Coagulation of humic acid by PACl with high content of Al_{13} : The role of aluminum speciation

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ABSTRACT

The role of aluminum speciation in coagulation–flocculation of humic acid (HA) by polyaluminum chloride (PACl) with high content of Al_{13} was investigated using ^{27}Al NMR spectroscopy, solid-state ^{27}Al NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS) and Al-Ferron method. Experimental results show that, in the coagulation process, the Al_{13} polymers are the dominant species in acidic pH and some of them change to Al precipitates at higher pH. The mechanism of HA removal is directly related to the form of aluminum in solution. The maximum removal of the HA is found to occur in the pH range from 5.0 to 6.0, which means that charge neutralization by Al_{13} polymer is the main mechanism of coagulation at slightly acidic pH. The results of zeta potential and solid-state ^{27}Al NMR spectroscopy of the flocs also confirm that positive polymers are very effective in charge neutralizing with HA molecules. Adsorption and sweep coagulation of HA by amorphous $Al(OH)_3(s)$ play an important role at pH > 6.0 or over dosing.

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1. Introduction

Humic substances, the major component of organic matter in natural waters, have received much attention in recent years due to the formation of toxic disinfection by-products (DBPs) during chlorination [1,2]. Although many advanced technologies, such as granular activated carbon adsorption, membrane filtration, and ozonation, are feasible for the control of DBPs formation, enhanced coagulation is considered to be among the best available techniques (BATs) for the removal of DBPs precursors.

Aluminum salts are widely used as coagulants to remove colloids, particles, and organics [3,4]. The hydrolyzed Al species, rather than the aqueous Al^{3+} ion, dominate the removal of different pollutants by aluminum coagulation. The four mechanisms of humic substances removal most commonly referred to are charge neutralization of negatively charged colloids by cationic hydrolysis products, incorporation of impurities in an amorphous hydroxide precipitate ‘sweep flocculation’, surface adsorption or chemical interaction of soluble pollutants with aluminum species [3,5]. The hydrolysis reactions of Al species are very complicated, which contribute to the formation of various hydrolyzed Al species, such as $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (Al_{13}) and Al_{13} aggregates [3]. In the past several decades, much attention has been paid to the partially pre-hydrolyzed Al salt, especially

to the polyaluminum chloride (PACl) with high content of Al_{13} polymer, due to its high efficiency for pollutants removal. Many studies have investigated the coagulation behaviors and effectiveness of Al salts in humic substances removal [6–9]. However, previous studies mainly speculated the presence of different Al species, which play significant roles in removing humic substances, based on indirect experiments and theoretical calculation [9,10]. Thoroughly understanding the Al species variation of PACl with high content of Al_{13} and its effect on humic acid removal during the coagulation process is not only valuable in water treatment but also meaningful for organic removal by coagulation.

The objectives of this study are as follows: (1) to qualitatively and quantitatively characterize the Al species with different techniques such as ^{27}Al NMR spectroscopy, solid-state ^{27}Al NMR, electrospray ionization/mass spectra (ESI-MS), and Al-Ferron method; (2) to investigate the distribution and transformation of Al species of PACl with high Al_{13} content at different pH conditions during coagulation process; (3) to study the effect and mechanisms of Al species transformation on the removal of humic acid (HA) by coagulation.

2. Materials and methods

2.1. Coagulants and water samples

The solid PACl with high content of Al_{13} polymer used in this study was prepared by electrolysis process [11,12]. The *B* value

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(molar ratio of OH and Al) and the content of Al_2O_3 of the PACI were 2.5 and 22.1%, respectively.

HA was obtained from Tianjin Chemistry Company (China). The molecular weight of the HA is in the range of 2000–50,000 Da. A stock HA solution was prepared by adding 1.5 g of HA into a 1 L 0.01 mol/L NaClO_4 solution, and the pH was adjusted to 10. Afterward, this stock solution was stirred for 5 h, and filtered for removing residual non-dissolved humic acid powder. Dissolved organic carbon (DOC) in the filtered solution measured by TOC analyzer (Tekmar-Dohrman Co., Phoenix 8000, USA) was with a concentration of 610 mg/L. The test HA solutions were prepared by diluting the stock solution to various concentrations. Ionic strength of the water was kept at 0.01 mol/L with NaClO_4 .

2.2. Jar test

Jar tests were performed at room temperature using a Phipps & Bird six-paddle stirrer. A total 300 mL volume of HA solution, previously adjusted to a desired pH value with diluted NaOH and HCl, was transferred to a 1 L beaker. Under rapid stirring conditions, the coagulant was added using a micropipette. After being dosed, 1 min rapid mixing at 250 rpm was applied, followed by 15 min of slow stirring at 30 rpm. The flocs were allowed to settle for 20 min. The pH values were recorded at the end of the settling period, after the completion of which the supernatants samples were passed through a 0.45 μm filter (cellulose nitrate, Whatman) and analyzed by means of UV analyzer (1 cm cell; Hitachi, U-3010 spectrophotometer, Japan) at a wavelength of 254 nm. The filtrates were tested for DOC (Tekmar-Dohrman Co., Phoenix, AZ). A small amount of sample was taken immediately to measure zeta potential (Malvern, Zetasizer 2000, UK) after 1 min rapid mix.

A parallel experiment was conducted with coagulation process to detect the adsorption ability of Al precipitates. The experiment procedure was as follows: certain amount of stock PACI was added to the beaker containing the distilled water (no HA) with 0.01 mol/L NaClO_4 and a given pH value. Rapid mixing (250 rpm) for 1 min was followed by 15 min of slow mixing (30 rpm) which was similar to jar tests to generate Al precipitates. And then, a given concentration of HA was added to the solution and followed by 15 min of slow mixing (30 rpm). Finally, the suspension was filtered and the filtrate was analyzed by means of the UV.

2.3. Characterization of aluminum speciation of coagulants

^{27}Al NMR spectroscopy was used to characterize the Al species with ^{27}Al NMR spectra obtained on a VARIAN^{UNITY} INOVA (500 MHz) spectrometer. Samples were placed in 5-mm tubes and the spectra were generated at 25 °C. To estimate the distribution of various species in solution, selected samples and standard solutions of known monomeric Al concentration were run using a coaxial sample tube, with a 0.2 mol/L Na aluminate solution in the inner insert as reference. The intensities for ^{27}Al signals relative to the aluminate reference were used for calculating the Al concentrations corresponding signals.

Solid-state ^{27}Al NMR was performed on solid PACI and freeze-dried flocs. Freeze-dried flocs were obtained from the precipitates of coagulation at pH 5.2. The flocs were separated from water samples with a refrigerating centrifuge (J2-HS, Beckman, U.S.A.) as soon as the jar tests finished and freeze-dried. Previous studies have shown that the structure of the metastable Al_{13} polymer remained unchanged after freeze-drying process [13]. MAS NMR spectra were recorded on VARIAN^{UNITY} INOVA (500 MHz) spectrometer at 78.2 MHz with 6 mm chemagnetics double resonance solid-state probe. Main experimental parameters included 0.3 μs pulse width, recycle delays of 1 s, line broadening of 60 Hz, and a

spinning speed of 7 kHz. The reference chemical shift (0 ppm) was adjusted with 1 mol/L AlCl_3 solution.

2.4. Al species distribution analysis in the coagulation process

The experimental procedure for characterizing the Al species in the coagulation process was as follows: the PACI was added to the beaker containing the distilled water with 0.01 mol/L NaClO_4 and a given pH value adjusted using diluted NaOH and HCl. Rapid mixing (250 rpm) for 1 min was followed by 15 min of slow mixing (30 rpm) and 30 min of settling which is similar to jar tests, but no HA was present in solution during these experiments. The entire solution was then vacuum filtered through a 0.45 μm membrane filter. The Al precipitates that remained on the filter were then dissolved in 5 mL of 2 mol/L HNO_3 solution and the concentration was analyzed. Because the Ferron method offers a simple alternative to ^{27}Al NMR analyses and allows quantification of Al speciation at a concentration of 10–100-fold lower than presently analyzable by NMR, a concentration range pertinent to water treatment process, the concentration of Al_T and Al speciation in filtrate was measured using Al-Ferron method [14]. Three categories of species, Al_a , Al_b and Al_c were analyzed by Al-Ferron method, which were corresponding to monomer, medium polymer, and larger polymer species and/or solid-phase $\text{Al}(\text{OH})_3$, respectively. Some investigations proved that the Al_b species could be regarded as the Al_{13} species [14]. Furthermore, the Al_a and Al_c species were approximately equal to the Al_m and Al_u species, respectively. With the concentration of insoluble Al, there were four Al speciation, Al_a , Al_b , Al_c and Al precipitates which were obtained as a function of pH.

In addition to the Al-Ferron method, ESI-MS was also used to detect the aluminum speciation variation of PACI. ESI-MS were recorded with a micromass hybrid quadrupole time of flight (TOF) mass spectrometer (2695XE micro, Waters, USA) equipped with an electrospray ion source with a positive ion mode. The solutions were introduced into the spectrometer at a flow-rate of 10 $\mu\text{L}/\text{min}$. The instrumental conditions were as follows: capillary voltage 3500.0 V, sample cone voltage 70 V, Ff lens 200 V, extraction cone voltage 5 V, source temperature 120 °C, cone gas (N_2) flow-rate 300 L/h, mass range 80–1000.

3. Results and discussion

3.1. Qualitative and quantitative characterization of Al species for PACI

Fig. 1 presents the solid-state ^{27}Al NMR spectrum of solid PACI and the aqueous ^{27}Al NMR spectrum of stock PACI solution (0.1 mol/L Al_T , pH 4.89). The tetrahedral coordination and octahedral coordination of oxygen atoms for aluminum are observed in Fig. 1a. The peak at ~ 10 ppm is assigned to the octahedral coordination, and the peak at ~ 63 ppm signifies the tetrahedral coordination, which corresponds to Al_{13} polymer [15]. The ^{27}Al NMR spectrum of PACI solution in Fig. 1b is in good accordance with that of solid PACI. The intensities of the ^{27}Al signals relative to the aluminate reference are used to calculate the Al concentrations. The intensities at 0 and 4.3 ppm resonances respectively represent the quantitative determinations of the monomeric and dimeric Al [16]. The monomeric and dimeric Al species are combined and named as Al_m . The intensity at 63 ppm resonance represents the quantitative determination of the Al_{13} polymer and that at 80 ppm resonance means sodium aluminate. The concentration for the 63 ppm signal is multiplied by 13 to obtain the concentration of Al_{13} . The difference between total aluminum (Al_T) and $[\text{Al}_\text{m} + \text{Al}_{13}]$ signifies the part that could not be detected by ^{27}Al NMR technique, namely the larger polymer species and/or solid-phase $\text{Al}(\text{OH})_3$ (Al_u). Based

Fig. 1. (a) Solid-state of ^{27}Al NMR spectrum of PACI produced by electrolysis process ($B = 2.5$) and (b) ^{27}Al NMR spectra of PACI solution used in the coagulation process (0.1 mol/L Al_r , pH 4.89).

on the methods for the classification and calculation of different Al species, the contents of Al_m , Al_{13} , and Al_u are 4.7%, 62.2% and 33.1%, respectively. The contents of Al_a , Al_b and Al_c analyzed by Al-Ferron are 7.2%, 65.3% and 27.5%, respectively. It is indicated that the Al_{13} polymers are the dominant species in this PACI solution.

3.2. Effect of pH on aluminum transformation and humic acid removal

The ^{27}Al NMR technique may analyze the aluminum species at high concentrations, but it is ineffective when the aluminum concentrations are low. This study employed the Al-Ferron method and ESI-MS to investigate the species transformation at different pH conditions, and the dominant species that contribute to HA removal.

Fig. 2 shows the ratio of different Al species of PACI with pH ranging from 3 to 9.5 at PACI dosage of 2 mg Al/L, which is the common dosage in practice. The results indicate that pH significantly affect the Al species distributions. As being indicated, at pHs lower than 3.5, the aluminum monomers (Al_a) is the dominate species with the content of 57%. In the range of pH 4–6, the Al_b is the dominated speciation with the content of 52–58%. When pH is higher than 6, the ratio of Al_b decreases whereas the ratio of Al precipitates increase due to the formation of $\text{Al}(\text{OH})_3$ or Al_{13} aggregates at higher pHs. The content of Al precipitates is about 50% in the pH range of 6.5–9. The higher pH (>8) contributes to the increased ratio of Al_a , mainly owing to the formation of $\text{Al}(\text{OH})_4^-$ species [3]. The ratio of Al_c reaches a maximum at pH 3.6, after that, the ratio of Al_c decreases and is relatively stable to be lower than 10% at pH 5–9. Consequently, the weak acidic conditions of pH from 4 to 6 are beneficial to the stabilization of Al_b polymer in dilute solutions for the time scales typical in water treatment.

Fig. 2. Aluminum speciation diagram for PACI with concentration of 2 mg Al/L.

In addition to the Al-Ferron method, the positive ion ESI-MS method also demonstrates the presence of Al_{13} polymer species, and indicates the species transformation of Al species at different pH conditions. The ESI-MS spectra of PACI solution (2 mg Al/L) at pH 4 and 7 are shown in Fig. 3. At pH 4, the total ion counts (TIC) value is 1.52×10^4 , and the most intensive peaks are at m/z 337 and m/z 328, which is assigned to the $[\text{Al}_{13}\text{O}_{17}(\text{OH})_3]^{2+}$ and $[\text{Al}_{13}\text{O}_{18}(\text{OH})]^{2+}$, respectively [17,18]. The dimeric aluminum species of $[\text{Al}_2\text{O}_2(\text{OH})(\text{H}_2\text{O})_{0-3}]^+$ with peaks at m/z 121, 139, and 157, are also observed. In this study, Al_{13} species in the PACI are stable at pH 4 which is similar with the previous study [17]. With pH increasing from 4 to 7, the TIC value decreases from 1.52×10^4 to 2.77×10^3 , indicating the formation of $\text{Al}(\text{OH})_3(\text{s})$ precipitates. The Al_{13} species are also detected at pH 7. Through aluminum speciation variation of PACI indicated by the results of ESI-MS and the Ferron method, the preformed Al_{13} polymers ($[\text{Al}_{13}\text{O}_4(\text{OH})_{24}]^{7+}$) in PACI are quite stable in pH 4–6 during the coagulation process and some of them change to Al precipitates when the pH is higher than 6.5.

The effect of pH on HA (initial DOC = 4 mg/L) removal was examined in the range of pH 3–9. As shown in Fig. 4, PACI at 2 mg Al/L contributes to the maximal UV_{254} removal, which is as much as 87.6%, in the pH range from 4.5 to 5.5. The higher pH inhibits UV_{254} removal, which decreases to about 50.0% at pH 9. Similar trends are observed for the variation of DOC removal at different pH conditions, and the optimal pH range is from 5 to 6. Comparatively, PACI is observed to lead to lower removal of DOC than that of UV_{254} .

Humic acid is acidic by virtue of ionizable carboxyl and hydroxyl groups, and solution pH has remarkable effect on electric characteristics of humic acid, which shows neutral charge at pH of near 3 [19]. Above this value, humic acid shows more negative charge with elevated pH, which is beneficial to the reactions between humic acid and positively charged Al species [19]. However, when pH is higher than 6, the removal of both UV_{254} and DOC decreases with higher pH. The distribution and transformation of Al species may dominate the removal of humic acid under these conditions, which would be discussed in detail below.

3.3. Mechanisms of aluminum species affecting humic acid removal by PACI coagulation

3.3.1. Electrostatic interaction between PACI and humic acid

The removal of HA by PACI coagulation is pH dependent (Fig. 4), which is relative to the Al species transformation at different pH conditions. In low pH ranges from 3.0 to 6.5, the removal of UV_{254} and DOC increases steadily with higher pH. Accordingly, the ratio of

Fig. 3. ESI-MS spectrum of PACI with concentration of 2 mg Al/L: (a) pH 4 and (b) pH 7.

Al monomer species (Al_a) decreases, and that of soluble Al_{13} polymer species (Al_b) increases steadily at elevated pH. Under these pH conditions, the charge neutralization–precipitation reactions between HA and Al species dominate the removal of HA, because the Al_b is the dominate species (Fig. 2).

In comparison, it may be inferred that Al_b exhibits higher capabilities of removing HA than that of Al_a , owing to the stronger electrostatic interactions between HA and soluble Al_{13} polymer species than Al_a . The Al_{13} exhibits much stronger positive charge than Al_a which contributes to the removal of negatively charged humic acid. To further demonstrate the interactions between HA and Al species, Fig. 5 followed the variation of zeta potential and residual UV_{254} absorbance at different PACI dosages at pH 5.2. It is indicated that the zeta potential of HA increased steadily from negative to positive with increased PACI dosages, and PACI at 2.2 mgAl/L contributes to the complete charge neutralization of HA. Further increasing the PACI dosage to be higher than 4 mgAl/L, the zeta potential approaches a plateau with a positive value of about 15 mV. The PACI dosage of 2.2 mgAl/L is a critical value for UV_{254} removal, at which the maximal UV_{254} removal is achieved. With PACI dosages increasing from 0 mg/L to 2.2 mgAl/L, UV_{254} absorbance decreases from 0.25 to 0.04. The higher PACI dosage would not improve, but inhibits the removal of HA, and the UV_{254} absorbance increases to 0.06 at PACI dosage of 5 mgAl/L. Overdose resulted in charge reversal, as being indicated from the positive zeta potential in Fig. 5a,

Fig. 4. Coagulation of HA (DOC = 4 mg/L) with 2 mg Al/L PACI as a function of pH.

Fig. 5. Coagulation of HA (4 mg/L) as a functions of PACI dose at pH 5.2: (a) zeta potential and (b) residual UV_{254} absorbance.

and decreases the removal of HA. Consequently, the electrostatic interaction of charge neutralization plays an important role in the removal of HA by coagulation.

The solid-state ^{27}Al NMR spectrum of the freeze-dried flocs obtained by coagulation of HA at pH 5.2 (Fig. 6) can prove above conclusion on another aspect. Fig. 6 displays two resonances: one strong asymmetric peak having a maximum at 2 ppm corresponding to octahedrally coordinated aluminum, and this peak can correspond to several Al species. Many researchers have stated that this shift corresponded to “free” Al dimers or complexed Al monomers and dimers [13]. It has been shown that increasing polymerization of Al resulted in increasing downfield chemical

Fig. 6. The solid-state ^{27}Al NMR spectrum of the freeze-dried floc (coagulation pH 5.2).

Fig. 7. The comparison of HA removal by coagulation process and adsorption by Al precipitates (initial HA concentration: 4 mg/L).

shifts, highly polymerized Al structure such as gibbsite having a resonance around 10 ppm [13]. The second line at 62.7 ppm is attributed to tetrahedral aluminum of Al_{13} polymer whose chemical shift has been reported to be in a 61–64 ppm range depending on the conditions of formation and aging. Thus, the largest possible Al species within the flocs is the Al_{13} polymer and Al monomers and dimers.

3.3.2. Comparison of HA removal between coagulation and adsorption by Al precipitates

In addition to the charge neutralization precipitates formed during the coagulation process, the adsorption on amorphous metal hydroxide precipitates contributes the HA removal [20–22]. Generally, charge neutralization occurs at low pH values only soluble species are present, while adsorption means the appearance of bulk hydroxide precipitation at high pH values or at high coagulant doses. When soluble aluminum species and Al precipitates are present at the same time, a simultaneous precipitation reaction should be considered.

Fig. 7 compares the UV_{254} removal by coagulation and adsorption by preformed Al precipitates at different pH conditions at PACl dosage of 2 mg Al/L and 5 mg Al/L, respectively. The removal efficiency of UV_{254} by adsorption is pH dependent. At pH from 4 to 6, the dominate aluminum species in the solution is Al monomers and Al_{13} polymers, the adsorption capacity of these species is lower than that of Al precipitates, which is abundant when the pH value exceed 6.0. With pH increasing from 4 to 6, the removal of HA by adsorption is relatively stable at a certain PACl dosage. However, the UV_{254} removal is significantly improved at pH 7.2, and the maximal removal efficiency of 60% and 63% is achieved for 2 mg Al/L and 5 mg Al/L, respectively.

The difference of UV_{254} removal between coagulation and adsorption (DIF_{UV}) provides valuable information on the mechanisms involved in the removal of HA by PACl at different pH conditions. The DIF_{UV} was calculated through the method as follows: $DIF_{UV} (\%) = UV_{254}$ removal by coagulation (%) – UV_{254} removal by adsorption (%).

When pH is lower than 6.2, the DIF_{UV} value is higher than 46% and the maximal DIF_{UV} is 65%. At higher pH, PACl coagulation decreases whereas aluminum precipitates adsorption increases the removal of HA, which contributes to the decrease of DIF_{UV} values. It is implied that the charge neutralization, with the high content of Al_{13} polymer, is the main mechanism for HA removal in lower pH ranges. However, the adsorption of HA onto Al precipitates, i.e., $Al(OH)_3(s)$, dominates HA removal beyond pH 6.0. At pH > 8.0, $Al(OH)_3(s)$ starts to redissolve and the humic substances adsorbed

on it are released back into solution, resulting in the HA removal decreased.

4. Conclusions

The role of aluminum speciation in coagulation–flocculation of HA by PACl with high content of Al_{13} was studied in this paper. The results of ESI-MS and Al-Ferron method show that Al_{13} polymers are stable in dilute solution at pH 4–6 and some of them change to Al precipitates when the pH higher than 6.5. The aluminum speciation directly influences the mechanism of HA removal. The maximum removal of the HA is found to occur in the pH range from 5 to 6. It can be concluded that charge neutralization is the main mechanism of coagulation at slightly acidic pH because the positively polymers are very effective in charge neutralizing with the HA molecules, while adsorption and sweep coagulation of HA by amorphous $Al(OH)_3(s)$ play an important role at pH > 6.0 or over dosing.

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