Coagulation of humic acid: The performance of preformed and non-preformed Al species

Baoyou Shi^{*}, Qunshan Wei, Dongsheng Wang, Zhe Zhu, Hongxiao Tang

*State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China*

Received 22 June 2006; received in revised form 20 September 2006; accepted 22 September 2006
Available online 28 September 2006

Abstract

Inorganic polymeric Al coagulants have been widely used in water treatment due to their advantages of applicability within broad pH and temperature ranges, high capacity of charge neutralization as well as less alkalinity consumption. However, the removal of dissolved organic matter (DOM) by such kind of coagulants has not been well understood because of the complexity of natural organic matter and the diversity of such polymeric Al coagulants. In this paper, coagulants with different Al speciation characteristics were prepared to conduct coagulation of humic acid (HA). The humic acid used was peat origin and was characterized physicochemically. The results showed that coagulants with preformed Al species were less effective than conventional Al salt in removing humic acid with large molecular and hydrophobic properties. The flocs formed by preformed Al species were smaller than those formed by conventional Al salt. Decreasing pH could improve the coagulation performance of all coagulants. Coagulation of humic acid might not follow the same charge neutralization rules associated with coagulation of mineral colloids. In the presence of humic acid, Al_{13} could be decomposed during coagulation process.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Coagulation; Humic acid; Polyaluminum chloride; Al_{13}

1. Introduction

Coagulation is one of the critical operation units for removing colloidal particles and dissolved organic matter (DOM) in surface water treatment. However, the mechanisms involved in colloidal particle and DOM removal could be significantly different. Charge neutralization and sweep flocculation (the incorporation of impurities in amorphous hydroxide precipitate) are considered to be the two most distinct mechanisms in removing mineral colloidal particles [1]. But much less has been understood on the mechanisms of DOM removal by coagulation. It was proposed that formation of insoluble complexes between DOM and coagulant species as well as the adsorption of DOM onto freshly formed hydroxide precipitate could be the determining mechanisms [2]. Due to the differences between coagulation of mineral colloids and DOM, the present designs and operating procedures that are effective for removing turbidity may not be the most effective for removing DOM [3].

The commonly used conventional coagulants in water treatment include alum, sodium aluminate, ferric chloride, ferric sulfate, etc. Preformed polymeric metal coagulants have been shown to improve some of the coagulation performance compared to conventional coagulants [4–6]. Polymeric forms of metal coagulants in water treatment have become increasingly used due to their wider availability and reduction in cost [7]. Polyaluminum chloride (PACl) is one of the most important pre-hydrolyzed coagulants. PACl is less sensitive to changes in pH and temperature [8–10]. In addition, the high positive charge of some polycations, such as Al_{13} [$AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$], is highly effective in neutralizing the negative charges of colloidal particles [11].

However, contradictory results have been reported concerning the effectiveness of PACl in DOM removal. Some researchers found that PACl was able to directly precipitate fulvic acids (FA) over a broad pH range and could be a better coagulant than alum at more acidic and basic pH values [3,12]. While some investigators observed that PACl did not reduce DOM as effectively as alum [13,14].

The discrepancies related to the coagulation of DOM by PACl are mainly due to the complexity of DOM and the vari-

^{*} Corresponding author. Tel.: +86 10 62849138; fax: +86 10 62923541.
E-mail address: byshi@rcees.ac.cn (B. Shi).

ety of PACl products. DOM consists of a large number of organic compounds including natural and synthetic matters. Humic substances are ubiquitous in surface water and are the major organic constituent of unpolluted water. The molecular weight and hydrophobic/hydrophilic properties of humic substances are important factors associated with their treatment efficiencies [15]. Typically, humic substances are operationally divided into the more soluble fulvic acids and the less soluble humic acids (HA). On the other hand, most of PACl coagulants used in past studies were commercial products, and little is known about their exact chemical composition. The content of Al_{13} in commercial products is usually very low. In addition, PACl products from different manufacturers may contain different additives, such as sulfate and organic polymers.

The objective of this work was to get more understanding on the coagulation mechanisms of PACl in removal of humic substances by using well-characterized materials. Since more in-depth studies had been reported on the coagulation of fulvic acids, the emphasis of this paper was placed on the effect of Al species on the coagulation of humic acid. AlCl_3 , laboratory prepared PACl and purified Al_{13} were selected as coagulants with different speciation characteristics; a kind of peat humic acid was chosen to conduct the coagulation experiments and the humic acid was characterized by ultrafiltration and resin fractionation. To avoid the interference of some cations and anions in natural water (e.g. calcium, magnesium, sulfate, phosphate), synthetic test water was prepared to conduct the investigation.

2. Materials and methods

2.1. Coagulants preparation and characterization

All the reagents used to prepare each coagulant were of analytical grade and deionized water was used to make all solutions. The procedures of preparing each coagulant can be described as follows: (1) conventional Al salt (AlCl_3): directly dissolving $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ into deionized water; (2) PACl: adding pre-determined amount of Na_2CO_3 slowly into AlCl_3 solution under intense agitation. The temperature was kept at 70°C by using recycling water bath. The target basicity (OH/Al molar ratio) of the PACl was 2.20; (3) Al_{13} : it was separated and purified from PACl using sulfate precipitation and nitrate metathesis reactions. The detailed procedures can be found in [16]. The total Al concentrations for all the coagulants were all adjusted to 0.1 mol l^{-1} . All the coagulants were stored in refrigerator after preparation for later use. No obvious turbidity appeared in the coagulant solutions during the study.

The speciation distributions of the three coagulants were characterized using both liquid-state ^{27}Al nuclear magnetic resonance (NMR) spectroscopy (Avance 500, Bruker, USA) and ferron colorimetric assay [8]. The ^{27}Al NMR patterns of the three coagulants are demonstrated in Fig. 1. The signal at 0 ppm corresponds to monomeric species and the signal at 62.5 ppm corresponds to Al_{13} species (only the central Al atom in Al_{13} structure can produce resonance signal), the signal at 80 ppm is ascribed to the inner standard of NaAl(OD)_4 . Other Al species, such as colloidal species cannot be observed by ^{27}Al NMR. No

Fig. 1. ^{27}Al NMR patterns of three coagulants ((a) AlCl_3 ; (b) PACl; (c) Al_{13}).

Al_{13} was detected from AlCl_3 solution, and the predominant species in AlCl_3 was monomers. Both Al_{13} and monomeric Al species existed in PACl while the content of monomers was relatively low. As to the purified Al_{13} , the signal of monomeric species was almost negligible.

Ferron assay can differentiate Al species into three categories: Al_a , monomeric (possibly some oligomeric) species; Al_b , polymeric species which could be rationally regarded as Al_{13} in this study; Al_c , colloidal species. The speciation characteristics of three coagulants are listed in Table 1. As evidenced by ^{27}Al

Table 1
Species distribution of three different coagulants

	pH	Al_a (%)	Al_b (%)	Al_c (%)
AlCl_3	3.28	91.7	8.3	0.0
PACl	4.02	6.2	29.5	64.3
Al_{13}	4.24	2.0	95.8	2.2

NMR patterns, the Al monomers (Al_a) of $AlCl_3$ accounted for 91.7%; while, the Al_b component (Al_{13}) of purified Al_{13} was as high as 95.8%; PACl was consisted of mixed species with Al_c being the dominant species.

2.2. Humic acid characterization

In order to examine the coagulation behaviors of higher molecular and less soluble humic acid, commercially available peat humic acid (Tianjin, China) was purchased and characterized.

Preparation of stock solution: 1.40 g humic acid was dissolved in 1000 ml of 0.01 mol l^{-1} NaOH with 6 h of continuous stirring, then filtered through $0.45 \mu\text{m}$ membrane filter and stored in refrigerator for later use.

Apparent molecular weight (AMW) distribution: AMW was determined using ultrafiltration membranes with a Amicon® cell device (Model 8200, Millipore, USA). For ultrafiltration operation, the stock humic acid solution was diluted 200 times with deionized water and the pH was adjusted to 7.50 using 0.05 mol l^{-1} HCl. Pure nitrogen gas ($0.25\text{--}0.35 \text{ MPa}$) was used as the driving force. The humic acid was divided into four classes: >30 , $10\text{--}30$, $3\text{--}10$ and $<3 \text{ kDa}$. The dissolved organic carbon (DOC) and UV_{254} absorbance of each class were measured using a total organic carbon analyzer (Phoenix 8000, USA) and UV–vis 8500 spectrophotometer (Shanghai, China), respectively. The AMW distribution of the humic acid in terms of DOC and UV_{254} values are shown in Table 2. The humic acid was mainly consisted of high AMW constituents with fraction greater than 30 kDa accounted for 70.1% of DOC and 86.3% of UV_{254} absorbance. The fractions with AMW of $10\text{--}30$, $3\text{--}10$ and $<3 \text{ kDa}$ were accounted for 17.6, 3.4 and 8.9% of DOC, respectively. It can be noticed that the percentage of UV_{254} absorbance was not equal to that of DOC for each fraction. It can be inferred that the specific ultraviolet absorbance value (SUVA) of higher AMW fraction ($>30 \text{ kDa}$) was greater than those of lower AMW fractions. For the fraction of $<3 \text{ kDa}$, no UV_{254} absorbance was detected.

Resin fractionation: the chemical property of the humic acid was further characterized by resin fractionation to reveal the distribution of hydrophobic or hydrophilic constituents. The fractionation operation used in this study was modified based on the method described by Chiang et al. [17]. The humic acid solution sample was the same as used for ultrafiltration.

A brief description of the procedures is as follows: the sample was passed slowly through a column ($3.5 \text{ cm} \times 50 \text{ cm}$) filled with 80 ml of XAD-8 resin at about 200 ml h^{-1} . The hydrophobic base and hydrophobic neutral parts (denoted as HoB and HoN, respectively), were adsorbed on the XAD-8 resin. The effluent was collected and adjusted to pH 2.0, and then flowed through another XAD-8 column, the hydrophobic acid (HoA) was adsorbed at this stage. Next, the effluent was fed into another column filled with XAD-4 resin, which adsorbed the weakly hydrophobic organics (WhoA), the residual organics in the final effluent was the hydrophilic fraction (HiO). Finally, the first XAD-8 column was back washed by 0.1 mol l^{-1} H_3PO_4 , and then HoB fraction could be released. During the whole operation process, the feed and effluent water volumes from each column were recorded. The DOC and UV_{254} absorbance of all samples were measured so that the content of each fraction could be calculated.

The resin fractionation results are also presented in Table 2. It can be seen that the major fraction was HoA, accounted for 50.2% of the total DOC and 57.1% of the total UV_{254} absorbance. WhoA and HiO fractions was 21.4 and 26.5% of total DOC, and 25.4 and 9.9% of total UV_{254} absorbance, respectively. These two fractions could be generally regarded as fulvic acid. Very little amount of HoB and no HoN were detected. Combined with the ultrafiltration fraction results, it could be deduced that the organic matter with AMW $>30 \text{ kDa}$ were mainly composed of hydrophobic acid and weakly hydrophobic acid fractions. While the fractions with AMW $<30 \text{ kDa}$ were primarily hydrophilic organics.

2.3. Jar tests

Synthetic test water was prepared by adding humic acid stock solution into deionized water (20 ml l^{-1}), meanwhile, $2.0 \times 10^{-3} \text{ mol l}^{-1}$ $NaHCO_3$ was added to provide a certain buffer capacity and ionic strength. The pH of test water was adjusted by 0.5 mol l^{-1} HCl and 0.1 mol l^{-1} NaOH solutions. Jar tests were performed on a program-controlled JTY-4 jar tester (Beijing, China). Test water of 500 ml was transferred into a 800 ml beaker; under rapid stirring of 200 rpm, pre-determined amount of coagulant was dosed; after 2 min, the stirring speed was changed to 40 rpm with a duration of 15 min; then after 20 min of quiescent settling, sample was collected from 2 cm below the surface for residual turbidity (RT) (2100N Tur-

Table 2
Ultrafiltration and resin fractionation results of the test humic acid

$>30 \text{ kDa}$ (%)		$10\text{--}30 \text{ kDa}$ (%)		$3\text{--}10 \text{ kDa}$ (%)		$<3 \text{ kDa}$ (%)	
DOC	UV_{254}	DOC	UV_{254}	DOC	UV_{254}	DOC	UV_{254}
70.1	86.3	17.6	8.5	3.4	5.2	8.9	0.0
HoB (%)		HoA (%)		WhoA (%)		HiO (%)	
DOC	UV_{254}	DOC	UV_{254}	DOC	UV_{254}	DOC	UV_{254}
1.9	7.6	50.2	57.1	21.4	25.4	26.5	9.9

Note: original humic acid solution DOC 2.93 mg l^{-1} , UV_{254} 0.3306 cm^{-1} .

bidimeter, Hach, USA) and pH (MP220 pH meter, Switzerland) measurements; at the same time, collected sample was filtered through 0.45 μm membrane to measure the UV_{254} absorbance. The removal of UV_{254} absorbance was used to evaluate the coagulation efficiency in this study.

To understand the Al species transformation after coagulation, flocs formed under some conditions were collected and freeze-dried for solid-state ^{27}Al MAS NMR (Varian Unity Inova 300, USA) examination. The instrument settings were: resonance frequency 78.2 MHz; pulse width 0.3 μs ; recycling delay time 1 s; magic angle spinning speed 5 kHz.

2.4. Flocculation kinetics

The flocculation kinetics after coagulant addition was monitored by using a photometric dispersion analyzer (PDA 2000, Rank Brothers Co., UK). The principle of this monitoring technique was described in literature [18,19]. The PDA apparatus can give a reading called flocculation index (FI) when suspension particles passing through a flow-through cell. FI is sensitive to particle size and can be effectively utilized to describe the aggregation progress of fine particles, such as the initial aggregation, breakage, and re-aggregation behaviors of particles. The flow rate was controlled by a peristaltic pump with rotation speed of 30 rpm. The coagulation procedures were the same as jar tests.

3. Results

3.1. Coagulation behaviors under neutral pH

The removal of humic acid by different coagulants was first examined under pH of 7.50. As shown in Fig. 2, the turbidity after coagulation increased first and then decreased with the increase of coagulant dosage, but the UV_{254} removal increased continuously and could reach 100% at high dosages for all coagulants. It can be seen that PACl and Al_{13} exhibited very similar coagulation behaviors in terms of residual turbidity, UV_{254} removal and post-coagulation pH values. However, the UV_{254} removal of AlCl_3 was much higher than those of PACl and Al_{13} before reaching complete removal. On the other hand, the maximal residual turbidity associated with AlCl_3 appeared at lower dosages than those with PACl and Al_{13} .

It was found that no appreciable floc was formed if the dosage was less than that corresponding to maximal turbidity value, which indicated that only small particles were formed within low dosage range. These small particles were not settleable but could be intercepted by filter membrane. When the dosage passed this point, large and settleable flocs were formed. The required dosage for floc formation was: $\text{AlCl}_3 < \text{PACl} \approx \text{Al}_{13}$.

The flocs formed by AlCl_3 were much larger than those formed by PACl and Al_{13} (Fig. 3). At dosage of $18 \times 10^{-5} \text{ mol l}^{-1}$, the systems associated with PACl and Al_{13} did not form any detectable flocs, but large flocs were developed rapidly in the system with AlCl_3 . At a higher dosage of $22 \times 10^{-5} \text{ mol l}^{-1}$, flocs appeared in the systems of PACl and Al_{13} , but they were much smaller than those formed by AlCl_3 .

Fig. 2. Residual turbidity (RT), UV_{254} removal, and pH as function of coagulant dosage.

Fig. 3. Flocculation kinetics of three coagulants at two different dosages.

3.2. Effect of pH on coagulation performance

3.2.1. Coagulation with pH changes at constant dosage

In order to investigate the effect of pH on humic acid coagulation performance, the test water pH was adjusted to different levels and the dosage was fixed at $10 \times 10^{-5} \text{ mol l}^{-1}$. The changes of residual turbidity and UV₂₅₄ removal with pH are shown in Fig. 4. For all three coagulants, the UV₂₅₄ removal increased with the decrease of pH and nearly complete removal was achieved when pH was less than 4.50. The removals by PACl and Al₁₃ were almost the same and significantly lower than that by AlCl₃ when the pH was greater than 4.50. However, the variations of residual turbidity with pH were rather complicated. When the pH was reduced from 8.50 to 4.50, the residual turbidities corresponding to three coagulants all experienced increase and subsequent decrease. During the turbidity increasing phase, no settable floc was developed. With further pH decreasing, large flocs were well formed, and residual turbidities were lowered accordingly. However, it was observed that the turbidity pertinent to AlCl₃ increased again when the pH was reduced further from 4.50. At pH of 2.50, no appreciable floc was formed. Since the filtered sample still exhibited nearly complete UV₂₅₄ removal, it could be inferred that small particles existed in the system, but they might be re-stabilized due to electrical charge reversion. No obvious re-stabilization phenomenon was observed in the cases of PACl and Al₁₃.

3.2.2. Coagulation with dosage changes at pH of 5.50 and 3.50

The UV₂₅₄ removal and residual turbidity variation as function of dosage were obtained at pH of 5.50 and 3.50, which represented the optimal and low pH values, respectively (Fig. 5). At pH 5.50, the UV₂₅₄ removal by AlCl₃ was much higher than those by PACl and Al₁₃. However, such difference was greatly reduced at pH of 3.50. In terms of the residual tur-

Fig. 4. Effect of pH on residual turbidity and UV₂₅₄ removal at constant dosage of $10 \times 10^{-5} \text{ mol l}^{-1}$.

bidity after coagulation, it is clear that severe re-stabilization phenomenon occurred with the increase of AlCl₃ dosage. While at high dosages, only slight turbidity increase was found for PACl and no re-stabilization was observed for Al₁₃.

Fig. 5. Coagulation as function of dosage at pH 5.50 and 3.50.

The pH after coagulation decreased continuously with the increase of AlCl_3 dosage when the original pH was 5.50, but there was no significant pH variation before and after coagulation when the original pH was 3.50.

It should be pointed out that the strong re-stabilization tendency associated with AlCl_3 is contradictory to the common knowledge on the charge neutralization abilities of different Al species when coagulation is used to remove mineral colloids, which will be discussed later.

3.2.3. Dosage required for complete UV_{254} removal

As mentioned above, the UV_{254} removal with dosage increased rapidly once observable flocs were developed, which was reflected by the steep rise of corresponding curves. If the point where the extrapolated steep portion of the UV_{254} removal curve intersects the 100% removal line was chosen as the required coagulant dosage for complete UV_{254} removal (RCDC), the coagulation capacity of different coagulant could be compared quantitatively. Fig. 6 illustrates the RCDC values of three coagulants at different pH levels. Obviously, PACl and Al_{13} exhibited the same coagulation capacity. And the RCDC values decreased with the decrease of pH: from pH 7.50 to 5.50, the RCDC values of AlCl_3 and PACl/ Al_{13} decreased 58 and 48%, respectively; from pH 5.50 to 3.50, the corresponding decreases were 44 and 72%, accordingly.

At pH of 7.50 and 5.50, AlCl_3 exhibited much higher coagulation capability than PACl and Al_{13} : the RCDC values of AlCl_3 were only 66 and 53% of those with PACl/ Al_{13} at pH 7.50 and 5.50, respectively. It implies that the coagulant constituted of monomeric Al species could have higher coagulation capacity than those constituted of preformed Al species in terms of large molecular humic acid removal.

Fig. 6. Required coagulant dosage for complete UV_{254} removal at different pH levels.

3.2.4. Coagulation kinetics at pH of 5.50 and 3.50

The coagulation kinetics at pH 5.50 and 3.50 with different dosages are shown in Fig. 7. At pH 5.50 and dosage $6 \times 10^{-5} \text{ mol l}^{-1}$, large flocs were formed in the case of AlCl_3 while no appreciable flocs were observed with PACl and Al_{13} . If the dosage increased to $12 \times 10^{-5} \text{ mol l}^{-1}$, small flocs were developed by PACl and Al_{13} . However, in the case of AlCl_3 , the size of flocs decreased compared to that at lower dosage ($6 \times 10^{-5} \text{ mol l}^{-1}$), which indicated that re-stabilization might have occurred. In addition, the floc size formed by AlCl_3 decreased slowly with the elapse of time.

When the test water pH was reduced to 3.50, the flocculation kinetics with AlCl_3 exhibited much different features compared to that at pH 5.50: the sizes of flocs were much smaller and there

Fig. 7. Coagulation kinetics at pH of 5.50 and 3.50 with different dosages.

existed a time lag (about 3 min) between dosing and formation of appreciable flocs. However, the pH reduction did not influence the flocculation kinetics of PACl and Al_{13} significantly.

4. Discussion

4.1. Interactions between humic acid and different Al species

As a typical kind of IPFs, PACl has the advantage of being more effective at lower temperatures and a broad pH range due to the presence of relatively stable preformed Al species (particularly Al_{13}). However, the coagulation/flocculation mechanisms of PACl have not been clearly understood. In the aspect of removing mineral colloids from water, the performance of PACl was mostly explained by the high positive charge associated with preformed Al species and the consequent high ability in neutralizing the negative charge of colloids [1].

It has been well known that humic substances can be effectively removed from water by hydrolyzing coagulants, such as aluminum and ferric salts. But it is still uncertain if the coagulants with preformed Al (or ferric) species are superior to conventional coagulants in removing humic substances. As shown in Table 1, the three coagulants used in this study have distinct speciation characteristics: AlCl_3 dominated by monomeric Al species, Al_{13} with high purity and PACl with mixed species of Al_{13} and colloidal Al species. After dosing into water, monomeric Al species will subject to a series of hydrolysis to form multinuclear species with different polymerization degree and finally form amorphous hydroxide solids. However, the Al_{13} species can be relatively stable after dosing and no hydroxide can be formed during the coagulation time scale [8].

Based on the above results, AlCl_3 demonstrated the most effective removal of humic acid, meanwhile the coagulation behaviors of PACl and Al_{13} were much similar. It can be concluded that the roles of preformed and non-preformed Al species in humic acid removal were distinctly different from those in mineral colloid removal. The high positive charge of preformed Al species, particularly Al_{13} , did not exhibit high coagulation efficiency in humic acid removal. Moreover, with the increase of dosage, strong re-stabilization occurred in the system of AlCl_3 dosed, while Al_{13} did not lead to re-stabilization (Fig. 5).

As characterized by ultrafiltration and resin fractionation, the humic acid used in this study was mainly consisted of large molecular and hydrophobic fractions, therefore it should be more inclined to be removed by forming insoluble complexes with Al species.

Under a given pH, there should be a certain charge density for the humic acid due to the dissociation of carboxylic and phenolic groups. But the interactions between the negatively charged functional groups and cationic Al species might not follow stoichiometric relations. Due to their relatively larger size and higher positive charge, the association of preformed Al species with humic acid could be stronger and such interactions might be able to induce reconfiguration of long humic acid molecules around the preformed Al species. Consequently the positive charges of preformed Al species can be greatly shielded and such interac-

tions are more approximate to stoichiometric relations. On the other hand, the reconfiguration of humic acid might be a reason of the smaller flocs formed by preformed Al species.

However, the interactions of non-preformed Al species with humic acid could be much weaker and might not be able to induce reconfiguration of humic acid molecules. Then partial neutralization of the negatively charged sites can lead to destabilization of humic acid and no stoichiometric relation exists for this kind of interaction. Hence, it is possible that the removal of humic acid by non-preformed Al species could be achieved at lower Al dosages and re-stabilization could occur at high dosages.

The reactions of humic acid with preformed or non-preformed Al species involve different pathways. It was reported that pre-hydrolyzed Al species could bind selectively to carboxylic groups at pH 6 and to phenolic moieties at pH 8 [20]. At higher coagulant concentrations, the remaining functional groups also interact with pre-hydrolyzed Al species. However, it was observed [21] that the tetrahedral Al in the Al_{13} –humic acid complexes could gradually be converted to octahedral Al, indicating that Al_{13} in Al_{13} –HA complexes could be decomposed into Al–HA complexes with time. Lu et al. also found that the existence of humic acid could significantly inhibit the formation of Al_{13} when base was added to Al solution [2].

In this study, the humic acid flocs formed by AlCl_3 and Al_{13} at test water pH of 7.50 and Al dosage of $22 \times 10^{-5} \text{ mol l}^{-1}$ was collected and freeze-dried to obtain the solid-state ^{27}Al MAS NMR spectra (Fig. 8). It is clear that no Al_{13} structure existed in the flocs formed by dosing AlCl_3 , and the only signal at 0 ppm indicated the Al species was octahedrally coordinated complexes (Fig. 8a). Although tetrahedrally coordinated Al still existed in the flocs formed by Al_{13} , part of Al had converted to octahedral Al–HA complexes after coagulation. It confirms that Al_{13} –HA complexes were not stable, and the Al_{13} could be decomposed by humic acid with time. It should be pointed

Fig. 8. Solid-state ^{27}Al NMR spectra of freeze-dried humic acid flocs formed by (a) AlCl_3 ; (b) Al_{13} .

out that the Al_{13} decomposition did not induce significant pH changes (Fig. 2) during coagulation process, which indicated that the Al_{13} decomposition and structure re-arrangement might take place at the same time.

4.2. Influences of pH on Al species and the structure of humic acid

The effect of pH on the coagulation of humic acid could be interpreted from two aspects. Firstly, with the decrease of pH, the carboxylic and phenolic groups on the humic acid molecular chain will become less negatively charged due to protonation reactions, therefore, less coagulant will be required to achieve neutralization or form insoluble complexes (Fig. 6). Secondly, pH can greatly affect the hydrolysis process of monomeric Al species. At higher pH, the reactions of monomeric Al complexing with humic acid and further hydrolyzing to form polymeric or hydroxide precipitate could occur simultaneously. Therefore, at least two mechanisms might be involved in the coagulation of humic acid: precipitation by forming insoluble complexes and adsorption of humic acid onto hydroxide solids. While at lower pH (e.g. 3.5), further hydrolysis of monomeric Al is greatly inhibited after dosing (as indicated in Fig. 5, no significant pH depression with the increase of dosage), formation of insoluble HA–Al complexes become the primary mechanism of humic acid removal. Moreover, the flocs formed at lower pH of 3.50 were smaller than those formed through the combination of complex formation and adsorption.

5. Conclusion

Although preformed polymeric Al coagulants are superior to conventional ones in removing mineral colloids, they might not be effective in removing dissolved organic matter. As revealed in this study, when large molecular and hydrophobic humic acid was treated, the coagulation efficiency of preformed Al species (Al_{13} and colloidal species) was much less than that of conventional Al salt. The flocs formed by preformed Al species were smaller than those formed by conventional Al salt.

Decreasing pH could significantly reduce the coagulant dosage required for complete UV_{254} removal regardless of the Al speciation differences.

Unlike the coagulation of mineral colloidal particles, forming insoluble complexes could be one of the primary mechanisms involved in humic acid removal. The complexes formed by Al_{13} and humic acid were not stable, and the Al_{13} structure could be decomposed in the presence of humic acid.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (Grant No. 20537020).

References

- [1] J. Duan, J. Gregory, Coagulation by hydrolyzing metal salts, *Adv. Colloid Interface Sci.* 100–102 (2003) 475–502.
- [2] X. Lu, Z. Chen, X. Yang, Spectroscopic study of the aluminum speciation in removing humic substances by Al coagulation, *Water Res.* 33 (1999) 3271–3280.
- [3] B.A. Dempsey, R.M. Ganho, C.R. O'Melia, The coagulation of humic substances by means of aluminum salts, *J. Am. Water Works Assoc.* 76 (4) (1984) 141–150.
- [4] J.K. Edzwald, Coagulation in drinking water treatment—particles, organics and coagulants, *Water Sci. Technol.* 27 (1993) 21–35.
- [5] Y. Matsui, A. Yuasa, Y. Furaya, T. Kamei, Dynamic analysis of coagulation with alum and PACl, *J. Am. Water Works Assoc.* 90 (10) (1998) 96–106.
- [6] W.P. Cheng, Comparison of hydrolysis/coagulation behavior of polymeric and monomeric iron coagulants, *Chemosphere* 47 (2002) 963–969.
- [7] S. Sinha, Y. Yoon, G. Amy, J. Yoon, Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes, *Chemosphere* 57 (2004) 1115–1122.
- [8] D. Wang, W. Sun, Y. Xu, H. Tang, J. Gregory, Speciation stability of inorganic polymer flocculant—PACl, *Colloid Surf. A* 243 (2004) 1–10.
- [9] K.N. Exall, G.W. Vanloon, Using coagulants to remove organic matter, *J. Am. Water Works Assoc.* 92 (11) (2000) 93–102.
- [10] Y.H. Shen, B.A. Dempsey, Synthesis and speciation of polyaluminum chloride for water treatment, *Environ. Int.* 24 (1998) 899–910.
- [11] H. Tang, Z. Luan, The differences of behavior and coagulating mechanism between inorganic polymer flocculants and traditional coagulants, in: H.H. Hahn, E. Hoffmann, H. Ødegaard (Eds.), *Chemical Water and Waste Water Treatment*, Springer, Berlin, 1996, pp. 83–93.
- [12] A.I. Zouboulis, G. Traskas, Comparable evaluation of various commercially available aluminum-based coagulants for the treatment of surface water and for the post-treatment of urban waste water, *J. Chem. Technol. Biotechnol.* 80 (2005) 1136–1147.
- [13] L. Rizzo, V. Belgiorno, M. Gallo, S. Meric, Removal of THM precursors from a high-alkaline surface water by enhanced coagulation and behavior of THMFP toxicity on *D. magna*, *Desalination* 176 (2005) 177–188.
- [14] C.R. O'Melia, W.C. Becker, K.K. Au, Removal of humic substances by coagulation, *Water Sci. Technol.* 40 (1999) 47–54.
- [15] M.R. Collins, G.L. Amy, C. Steelink, Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter: implications for removal during water treatment, *Environ. Sci. Technol.* 20 (1986) 1028–1032.
- [16] B. Shi, G. Li, D. Wang, H. Tang, Separation of Al_{13} from polyaluminum chloride by sulfate precipitation and nitrate metathesis, *Sep. Purif. Technol.* 54 (2007) 88–95.
- [17] P.C. Chiang, E.E. Chang, C.H. Liang, NOM characteristics and treatabilities of ozonation processes, *Chemosphere* 46 (2002) 929–936.
- [18] J. Gregory, Turbidity fluctuations in flowing suspensions, *J. Colloid Interface Sci.* 105 (1985) 357–371.
- [19] D. Wang, H. Tang, J. Gregory, Relative importance of charge neutralization and precipitation on coagulation of kaolin with PACl: effect of sulfate, *Environ. Sci. Technol.* 36 (2002) 1815–1820.
- [20] V. Kazpard, B.S. Lartiges, C. Frochot, J.B. d'Espinoise, Fate of coagulant species and conformational effects during the aggregation of a model of humic substances with Al_{13} polycations, *Water Res.* 40 (2006) 1965–1974.
- [21] S. Hiradate, N.U. Yamaguchi, Chemical species of Al reacting with soil humic acids, *J. Inorg. Biochem.* 97 (2003) 26–31.