



# Effect of pH on the coagulation performance of Al-based coagulants and residual aluminum speciation during the treatment of humic acid–kaolin synthetic water

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## ABSTRACT

The fractionation and measurement of residual aluminum was conducted during the treatment of humic (HA)–kaolin synthetic water with  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{AlCl}_3$  and polyaluminum chloride (PAC) in order to investigate the effect of pH on the coagulation performance as well as residual aluminum speciation. Experimental results suggested that turbidity removal performance varied according to the following order:  $\text{AlCl}_3 > \text{PAC} > \text{Al}_2(\text{SO}_4)_3$ . HA removal performance of PAC was better than that of  $\text{AlCl}_3$  under acidic condition. The optimum pH range for  $\text{AlCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  was between 6.0 and 7.0 while PAC showed stable HA and  $\text{UV}_{254}$  removal capacity with broader pH variation (5.0–8.0). For the three coagulants, majority of residual aluminum existed in the form of total dissolved Al (60–80%), which existed mostly in oligomers or complexes formed between Al and natural organic matter or polymeric colloidal materials. PAC exhibited the least concentration for each kind of residual aluminum species as well as their percentage in total residual aluminum, followed by  $\text{AlCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  (in increasing order). Moreover, PAC could effectively reduce the concentration of dissolved monomeric Al and its residual aluminum ratio was the least among the three coagulants and varied little at an initial pH between 7.0 and 9.0.

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## 1. Introduction

Conventional drinking water treatment processes mainly consist of coagulation, sedimentation, and gravity filtration [1–3], in which, some Al-based compounds or polymers such as alum, aluminum chloride, PAC and so on are widely used as coagulants in drinking water treatment to enhance the removal of particulate, colloidal, and dissolved substances via coagulation process [4,5]. Although effective for removing turbidity and dissolved organic materials, Al-based coagulants, particularly alum, may result in elevated concentrations of Al in treated water.

The occurrence of Al in treated water or as a precipitate in the distribution system has been considered for many years to be an undesirable aspect of treatment practice and it has been associated with several problems, including increased turbidity, reduced disinfection efficiency, and a loss in hydraulic capacity [6]. There is considerable concern throughout the world over the level of aluminum in drinking water sources (raw water) and treated water. The ingestion of high concentrations of Al is also of concern because of potential adverse health effects. Furthermore, scientific issues about the association between Al and Alzheimer's disease are pending resolution [7–9]. From the standpoint of treatment plant performance, high concentrations of residual dissolved Al indicate

incorrect coagulant dosing, inefficient use of the coagulant, or problems in the chemistry of treatment process. High concentrations of particulate Al may lead to problems in solid–liquid separation of postprecipitation of Al. Thus, Al fractionation measurements can provide the treatment plant operator with valuable information about various aspects of plant performance [6].

In addition, most regulatory agencies have established guidelines/standards for the control of Al in drinking water. However, it should be stressed that all guidelines refer to total Al and most water treatment plants and researchers pay close attention to only total Al or total dissolved Al. That is to say, profiles of various forms of Al levels in raw and treated water are rarely performed [10]. Considerable differences exist in the toxicity of the different Al species, so reports of compliance with guidelines may have less toxicological significance than indicated by the total concentration data. From a research perspective, knowledge of Al speciation can provide insights into coagulation chemistry and the mechanisms for contaminant removal.

So it seems reasonable to carry out the Al fractionation studies systemically. Moreover, pH was an essential parameter influencing the coagulation performance of Al-based coagulants as well as the contents of different residual Al species [9,11–14]. In this paper, the Al characterization (speciation) studies was conducted with respect to the treatment of HA–kaolin synthetic water, and the effect of pH on the coagulation performance of three Al-based coagulants –  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{AlCl}_3$  and PAC – were also studied as well as the contents of different residual aluminum species. It was intended to investi-

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gate the relationship between the coagulation performance of the three coagulants and content and speciation of residual aluminum.

## 2. Materials and methods

### 2.1. Experimental materials

The commercial HA with a carbon content of 52.6% (w/w), biochemical reagent, was purchased from the Jufeng Chemical Technology Co. Ltd., Shanghai, China. High purity Al sheet, obtained from Beijing Purchasing and Supply Station of Chinese Medicine Company, was used for the preparation of standard stock solution of Al. Concentrated nitric acid (Sinopharm Chemical Reagent Co. Ltd., Beijing, China), a guaranteed reagent, was used for the acidification of the test water samples. Cetyl pyridinium bromide (CPB) and Triton X-100 (OP) were chemically pure grade agents and were purchased from Sinopharm Chemical Reagent Co. Ltd., Beijing, China.  $\text{CH}_3\text{COONa}$ , Chrome azurol S, xylenol orange, ascorbic acid, NaCl, NaOH,  $\text{Na}_2\text{CO}_3$ , anhydrous ethanol and EDTA were analytically pure grade agents and were obtained from Guangcheng Chemical Reagent Plant, Tianjin, China. Other analytically pure grade agents, including concentrated hydrochloric acid (HCl), kaolin,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , KF, 4-nitrophenol, anhydrous ethylenediamine and ammonia solution were purchased from Sinopharm Chemical Reagent Co. Ltd., Beijing, China. All the reagents exploited were used as received, without any further purification. The water used for dilution of stock solutions as well as for any reagent preparation during the whole experiment was deionized with an all-glass apparatus.

All containers used in this study were cleaned using deionized water as follows: cleaned with 1 + 9  $\text{HNO}_3$  solution and then stored in 1 + 9  $\text{HNO}_3$  solution for 12 h; rinsed with deionized water. It was reported that membrane filters should be used freshly and the first 50 ml of sample should be avoided to prevent any contamination due to filters [10].

### 2.2. Experimental methods

#### 2.2.1. Preparation of HA–kaolin synthetic water

The HA stock solution was prepared as follows: 1.00 g HA was dissolved in 1000 mL of  $1.0 \times 10^{-4}$  mol/L NaOH solution with 3 h of continuous stirring and stored in refrigerator for later use. Under this condition, the HA was soluble [15]. HA–kaolin synthetic water was prepared by adding a certain amount of HA stock solution and kaolin into deionized water and tap water (the volume ratio of deionized water and tap water was 1:1). The properties of the synthetic water used were shown as following: HA content = 10 mg/L,  $\text{UV}_{254}$  absorbance =  $0.500 \pm 0.002$ , pH =  $8.25 \pm 0.10$ , Turbidity =  $15.0 \pm 0.5$  NTU. The pH of synthetic water was adjusted to the predetermined pH by 0.1 mol/L HCl and 0.1 mol/L NaOH solutions.

#### 2.2.2. Coagulation experiments

Standard jar tests for HA–kaolin synthetic water treatment were conducted on a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) at a room temperature of  $20 \pm 1$  °C. The synthetic water of 1000 ml with different pH was transferred into each of the 2.0L plexiglass beakers and a six-paddled stirrer was used for mixing. Under rapid stirring of 200 rpm ( $G = 102.5 \text{ s}^{-1}$ ), predetermined amount of coagulant was dosed. And then the solutions were stirred rapidly at 200 r/min for 60 s after coagulant addition, followed by slow stirring at 40 r/min ( $G = 11.8 \text{ s}^{-1}$ ) with a duration of 15 min and then 25 min of quiescent settling. After depositing, samples were collected from 2 cm below the solution surface for subsequent measurements.

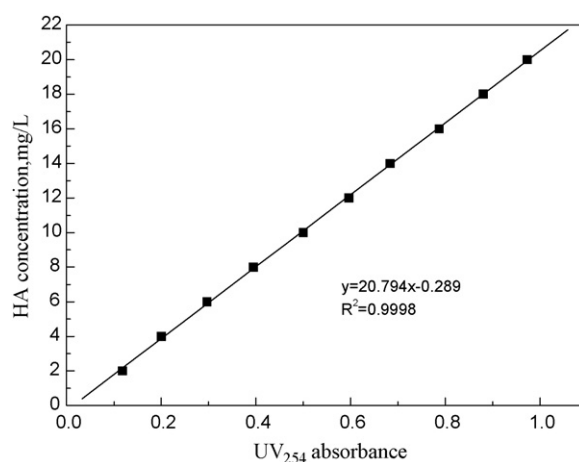


Fig. 1. Linear relationship of  $\text{UV}_{254}$  and HA concentration.

Collected water sample was filtrated through a  $0.45 \mu\text{m}$  filtration membrane to measure the  $\text{UV}_{254}$  absorbance at a 254 nm wavelength with a UV-754 UV/VIS spectrophotometer (Jinghua Precision Scientific Instrument Co. Ltd., Shanghai, China). The relationship between  $\text{UV}_{254}$  absorbance and HA concentration is linear and was shown in Fig. 1, constituting a basis of conversion of  $\text{UV}_{254}$  absorbance data to an equivalent HA concentration. The removal of  $\text{UV}_{254}$  absorbance was used to evaluate the HA removal efficiency in this study. The zeta potential was measured with a Zetasizer 3000HSa (Malvern Instruments, UK). Turbidity was measured using a portable turbidimeter 2100P (Hach, USA).

#### 2.2.3. Preparation and synthesis of Al-based coagulants and measurement of total Al content in PAC

$\text{AlCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  were prepared by directly dissolving a certain amount of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  to deionized water. PAC was synthesis by solid–solid mixed method [16,17]. In this technique, each reaction was conducted in a 250 ml, three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer and glass plug. After the reactor was heated to about 80 °C from ambient temperature using a thermostated water bath, a predetermined amount of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$  was continuously added into the beforehand added 100 ml deionized water with vigorous agitation within 30 min. After that, the reactor was still kept at the constant temperature with continuous and intense stirring for about 1 h until the solid mixture was solubilized and the solution was optically transparent. At the end of the reaction the product was homogeneous and clear and then was stored in refrigerator for later use.

The total Al content in PAC was determined by titrimetric method according to the national standard of China [18]. The properties of PAC used were indicated as follows: total Al ( $\text{Al}_T$ ) content = 0.8556 mol/L, basicity value (B, molar ratio of OH and Al) = 2.0, pH =  $2.85 \pm 0.10$ . The dosage of the three Al-based coagulants was 10.0 mg/L  $\text{Al}_2\text{O}_3$ , which was determined through preparatory experiments.

#### 2.2.4. Separation method of different residual aluminum speciation

Nalgene 500 ml high-density polyethylene bottles were used for water sample collection and storage. Nucleopore polycarbonate  $0.45 \mu\text{m}$  filters were used for the separation of total and dissolved Al. Filters have “self-adsorption/absorption” capacity for Al and, hence, initial filtrates would not have the same Al content as samples. After discarding the initial filtrate volume of 50 ml, samples then should be collected for next Al fractionation analysis [10].

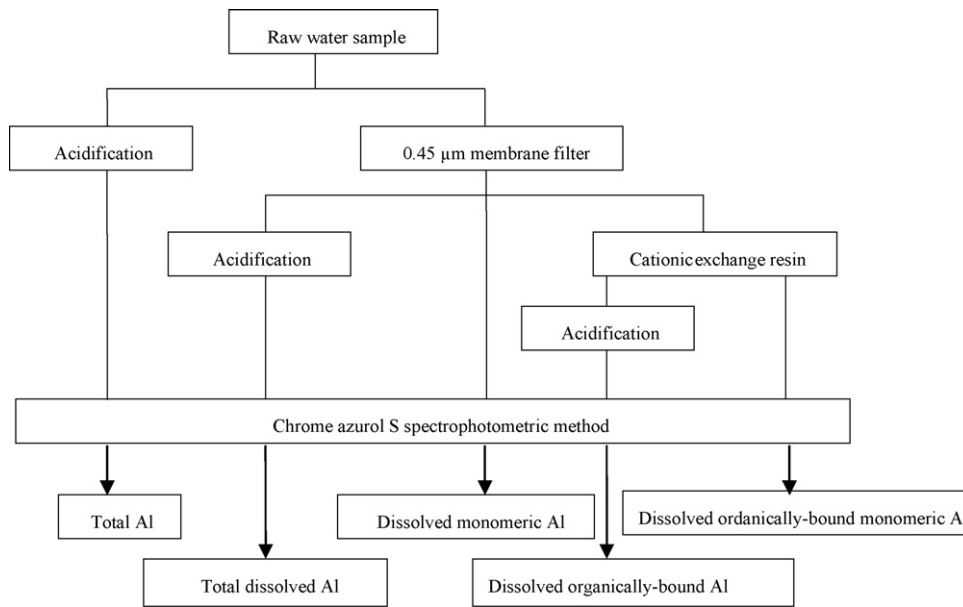


Fig. 2. Separation procedure of different residual aluminum speciation.

The strongly acidic styrene type cation exchange resin (hydrogen form, 20–40 mesh standard screens) was purchased from Damao Chemical Reagent Plant, Tianjin, China, and was used for speciation of organic-bound Al. The pretreatment procedures of the cation exchange resin were revealed as following: cleaned with 1 mol/L HCl solution and then stored in 1 mol/L HCl for 30 min; rinsed with deionized water; cleaned with 1 mol/L NaOH solution and then stored in 1 mol/L NaOH for 30 min; rinsed with deionized water; washed with 1 mol/L NaCl solution to convert hydrogen form resin to sodium form resin. All the procedures were implemented in a column of strongly acidic cation exchange resin [19].

The Al fractionation method was carried out under a modification of previously developed procedures—the Van Benschoten and Edzwald method [6] and allowed the determination of the following operationally defined Al fractions (the analytical scheme was presented in Fig. 2) [20]:

- Total Al: an unfiltered sample was acidified with nitric acid and was then analyzed.
- Total dissolved Al: particulate and dissolved Al forms were operationally isolated by filtering the water samples with a 0.45 μm membrane filter, acidified and analyzed.
- Dissolved monomeric Al: a filtered sample was analyzed without acidification.
- Dissolved organically bound Al: a strong acidic cation exchange resin was used to fractionate dissolved Al into two fractions, namely, inorganic and organically bound Al; a filtered sample was passed slowly (about 13–14 ml/min) through a column of the strongly acidic cation exchange resin and effluent was analyzed after acidification.
- Dissolved organic monomeric Al: a filtered sample was passed through the cation exchange column and analyzed without acidification.

Additional fractions were obtained by subtraction, i.e.:

- Particulate Al is the difference between total reactive and total dissolved Al.
- Dissolved inorganically bound Al is the difference between total dissolved and dissolved organically bound Al.

- Polymeric colloidal and strongly bound Al is the difference between total dissolved and dissolved monomeric Al.

All the digestion procedure (for total Al/dissolved plus colloidal Al) involved lowering sample pH to 1 using guaranteed grade concentrated nitric acid and then heating the sample for 1 min after the sample was boiled at pH = 1 before the subsequent cooling and measurement.

#### 2.2.5. Measurement of residual aluminum content

The different residual aluminum speciation concentration was measured by spectrophotometer according to the national standard GB/T5750.6–2006 of People's Republic of China. During the experiment, the residual Al contents of raw and purified water after flocculation were analyzed by chrome azurol S colorimetric analysis [21]. The residual Al content was obtained through consulting the standard curve of Al content after measuring the absorbances at 620 nm wavelength with spectrophotometer of UV-754 type spectrophotometer. The Al content–absorbance standard curve was shown in Fig. 3. Precision and accuracy of the method were verified by analyzing 10 replicates of a raw water sample. Precision for total, total dissolved, and dissolved organic Al deter-

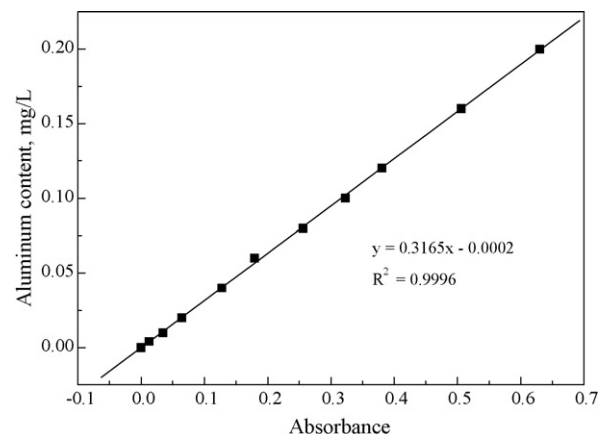


Fig. 3. Standard curve of aluminum content.

**Table 1**

The pH of the treated water after coagulation and sedimentation with three Al-based coagulants.

Water samples	pH					
Raw water	4.00	5.00	6.00	7.00	8.00	9.00
Purified water after coagulation with AlCl <sub>3</sub>	4.42	4.55	4.97	6.71	7.06	7.20
Purified water after coagulation with Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	4.31	4.83	5.49	7.04	6.93	7.22
Purified water after coagulation with PAC	5.16	6.41	6.91	7.20	7.50	7.99

minations, measured several times as relative standard deviation of 10 samples, was within 10%. The detection limit was 0.008 mg/L.

### 3. Results and discussion

Considering the acidic, alkaline and neutral ambience together, the initial pH of the raw water was adjusted to 4.00, 5.00, 6.00, 7.00, 8.00, and 9.00, respectively, in order to investigate the effect of different pH on the coagulation performance of the three Al-based coagulants as well as the speciation and contents of residual Al during the treatment of HA–kaolin synthetic water.

#### 3.1. Coagulation performance of the three Al-based coagulants at different pH

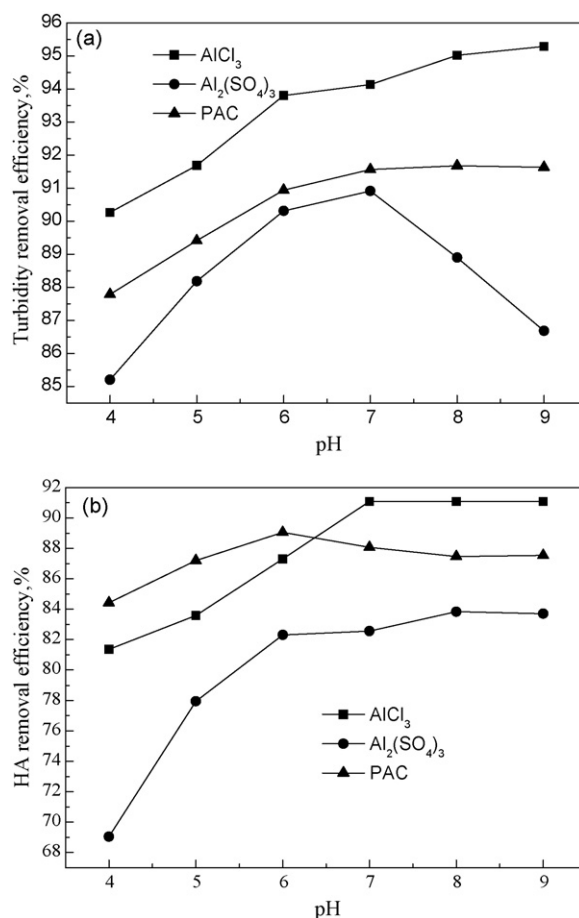
The mechanisms to explain the coagulation of HA–kaolin substances include charge neutralization, precipitation, bridge-aggregation, adsorption and sweep-flocculation [22]. Under different conditions, the different mechanisms or their combination may be dominant. The effect of initial pH on turbidity removal (a) and HA removal (b) was shown in Fig. 4. The pH of the effluent after coagulation and sedimentation was shown in Table 1. During all the experiments, the dosage of three Al salts coagulants was 10.0 mg/L (Al<sub>2</sub>O<sub>3</sub>).

Consistent with the reported results [23], initial pH had an important effect on the coagulation behavior of the three Al-based coagulants. As indicated in Fig. 4(a), turbidity removal efficiency increased obviously with pH when initial pH is lower than 6.0 and could reach about 94%, 91.5% and 90.5% for AlCl<sub>3</sub>, PAC, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, respectively, at the dosage of 10.0 mg/L (Al<sub>2</sub>O<sub>3</sub>). When the initial pH is between 7.0 and 9.0, the turbidity removal efficiency increased insignificantly for AlCl<sub>3</sub> and PAC, while it decreased sharply for Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. And the turbidity removal performance of the three coagulants varied according to the following order: AlCl<sub>3</sub> > PAC > Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Similarly, as seen in Fig. 4(b), HA removal efficiency increased obviously with pH when initial pH is lower than 6.0 and could reach about 87%, 88.5% and 82% for AlCl<sub>3</sub>, PAC, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, respectively, at the dosage of 10.0 mg/L (Al<sub>2</sub>O<sub>3</sub>). When the initial pH range is between 7.0 and 9.0, the HA removal efficiency increased slightly for all the three coagulants. The HA removal performance of PAC was better than that of AlCl<sub>3</sub> under the acidic atmosphere; while the residual UV<sub>254</sub> with PAC was a little higher than that with AlCl<sub>3</sub> under the neutral and alkaline atmosphere. Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> showed the poorest HA removal effect among the three coagulants. For PAC, the suitable initial pH range was slightly broader compared with AlCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The optimum pH range for AlCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was between 6.0 and 7.0, which corresponded well with the reported optimums for Al coagulants [24]. However, PAC showed stable turbidity and HA removal capacity with broad pH variation (5.0–8.0).

As indicated in the pH of raw and treated water, the effect of the initial pH on HA and kaolin removal was correlated with the coagulant hydrolyzates. When pH was lower than 5.0, the primary hydrolyzates of AlCl<sub>3</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and PAC were some positive hydrolyzates, like Al(OH)<sup>2+</sup>, Al(OH)<sub>2</sub><sup>+</sup>, Al<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>, and Al<sub>3</sub>(OH)<sub>4</sub><sup>5+</sup> [25]. These positive hydrolyzates were easy to neutralize the exterior negative charges of HA and kaolin, and further destabilize

the colloids. They are also of benefit to the physical or chemical adsorption of the destabilized HA–kaolin colloids, which lead to floc growth. When the initial pH range was between 6.0 and 8.0, there were some high polymeric positive hydrolyzates and Al(OH)<sub>3</sub> formed in solution [25]. The colloids were easily adsorbed and co-precipitated by the hydrolyzates, which had low solubility and large surface area. When pH was higher than 8.0, the suspension system was difficult to be destabilized because the hydrolyzates were transformed to Al(OH)<sub>4</sub><sup>-</sup> [25].

Fig. 5 presented the Zeta potential of flocs formed after coagulation with the three Al-based coagulants. In acid region, the Zeta potential of flocs formed after coagulation with AlCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> increased dramatically with the increase of pH, while it reduced significantly at an initial pH range between 6.0 and 9.0. As pH increased, Zeta potential moved into the positive side first and then the negative side and it reached a peak value at pH=6.0. This indicated that the charge neutralization effect of AlCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> at acid ambience was superior to that at alkaline and neutral ambience. For PAC, Zeta potential of flocs formed after coagulation decreased directly and moved from the positive side into



**Fig. 4.** Effect of pH on coagulation performance in HA–kaolin synthetic water treatment.

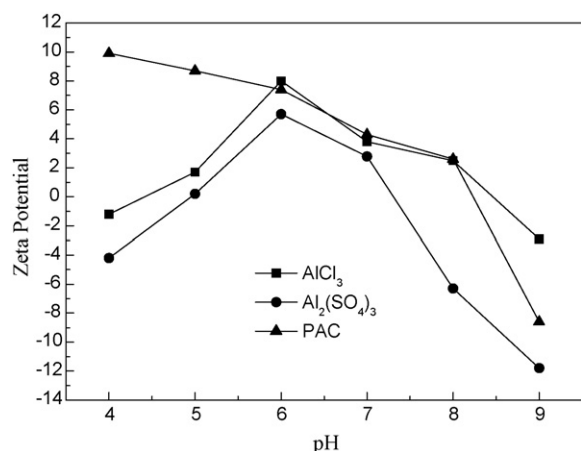


Fig. 5. Zeta potential of flocs formed of the three coagulants in HA–kaolin synthetic water treatment.

the negative side at an initial pH range from 4.0 to 9.0. In addition, at lower pH range, the Zeta potential of flocs formed after coagulation with PAC was obviously higher than that of flocs formed after coagulation with AlCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and it seemed reasonable to contribute to the superior coagulation performance of PAC.

Furthermore, pH also affected the physical or chemical properties of HA in water. The HA were less hydrophilic and the protonation was improved at lower pH to make HA easier to be charge-neutralized and destabilized. Not merely, pH could affect the balance between the reactions of organic functional groups with hydrogen ions and Al hydrolysis products [26]. At lower pH, hydrogen ions could outcompete the metal hydrolysis products for organic ligands; thus, the amount of unsatisfied organic ligands is decreased and then HA could be removed more efficiently by metal salts.

### 3.2. Different residual aluminum speciation content in the effluent

In recent years, the physiological toxicity of aluminum is more and more recognized by people, and standards of aluminum concentration in drinking water were issued by some organizations and governments. Since the toxicity of Al is highly dependent on its speciation (“free” and complexed Al) and mobility (soluble, colloidal or precipitated) [27], the fractionation and measurement of different Al speciation were conducted in this paper, in order to discuss the effect of pH on the content and speciation of residual aluminum of the three Al-based coagulants with respect to the

treatment of HA–kaolin synthetic water. The results were shown in Fig. 6.

As suggested in Fig. 6, the concentration of different Al speciation varied regularly along with the pH variation. The concentration of the tested several Al species represented the similar tendency, expressing as going down at the beginning and then going up later, except for the dissolved organically bound Al species, which showed deucedly low concentration and altered little. It seemed reasonable to attribute to the pH variation and the solubility of Al species. Unstable suspended or particulate aluminum could be simply wiped off from the water during the coagulation and sedimentation process, while, dissolved Al fraction exhibited high activity and was partially removed in the treatment. Al was soluble almost completely at strong acidic condition and formed Al(OH)<sub>3</sub> precipitate under neutral or weakly alkaline atmosphere while soluble Al(OH)<sub>4</sub><sup>-</sup> existed in the solution [28], which were in accordance with the change trends of residual aluminum concentration.

The higher total residual aluminum concentration (more than 1.0 mg/L) can be explained by the high Al concentration in the raw water (Al<sub>2</sub>O<sub>3</sub> component in kaolin as well as some possible impurities in the tap water) together with the fraction caused by the Al-based coagulants. The total dissolved Al concentration consists of inorganic Al species (e.g., Al<sup>3+</sup>, Al(OH)<sub>2</sub><sup>+</sup>, AlF<sub>2</sub><sup>+</sup>) and soluble complexes of Al with dissolved organic carbon. The speciation and fate of dissolved Al in treatment plants are determined by the competition of the Al cation with ligands such as hydroxyl ion, fluoride, sulfate and the functional groups of dissolved organic materials. The humic material with a high Al complexation capacity was partially removed in the coagulation progress and the residual organic matter exhibited a different Al-binding capacity. The results revealed that most of the dissolved Al in raw water was strongly bound or polymeric colloidal, while percentages of monomeric Al ranging from 34% to 66% were present in the finished water. This was probably due to the particle aggregation produced by the water treatment.

Besides, PAC exhibited the least concentration for each kind of residual aluminum species implied in Fig. 6, especially the concentration of dissolved monomeric Al, followed by AlCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (in increasing order), which seemed consistent with the results appeared in the previous research [20].

### 3.3. Proportion of different residual aluminum speciation in the total residual aluminum

Aluminum present in Al-based coagulants and naturally present in raw water are transformed into various forms during water treatment. Proportion of different residual aluminum speciation in the total residual aluminum varied with pH for each kind of Al-based coagulants, as indicated in Table 2.

Table 2  
Proportion of different residual aluminum speciation in the total residual aluminum at different pH.

Proportion in the total Al (%)	Coagulants	pH					
		4.00	5.00	6.00	7.00	8.00	9.00
Proportion of total dissolved Al (%)	AlCl <sub>3</sub>	72.71	76.90	71.89	64.73	61.34	61.77
	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	84.11	77.29	75.41	57.82	76.47	79.47
	PAC	70.99	76.38	64.99	77.15	76.05	83.09
Proportion of dissolved monomeric Al (%)	AlCl <sub>3</sub>	63.69	62.99	55.26	47.77	44.22	46.94
	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	74.97	66.60	45.60	49.97	52.95	49.91
	PAC	55.72	57.51	19.34	3.30	13.44	34.47
Proportion of dissolved organically bound Al (%)	AlCl <sub>3</sub>	54.75	48.67	44.96	53.28	49.97	53.65
	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	33.89	33.59	32.54	46.77	68.26	70.21
	PAC	35.87	41.69	47.55	63.16	56.72	60.80
Proportion of dissolved organically bound monomeric Al (%)	AlCl <sub>3</sub>	0	0	0	0	0	0
	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	6.23	4.59	1.13	0	0	0
	PAC	3.00	2.67	1.28	0.74	1.38	0

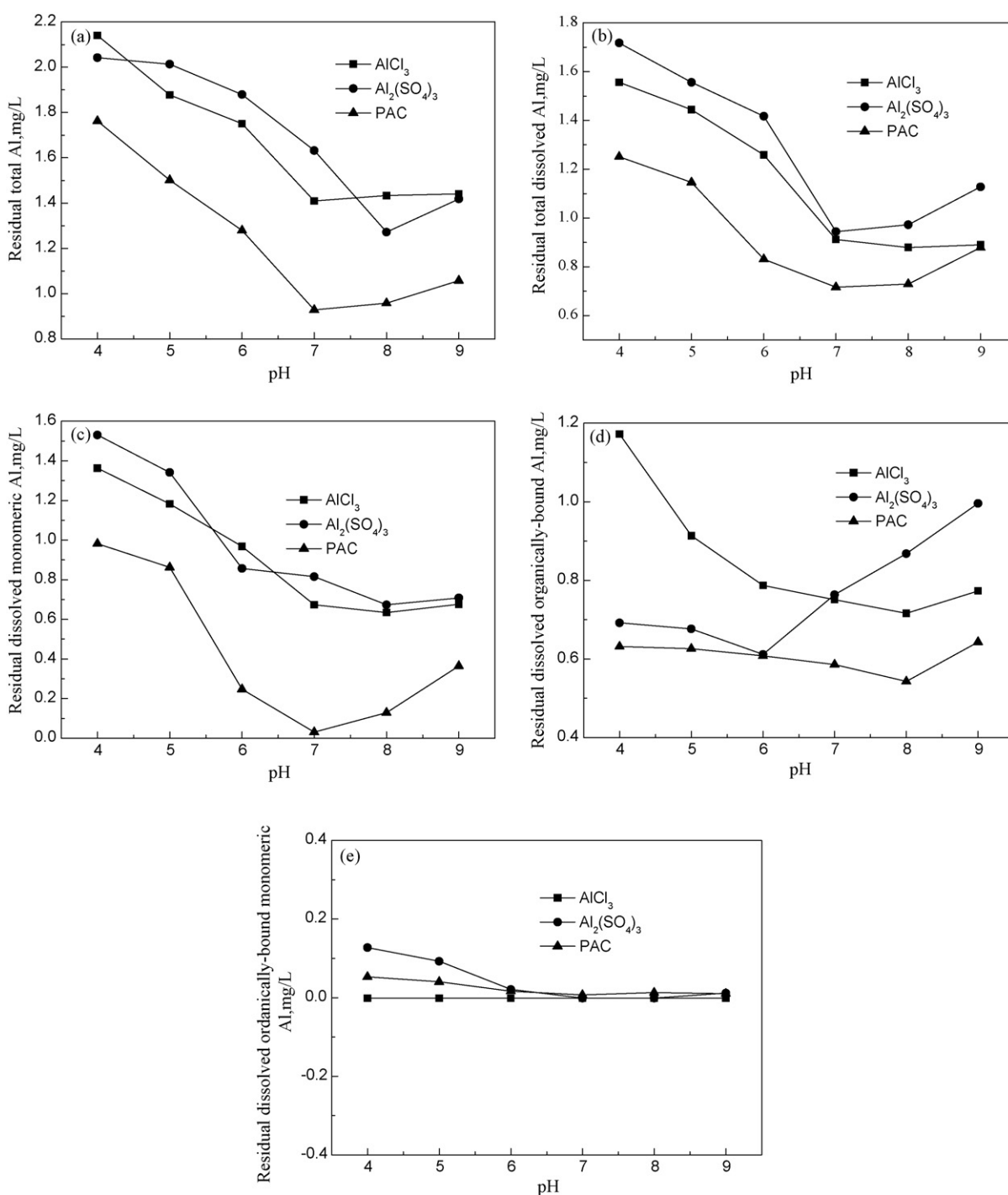


Fig. 6. Different residual aluminum speciation content of the three coagulants in HA-kaolin synthetic water treatment.

These results revealed that, for all the three coagulants, the majority of total residual aluminum existed in the form of total dissolved Al (accounting for about 60–80%), among which, dissolved organically bound Al was the predominant speciation. And, dissolved inorganically bound monomeric Al was the main component in the dissolved monomeric Al. Dissolved organically bound Al existed mostly in oligomers or complexes formed between Al and natural organic matter or polymeric colloidal materials in the water. Apart from these, PAC exhibited the least percentage of each kind of residual aluminum speciations in the total residual aluminum, especially the percentage of dissolved monomeric Al, followed by  $\text{AlCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  (in increasing order). This was con-

sistent with the results shown in Fig. 6, and mean that PAC could effectively reduce the concentration of dissolved monomeric Al, which had comparatively high toxicity to human health.

### 3.4. Residual aluminum ratio of the three Al-based coagulants

The use of Al salts coagulants may either increase or decrease Al concentration in the solution, depending on Al speciation in the source water, Al species in the coagulants, Al species transformation during water treatment and water treatment conditions [10]. The residual aluminum ratio present the total residual aluminum induced by the coagulants used and it is an important parameter of

**Table 3**  
Residual aluminum ratio of three Al-based coagulants at different pH.

Residual aluminum ratio (%)	pH					
	4.00	5.00	6.00	7.00	8.00	9.00
AlCl <sub>3</sub>	8.13	5.51	4.24	0.82	1.06	1.14
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	12.21	11.93	10.59	8.12	4.51	5.98
PAC	7.63	5.02	2.80	0.71	0.41	0.59

various coagulants. Table 3 shows the residual aluminum ratio of the three Al-based coagulants at different pH during the treatment of HA–kaolin synthetic water. The residual aluminum ratio can be calculated according to the following equation:

$$\text{residual aluminum ratio}(\%) = \frac{\text{residual total Al in the purified water}(\text{mg/L}) - \text{total Al in raw water}(\text{mg/L})}{\text{coagulant dosage}(\text{mg/L})} \times 100\% \quad (1)$$

It was found from the results shown in Table 3 that, along with the increase of pH, the residual aluminum ratio of the three coagulants decreased first and then increased at higher pH. When the initial pH was higher than 6.0, residual aluminum ratio of all the coagulants was relatively low, compared with those under the lower initial pH. And the residual aluminum ratio of the three coagulants varied according to the following order: Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> > AlCl<sub>3</sub> > PAC. For PAC, its residual aluminum ratio was the least among the three coagulants and varied little at an initial pH range between 7.0 and 9.0. The reasons can be explained by considering the pH variations. When pH was lower than 7.0, Al in the solution existed mostly in soluble and high-reactive form, which was hardly removed by coagulation and sedimentation process, and tended to remain in the purified water. While under the neutral and the weak alkaline ambience, the gel-Al(OH)<sub>3</sub> and suspended Al together were the predominant species and were conveniently removed during water treatment. It seemed reasonable to induce the lower residual aluminum ratio of the coagulants at an initial pH range from 6.0 to 8.0. Furthermore, correlated with the total residual aluminum concentration as shown in Fig. 6(a), residual aluminum ratio of PAC was obviously lower than those of the other two coagulants.

From the standpoint of coagulation performance together with the residual aluminum ratio, PAC was an excellent coagulant for the treatment of HA–kaolin synthetic water.

#### 4. Conclusions

The Al characterization (speciation) studies was conducted with respect to the treatment of HA–kaolin synthetic water with three Al-based coagulants – Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, AlCl<sub>3</sub> and PAC – and the effect of pH on the coagulation performance of the three Al-based coagulants were investigated as well as the residual aluminum speciation in this paper. The main conclusions from this work were listed as the following:

(1) The turbidity and HA removal efficiency increased obviously when initial pH is lower than 6.0 and then enhanced insignificantly or decreased slightly at the neutral and alkaline atmosphere. The turbidity removal performance of the three coagulants varied according to the following order: AlCl<sub>3</sub> > PAC > Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and it could reach about 94%, 91.5% and 90.5% for AlCl<sub>3</sub>, PAC, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, respectively. The HA removal efficiency could reach about 87%, 88.5% and 82% for AlCl<sub>3</sub>, PAC, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, respectively. The HA removal performance of PAC was better than that of AlCl<sub>3</sub> under the acidic atmosphere. The optimum pH for AlCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> could be determined between 6.0 and 7.0 but PAC showed stable HA and turbidity removal capacity with broad pH variation (5.0–8.0).

(2) The concentration of the tested several Al species represented the similar tendency, expressing as going down at the beginning and then going up later, except for the dissolved organically bound Al species, which showed significantly low concentration and changed little. For all the three Al salts coagulants, the majority of total residual aluminum existed in the form of total dissolved Al (accounting for about 60–80%), among which, dissolved organically bound Al was the predominant speciation. And, dissolved inorganically bound monomeric Al was the main component in the dissolved monomeric Al. Dissolved organically bound Al existed mostly in oligomers or complexes formed between Al and natural organic matter or polymeric colloidal materials in the water.

(3) PAC exhibited the least concentration for each kind of residual aluminum species as well as their percentage in the total residual aluminum, followed by AlCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (in increasing order). PAC can effectively reduce the concentration of dissolved monomeric Al, which had comparatively high toxicity to human health.

(4) Along with the increase of pH, the residual aluminum ratio of the three coagulants decreased first and then increased at higher pH. For PAC, its residual aluminum ratio was the least among the three Al salts coagulants and varied little at an initial pH between 7.0 and 9.0.

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