Effect of aluminum speciation on arsenic removal during coagulation process

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ABSTRACT

The effect of Al speciation on arsenate [As(V)] removal during coagulation process was investigated from the viewpoint of Al hydrolysis species transformation. The As(V) removal efficiency of preformed Al₁₃ was compared with that of in situ formed Al₁₃ considering various Al dosages and pH values. The mechanisms of As(V) removal by Al salt coagulation were explored, and adsorption ability of the flocs formed from Al₁₃ species were evaluated. The results showed that As(V) removal efficiency was positively correlated with the content of Al₁₃ species during coagulation process. Weak acidic condition (pH 5–7) is the optimal pH range to remove As(V) because Al₁₃ species, especially for AlCl₃, is largely in situ formed from the transformation of monomeric Al species. Through regulating Al speciation, pH adjustment could improve As(V) removal and AlCl₃ could benefit most from this. In contrast, the improvement induced by pH control for polyaluminum (PACl) was slighter because Al speciation of PACl was less dependent upon water pH. This present study confirmed that adsorption on formed hydroxide flocs was the most active mechanism for As(V) removal by Al based coagulants. The flocs generated from in situ formed Al₁₃ presented better As(V) adsorption ability than the flocs generated from preformed Al₁₃. These findings are important to understand the coagulation mechanisms of arsenic removal by Al based coagulants.

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1. Introduction

The removal of arsenic (As) from natural water has been the subject of many studies [1] because drinking water is considered as the main source of exposure to arsenic [2]. Many studies have shown that long-term exposure to As has adverse health effects [2,3], which lead the World Health Organization in 1993 to decrease As standards for drinking water from 50 to 10 µg/L. Since July 1, 2007, China's newly revised drinking water standards for the maximum contaminant level (MCL) of As reduced from 50 to 10 µg/L. As removal from drinking water is a key measure of endemic arsenism prevention and cure. Drinking water sources in various parts of China and other developing countries contained much higher levels of As (20–2000 µg/L) than MCL requirements [1,4,5].

Enhanced coagulation, is intended to improve natural organic matter (NOM) removal, but is also in many cases the least-cost option for water utilities to comply with the new As MCL [6,7]. Early bench, pilot, and demonstration scale studies have shown that As(V) can be efficiently removed during coagulation with ferric chloride and alum even when present at low or high concentration in influent waters [8,9]. Aluminum (Al) based salts, e.g., polyaluminum chloride (PACl), aluminum chloride (AlCl₃), and alum (traditional Al coagulants), are most commonly used in water treatment plant. The hydrolysis reactions of Al species are very

complicated depending on water quality and coagulant type [10,11], which contribute to the formation of various hydrolyzed Al species. According to the analysis method of Al–feron complexation timed spectrophotometry or ²⁷Al nuclear magnetic resonance, the Al species are usually divided into monomeric species (e.g., Al(OH)₂⁺, Al₂(OH)₂⁴⁺, Al₃(OH)₄⁵⁺), medium polymer species (i.e. AlO₄Al₁₂(OH)₂₄(H₂O)₁₂⁷⁺, Al₁₃), colloidal or solid species [12–14]. Many researchers [15–17] believed that PACl was superior to traditional Al coagulants (i.e. AlCl₃ and alum) in removing particulate and NOM due to the preformed Al₁₃, which has inherent characteristics of high positive charge and strong binding ability [18–20]. Recently, many investigations [21–24] demonstrated the existence of in situ formed Al₁₃ species in AlCl₃ at pH 5–7, which made AlCl₃ exhibit better removal ability for turbidity and NOM than PACl at weak acidic pH conditions.

Al species during coagulation process play a key role in determining the behavior and efficiency of Al based coagulants. Thus, researchers paid more attention to the effect of Al speciation on coagulation performance. During coagulation, As(V) is generally removed through two main mechanisms including coprecipitation into growing hydroxide and adsorption on formed hydroxide floc [25,26]. Which one is the dominant mechanism depends on the water quality and coagulant dose [27,28]. Al hydrolysates in coagulation process varied greatly with the difference of Al species distribution in coagulant and coagulation pH condition, which may significantly influence the As(V) removal performance. Although Al based coagulants have been widely used to meet the standard

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of As MCL in drinking treatment process, the relationship between the different Al species and As(V) removal efficiency is still unclear to date. Moreover, few studies focused on the coagulation mechanisms of As removal with Al based coagulants and the role of Al_{13} species.

The purpose of this study was to examine the effect of Al species on As(V) removal during coagulation process. Particular emphasis was placed on understanding the effect of preformed and in situ formed Al_{13} species on the coagulation performance for As(V) removal in surface water. 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 As removal by Al based coagulants with different species distribution character.

2. Materials and methods

2.1. Water samples

Water samples were synthesized by spiking 280 $\mu\text{g/L}$ As(V) into tap water. Table 1 summarizes the characteristics of the water sample, which simulated natural surface water. Since As(V) is the prevalent form of arsenic found in surface water, all arsenic removal tests were performed with As(V). Sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) was used to provide a stock As(V) solution.

2.2. Jar test

Jar tests were performed using a six-paddle stirrer. The procedures consisted of a 2 min rapid mix (200 rpm), 15 min slow mix (40 rpm), and a 30 min settling period. A small amount of sample was taken immediately to measure zeta potential (Malvern, Zetasizer 2000, UK) after 1 min rapid mix. After settling for 30 min, supernatants were sampled and filtered by 0.45 μm pore size membrane filter. The filtrates were tested for As(V) concentration using spectroscopy equipment (AF-610, Beijing Rull Analytical Instrument Co., Ltd., China) on the basis of hybrid generation-atomic fluorescence spectrometry. Finished pH values were determined with a pH meter (Orion 720A, USA). A pre-determined amount of 0.2 or 0.05 mol/L NaOH or HCl solution was used to adjust pH values during rapid mix process. All reagents used are analytical grade chemicals.

2.3. Characterization of Al speciation in coagulants

^{27}Al nuclear magnetic resonance (NMR) spectroscopy was used to characterize the Al species with ^{27}Al NMR spectra obtained on a VARIANUNITY INOVA (500 MHz) spectrometer. Samples were placed in 5-mm tubes and the spectra were generated at 25 °C. Al_m (i.e. monomer + dimer), Al_{13} , and Al_u [i.e. larger polymer species and/or solid phase $Al(OH)_3$] can be quantitatively analyzed according to the intensities of ^{27}Al signals. Details of the quantitative analysis of the Al species can be found in the literature [12,29].

Ferron colorimetric method was also used to analyze initial Al species distributions of Al coagulants. The reagents preparation and procedures for the ferron colorimetric method are illustrated in the literature [10,13]. Absorbance increase was monitored for 120 min such that three fractions could be operationally defined: Al_a , Al_b , and Al_c , corresponding to monomeric species, medium polymer species and larger polymer species and/or solid phase $Al(OH)_3$, respectively.

Total Al concentrations (Al_T) were determined using ICP-AES (PerkinElmer, Optima 2000, UK). Basicity values (B, OH/Al molar ratios) were determined by titrimetric methods (Standard method of the chemical industry of China).

2.4. Analysis of Al species distribution during coagulation process

To study the nature of Al speciation distributions in the coagulation process, we designed experiments to clarify what happen after dosing coagulants. Synthetic water containing 5×10^{-4} mol/L $NaHCO_3$ and $NaNO_3$ in deionized water was prepared. Then, the solution was analyzed subsequently by ferron assay after coagulants was added under rapid stirring at 200 rpm for 2 min. The final solution was 2×10^{-4} mol Al/L and a pre-determined 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 can affect Al species distributions, deionized water was used for this research to provide baseline species distributions data during coagulation processes, and highlight differences in Al species distribution among the different coagulants examined.

2.5. Adsorption experiments

Adsorption experiments were initiated to evaluate As(V) removal by adsorption on Al hydroxide flocs. Al hydroxide flocs were preformed in the tap water by using the jar test method under the same coagulation experimental conditions as during coagulation/flocculation experiments. Just after the flocculation step, 280 $\mu\text{g/L}$ As(V) was added to the colloidal suspension and the slow mixing (30 rpm) was maintained for 1 h to allow arsenic adsorption. After the adsorption step, the settling step was applied. $AlCl_3$ and PACI were used to form flocs under the same concentrations as during coagulation/flocculation experiments to be able to compare arsenic removal by coagulation and adsorption. Adsorption isotherms experiments were carried out at the same conditions.

3. Results and discussion

3.1. Characterization of Al speciation during coagulation process

Three coagulants with different Al speciation distributions were selected to make a comparison on their coagulation behaviors in removing As(V). $AlCl_3$ (AC) was used as traditional Al coagulant. Two PACIs (PACI1 and PACI2) were prepared using the electrolysis process [29]. The Al species character of the three coagulants was analyzed by ^{27}Al NMR spectroscopy and ferron colorimetric method. As shown in Table 2, the Al_{13} contents of the three coagulants followed an increasing order of $AC < PACI1 < PACI2$, which was in good accordance with that of B value. Many investigations [13,30] proved that the Al_b species could be regarded as Al_{13} species. Furthermore, the Al_a and Al_c species were approximately equal to the Al_m and Al_u species, respectively. From the present study of Al species distribution similar results were obtained. From Table 2, the content of preformed Al_{13} polymer and Al_b in PACI2 reached 73.5% and 76.9%, respectively. Preformed Al_{13} polymer

Table 1
Characteristics of water sample.

pH (20 °C)	8.10 $\pm$ 0.05
Turbidity (NTU)	0.35 $\pm$ 0.02
DOC (mg/L)	0.62
Spiked As(V) ($\mu\text{g/L}$)	280
Alkalinity (mg $CaCO_3/L$)	150
Hardness (mg $CaCO_3/L$)	155
Aluminum (mg/L)	0.08
Iron (mg/L)	0.05
Total phosphorus (mg/L)	0.06
SO_4^{2-} (mg/L)	31.7
Cl^- (mg/L)	8.9

Table 2Characterization of coagulants by ^{27}Al NMR and ferron assay.

Coagulant	Al_T (mol/L)	B	pH	Al_m (%)	Al_a	Al_{13}	Al_b	Al_u	Al_c
AC	0.50	0	2.38	100	96.2	0	3.8	0	0
PAC1	0.58	1.15	3.50	44.8	48.7	36.3	37.9	18.9	15.4
PAC2	0.58	2.41	4.11	8.8	10.9	73.5	76.9	17.7	12.2

was the predominant species in PAC12, while there was almost no other species in AC except Al_m .

The Al speciation distributions of three coagulants during coagulation were studied in the range of pH 4–9. Fig. 1c showed Al speciation distributions of PAC12 were relatively stable and tended to maintain the original speciation distributions in coagulation process. The content of preformed Al_b was almost unchanged throughout the pH range investigated. In contrast, the results (Fig. 1a) indicated the Al speciation distributions of AC during coagulation process changed greatly compared with the initial speciation distributions. In the acidic region, Al_a decreased rapidly with increase of pH, and reached a minimum in the near neutral pH region. With increase of pH to the basic region, the Al_a species increased sharply again. At the same time, 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 5.5–7.5). In the basic region, a rapid decrease for Al_b occurred when pH was raised. The distribution of Al_c was similar to that of Al_b , but the scale of change was smaller. Similar trends of the change in Al_a , Al_b , and Al_c species was also observable for PAC11 (Fig. 1b), but the scale of change largely decreased.

Obviously, further transformation of Al species after dosing occurred and depended largely on the original composition of coagulants and water pH. 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 PAC12, the Al_b fraction still accounted for 74.4%, which was almost equal to the initial content of Al_{13} (73.5%). However, at pH 6 in AlCl_3 , at least 75% of Al_a species transformed into Al_b species, and 15% further into Al_c . During coagulation process, Al_b was largely in situ formed under using traditional Al coagulant while the preformed Al_b of PAC1 was relatively constant, which made their coagulation efficiency different at different pH conditions.

3.2. As removal by Al coagulants with different Al species distribution

As shown in Fig. 2, with the increase of coagulant dosage, As(V) concentration initially decreased, gradually stabilized, then changed to an upward trend. Due to charge neutralization function of coagulants, the surface potential of particles in model water developed from electronegative to electropositive. The As(V) removal efficiency and zeta potentials increased with the increase of preformed Al_{13} content in coagulants at low dosages (1 to ~4 mg/L) and high dosages (40 to ~60 mg/L). At medium dosages (8 to ~32 mg/L), the As(V) removal efficiency and zeta potentials decreased with the increase of preformed Al_{13} content in coagulants. All three coagulants had the ability to reduce As(V) concentration down less than 10 $\mu\text{g/L}$ at initial As(V) of 280 $\mu\text{g/L}$ in model water, but the required dosages to obtain residual As(V) of 10 $\mu\text{g/L}$ were different. The minimum dose to satisfy MCL was about 6 mg/L for AC, however, about 16 mg/L for PAC12. As far as the lowest dose to satisfy MCL, the ability of the coagulants for removing As followed the order: AC > PAC11 > PAC12.

Fig. 2 shows that water pH was depressed by coagulant additions. The dropped ability was inverse to the coagulant basicity. From the lowest dosage to highest dosage, the pH value decreased from 7.7 to 4.2 with AC addition. It was noted that the finished pH values with the medium doses of AC lie in the pH range of 7 to 5,

Fig. 1. The speciation characterization after dosing Al coagulants at dosage of 2×10^{-4} mol Al/L.

Fig. 2. The removal of As(V) and zeta potentials of coagulated material as a function of coagulant dose.

which was the optimal pH environment for in situ Al_{13} formation (Fig. 2). The results showed that the ability of removing As(V) at the medium dosages was $AC > PACI1 > PACI2$, and the coagulation efficiency negatively correlated with the preformed Al_{13} content but positively correlated with the in situ formed Al_{13} content. At the medium dosages, AC was more effective than PACI in removing As(V) because AC could function as pH control agent and then generate Al_{13} species in the coagulation process. At low and high dosages of AC, the finished pH values were outside of the weak acidic environment (up pH 7 and below pH 5), where Al_{13} species could not in situ formed and Al_m was predominant species during coagulation process for AC. In contrast, preformed Al_{13} species was independent of pH, thus the dominant species of PACI2 during coagulation process was still Al_{13} species under all dosages. Therefore, PACI performed better for removing As(V) than AC at low and high dosages. This phenomenon is consistent with the findings reported by Fan [31]: the As removal efficiencies of PACI were higher than those of its traditional coagulant counterparts at low dosages (0.81–1.89 mg Al/L).

It showed that, despite preformed Al_{13} and in situ formed one, Al_{13} species was the active species in Al coagulants responsible for As(V) removal, which was similar with the results of Al species on removing NOM and particles during coagulation process. Many researchers [19,20,32] claimed that Al_{13} species had higher charge neutralization ability than Al_m and Al_c species, which was also proved by our present research. Fig. 3 showed that zeta potential as a function of coagulant dosages resembled the changing trends of As(V) removal. The relative As(V) removal efficiency corresponded well with the charge neutralization ability of the three coagulants. Al_{13} species, both preformed polymer or in situ formed one, exhibited a stronger charge neutralization ability and thus was more effective on As(V) removal.

3.3. Effect of pH on As(V) removal by coagulation

The effect of pH on As(V) removal by coagulation and zeta potential of coagulated material was also examined in the range of

Fig. 3. Finished pH of water samples as a function of coagulant dose.

pH 4 to ~9 at two dosages of 2 and 20 mg/L. Fig. 4 showed that the As(V) removal efficiency and zeta potential of the 20 mg/L dosage was higher than that of the 2 mg/L dosage, but the growing trends of their curves were similar. The As(V) removal efficiency was positively correlated with the zeta potential. It was noted that the As(V) removal efficiency of AC could be significantly improved by pH adjustment. The As(V) removal efficiency of AC with 2 mg/L was about 73% at pH 7.6 (Figs. 2 and 3), while the As(V) removal efficiency with same dosage could reach 83% under pH 6 (Fig. 4). The optimal pH region for removing As(V) was pH 5 to ~7. The obtained optimum pH range for As(V) removal with Al based coagulants from this study is in good agreement with the values given in literature [5,33,34].

Comparison of Al_{13} fraction (Fig. 4a) with effect of pH on As(V) removal (Fig. 4c) displayed that Al_{13} species content in the coagulation process corresponded well to As(V) removal efficiency at the same pH values. The pH region of 5 to ~7 is not only the optimal pH range for As(V) removal but also the optimal pH environment for in situ Al_{13} formation. The effect of pH on the As removal efficiency is related to the Al species distribution character of Al based coagulants. The higher ability of removing As(V) for AC might come from the higher content of Al_{13} species than that of PACI2 at weak acidic pH range. However, at the acidic and alkaline range (i.e. pH 4 and pH 8 to ~9), the ability of removing As(V) was $PACI2 > AC$, where the As(V) removal efficiency was positively correlated with the preformed Al_{13} species. Preformed Al_{13} species was more stable during coagulation process, and could maintain high fraction even in the acidic and alkaline range. With a higher content of preformed Al_{13} species, PACI2 was less dependent on pH to remove As(V). pH adjustment could improve As(V) removal efficiency through regulating Al species distribution. Especially for traditional Al coagulants, weak acidic condition is the optimal pH range to remove As(V) because in situ Al_{13} is largely formed from the

Fig. 4. Effect of pH on Al_{13} species distribution, zeta potential of coagulated material, and As(V) removal efficiency by Al coagulants.

transformation of Al_m . However, the improvement induced by pH control for PACl was slighter because Al speciation of PACl was more independent upon water pH.

3.4. Mechanisms of As(V) removal by Al based coagulants

As mentioned above, coprecipitation and adsorption are both active As(V) removal mechanisms. Special experiments were performed to discriminate which one is predominant and the differences between AC and PACl during As(V) coagulation removal. Adsorption and coagulation data for model water at pH 6 are shown together in Fig. 5. Similar trends were observed in adsorption and coagulation experiments with AC and PACl2. Although As(V) removal by coagulation was more efficient than As(V) adsorption removal, the differences in As(V) removal efficiency between adsorption and coagulation were low. Moreover, especially for AC, the differences were more pronounced at low dosages than that at high dosages. The results from these experiments indicate that adsorption onto precipitated Al hydroxides is the main mechanism for As(V) removal by Al coagulants but precipitation/coprecipitation also play specific roles at low dosages. Pallier et al. [28] gained similar results when they studied the behavior of $FeCl_3$ to remove As(V).

During adsorption on preformed flocs, As(V) removal depended on the coagulant dose and consequently on the number of active sites on the hydroxide surface [27,28]. The more numerous active sites on the hydroxide Al surface, the higher As(V) removal efficiency. As shown in Fig. 5, the preformed flocs from AC exhibited better As(V) adsorption efficiency than the preformed flocs from PACl2. The different ability of preformed flocs of AC and PACl2 in adsorbing As(V) might be a result of the different flocs structure that was caused by the different Al species distribution. Xu et al. [24] pointed out the flocs from in situ formed Al_{13} were larger than that from preformed Al_{13} . Larger flocs may bring an increased collision frequency that lead to adhesion between Al hydrolysates and As(V). Beside, owing to the higher positive potential at pH 6 (Fig. 4b), the flocs of AC might give rise to higher adsorption ability than the flocs of PACl2. This were the reason why a higher As(V) removal efficiency with AC flocs was obtained at pH 6 in adsorption experiment.

The adsorption capacity of the preformed flocs from AC and PACl2 was further investigated. As shown in Fig. 6, the adsorption capacity of AC flocs was significantly higher than PACl2 flocs. Many researches [20,23] proved the existence of aggregated Al_{13} in flocs of PACl and the flocs of $AlCl_3$ at pH 6, however, which were differ-

Fig. 5. Comparison of As(V) removal by coagulation and adsorption on preformed flocs at pH 6.

Fig. 6. Adsorption isotherms of As(V) onto preformed flocs of AC and PACl2 at pH 6 (The flocs formed at the dosage of 20 mg Al/L).

ent in crystal type. Previous results [21,24] showed preformed Al_{13} was quite stable throughout the whole coagulation process even in flocs, but the in situ formed Al_{13} was not stable and further hydrolyzed into larger polymers, and finally into amorphous hydroxide. Generally, the surface area of amorphous hydroxide is larger than that of crystal hydroxide. Therefore, the flocs of AC could present more adsorption sites than the flocs of PACl2.

4. Conclusions

The results of this paper indicated that, despite preformed Al_{13} and in situ formed one, Al_{13} species was the active species in Al based coagulants responsible for As(V) removal, and As(V) removal efficiency was positively correlated with the content of Al_{13} species during coagulation process. pH adjustment could improve As(V) removal efficiency through regulating Al species distribution. Especially for traditional Al coagulants, weak acidic condition is the optimal pH range to remove As(V) because in situ Al_{13} is largely formed from the transformation of Al_m . In contrast, the improvement induced by pH control for PACl was slighter because Al speciation of PACl was more independent upon water pH. Present study confirmed that adsorption on formed hydroxide flocs was the most active mechanism of As(V) removal by Al based coagulants. With larger surface area, the flocs formed from in situ formed Al_{13} presented better ability of As(V) adsorption than the flocs formed from preformed Al_{13} .

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