective coagulation efficiency at low dosages. Whereafter, at the higher coagulant doses, extensive hydroxide precipitation occurred rapidly, yielding sweep flocculation. At optimal dosages, all coagulation pH values depressed by coagulant additions were near 7, which closely coincided with the pH of minimum solubility for Al salts (37). With AlCl_3 addition in eutrophic water, the coagulation pH could more easily be depressed into the optimal pH range. This pH range took full advantage of the Al species transformation, preparing an ideal environment for Al_{13} formation (Figure 6). However, for PACl_1 ,

eutrophic water with high alkalinity must require higher coagulant dosages to depress pH values favorable for coagulation.

Although both AlCl_3 and PACl_2 removed particles and DOC through the mechanism of sweep flocculation at optimal dosages, their precipitates were significantly different according to the results of the solid-state ^{27}Al NMR spectra. Al_{13} polymer was largely transformed from monomer in the coagulation process of AlCl_3 , but the in situ formed Al_{13} polymer was not stable and further hydrolyzed into larger polymer species soon (38), and finally into amorphous hydroxide. In contrast to AlCl_3 , the preformed Al_{13} polymer in PACl_2 was quite stable throughout the whole coagulation process. Figure 7 clearly displayed the existence of Al_{13} in the precipitates of PACl_1 and PACl_2 . This indicated that the polymeric structure was maintained in the PACl_2 precipitate, i.e., the PACl_2 precipitate might be generated from the clusters of Al_{13} polymer. Interestingly, besides Al_{13} polymer monomer was also detected by solid-state ^{27}Al NMR in the precipitate of PACl_2 . This part of the monomer might come from the depolymerization of Al_{13} polymer by NOM in raw water (39).

Comparison of the Al_{13} fraction (Figure 6) with effect of pH on coagulation (Figure 5) gave an interesting finding. Al_{13} species fractions in the coagulation process corresponded well to turbidity and DOC removals at the same pH values. The Al_{13} content positively correlated with coagulation efficiencies. In the optimal pH region, the turbidity and DOC removals were $\text{AlCl}_3 > \text{PACl}_1 > \text{PACl}_2$ (Figure 5), whose contents of Al_{13} were consistent with the order in this pH region (Figure 6). In the acidic and alkaline regions, the turbidity and DOC removals were $\text{PACl}_2 > \text{PACl}_1 > \text{AlCl}_3$, whose contents of Al_{13} also were the same order in the two ranges. The results indicated that, despite preformed Al_{13} polymer or the in situ formed one, Al_{13} species no doubt was the active species in Al salts responsible for coagulation, and coagulation efficiency positively correlated with the content

of Al_{13} species in the coagulation process rather than in the original coagulants. As noted by previous researchers (40, 41), NOM removal could be optimized by pH control in coagulation or filtration processes with alum. The present results indicated that pH control could improve the coagulation process through regulating Al species distributions. If the coagulation pH value is adjusted into the appropriate pH region (5 to ~7), where in situ Al_{13} polymer is largely formed, the coagulation efficiency of AlCl_3 in eutrophic water will be significantly improved. Figure 5 showed that AlCl_3 benefited most from pH control, especially for DOC removal at pH 5 to ~6. However, the improvement induced by pH control for PACls was slighter because the Al speciation of PACls was less dependent upon water pH.

In summary, AlCl_3 was more effective than PACl on removing turbidity and dissolved organic matter in eutrophic water. Compared with PACl, AlCl_3 could not only generate Al_{13} species but also function as a pH control agent in the coagulation process. The present study suggests that traditional coagulants are a better selection for eutrophic water treatment than inorganic polymer flocculants. Moreover, pH control in the coagulation process may be an effective method to optimize particle and DOC removals with AlCl_3 in eutrophic water. This work also clarifies how pH control can maximize turbidity and DOC removals in eutrophic water by appropriately regulating Al speciation.

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