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The effect of total hardness and ionic strength on the coagulation performance and kinetics of aluminum salts to remove humic acid

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ABSTRACT

In order to investigate the effect of total hardness and ionic strength on the coagulation of natural organic matter, different Al coagulants – conventional Al salt ($AlCl_3$), polyaluminum chloride (PAC) and Nano polyaluminum chloride (Nano-PAC) – were used to treat humic acid (HA) in this study. The effects of total hardness and ionic strength on coagulation performance and coagulation kinetics of different aluminum were studied. Results show that when total hardness increases from 10 mg L^{-1} as $CaCO_3$ to 160 mg L^{-1} as $CaCO_3$, the highest HA removing efficiency of HA water decreases from 94.2% to 93.6%, while the highest HA removing efficiency in HA–kaoline water treatment increases from 94.3% to 95.3%. When ionic strength increases from 0.05 mol L^{-1} to 0.25 mol L^{-1}, the highest HA removing efficiency of HA water decreases from 92.3% to 88.4%, while the highest HA removing efficiency in HA–kaoline water increases from 88.1% to 85.6%. Nano-PAC, which is thought of as a highly efficient aluminum salt in other studies, does not perform well for removing HA from water.

1. Introduction

Humic acid (HA) is a natural organic matter, resulting from the weathering and/or the biodegradation of dead plants and animals [1]. The presence of HA in water presents a yellowish to brown color. Moreover, high affinity of HA for complexation with various pollutants including heavy metals and pesticides causes contamination of ground and surface water. In addition, HA will form toxic disinfection (chlorinated organic compounds including trihalomethanes) by-products which exhibit mutagenic properties during chlorination step in drinking water treatment [2]. Therefore, considerable attention has been focused on removing HA from water.

Coagulation is an essential method to remove contamination from water. In the past years, many kinds of inorganic aluminum salts have been developed including traditional Al coagulants (e.g. $AlCl_3$ and alum), prehydrolyzed aluminum coagulants (e.g. PAC and PAS), Nano-PAC coagulants and composite aluminum flocculants (e.g. PASC and PASS) [3,4]. Application of prehydrolyzed aluminum coagulants, especially PAC, is on the rise, particularly in China, Japan, Russia and Western Europe [5]. PAC contains species of superior quality and possesses structure that is fairly stable for further hydrolysis and solution chemistry, resulting in higher coagulation efficiency [6]. Recently the most widely used aluminum salts are Nano-PAC coagulants. Nano-PAC coagulants are constituted mainly of Al_{13} ($[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) [7,8]. Al_{13} has high positive charge and strong binding ability to aggregate [9]. These special properties of Al_{13} contribute to the superior behavior of Nano-Al coagulants in coagulation.

At present, aluminum salts have attracted much attention with regard to removing HA in water. However, there is no consensus on the selection of appropriate aluminum salts as given raw water are not uniform. Some researchers claimed that the Al_{13} content of coagulants positively correlates with coagulation efficiency [10]. However, other studies found that Al_{13} showed no significant improvement over alum on natural organic matter [11]. Therefore, it is necessary to investigate the coagulation properties of various aluminum salts on HA removal.

Coagulation efficiency not only depends on the characteristics of coagulants but also on the certain water quality parameters, such as pH, total hardness, and ionic strength. The interactions of coagulants and contamination are determined by the actual Al species in the coagulation process [12]. Although much attention has been paid to the effect of dosage and pH on the coagulation performance of various aluminum salts, the effect of total hardness and ionic strength has not been systemically studied. Therefore, the purpose of this study is to examine the effect of total hardness and ionic strength on coagulation performance and kinetics of aluminum salts in HA water and HA–kaolin water, and understand the relation of water quality parameters with the coagulation efficiency.

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2. Materials and methods

2.1. Coagulants

All the reagents used to prepare each coagulant were of analytical grade. Deionized water was used to make all solutions. The procedures of preparing each coagulant are as follows: (1) conventional Al salt ($AlCl_3$): directly dissolving 3.7 g $AlCl_3{\cdot}6H_2O$ to 100 mL deionized water; (2) polyaluminum chloride (PAC): adding 14 g $NaCO_3$ slowly into $AlCl_3$ solution (0.84 mol L^{-1}) under intense agitation. The temperature was kept at 70 °C by using recycling water bath [10]; (3) Nano-PAC: it was separated and purified from PAC by adding ethanol and acetone method [13]. Ethanol and acetone mixture ($V_{ethanol}/V_{acetone} = 1{:}4$) dripped to 20 mL PAC. After the solution turned to turbid, the precipitate was filtrated every 30 mL ethanol and acetone mixture until no precipitate was produced. These precipitates were marked as No. 1, No. 2, No. 3, etc. No. 3 precipitate was Nano-PAC.

Total Al concentrations (Al_T) were determined by ICP-AES (PerkinElmer, Optima 2000, UK). Basicity values (B, OH/Al molar ratios) were determined by titrimetric methods (Standard Method of the Chemical Industry of China) [23]. The Al species in $AlCl_3$, PAC and Nano-PAC were analyzed by a JEOL FX-90 Q NMR spectrophotometer with a 10 mm diameter sample tube. A diameter capillary (diameter = 1 mm) was inserted in the center of the sample tube. The 0.20 M $NaAl(OH)_4$ aqueous solution and an equal volume of heavy water (D_2O), which was used as the internal standard, were added to the capillary. The scanning frequency data was: pulse = 90°, pulse delay time = 0.1 s, data point = 8K, and the spectrum width = 200 ppm. There are three signals in the NMR spectra: the signal near 0.0 ppm represents the monomeric and dimeric aluminum species (denoted as Al_{mono}); the signal at 62.5 ppm represents the Al_{13} species (denoted as Al_{13}); and the signal at 80.0 ppm indicates the formation of $Al(OH)_4{}^-$ (the internal standard). The other Al species (denoted as Al_{other}) – large polymer aluminum species and solid-phase $Al(OH)_3$ – are calculated by the following equation.

$$Al_{other} = Al_{total} - Al_{mono} - Al_{13} \tag{1}$$

where Al_{other} is the concentration of the large polymer aluminum species and solid-phase $Al(OH)_3$ species, Al_{total} is the concentration of all aluminium species, Al_{mono} is the concentration of the monomeric and dimeric aluminum species, and Al_{13} is the concentration of the Al_{13} species.

The properties of coagulants used are summarized in Table 1. $AlCl_3$ can be considered as Al_{mono}, PAC can be considered as the mixture of various Al species, and Nano-PAC can be considered as the Al_{13} species.

Table 1
The properties of coagulants.

Coagulants	Al_T (mol/L)	Al_{mono} (%)	Al_{13} (%)	Al_{other} (%)
$AlCl_3$	0.017	98.5	1.5	0.0
PAC	0.91	32.5	31.8	35.7
Nano-PAC	0.076	0.4	96.7	2.9

2.2. Synthetic test water

HA in this study was purchased from Shanghai Chemical Co., China. Because HA is mixture of aromatic hydrocarbon, apparent molecular weight (AMW) distribution, which is an important parameter for HA, was determined by 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. Pure nitrogen gas (0.35 MPa) was used as the driving force. The HA was divided into four classes: >30 kDa, 10–30 kDa, 3–10 kDa and <3 kDa. The total organic carbon (TOC) and UV_{254} absorbance of each class were measured. The humic acid mainly consisted of high AMW constituents with fraction >30 kDa accounting for 80.1% of DOC and 87.5% of UV_{254} absorbance. Kaolin clay in this study was purchased from Tianjin Chemical Co., China. The median diameter of the kaolie clay is 8.37 μm.

The HA stock solution was prepared as follows: 1 g of HA was dissolved in 1000 mL deionized water that contained 4.2 g of $NaHCO_3$. Under this condition, the HA was soluble.

Two types of the synthetic test water were prepared in this study: (1) HA water: directly dissolving the HA stock solution (5 mL) in deionized water (500 mL); (2) HA–kaolin water: adding the HA stock solution (5 mL) and kaolin clay (10 mg) in deionized water (500 mL). The property of the synthetic test water used is as following: (1) HA water: TOC = 11.3 mg L^{-1}, pH 7.78; (2) HA–kaolin water: TOC = 12.3 mg L^{-1}, pH 7.32. Total hardness of test water was adjusted to different levels by $CaCl_2$ solids, and the ionic strength of synthetic water was adjusted from 0.05 mol L^{-1} to 0.25 mol L^{-1} by NaCl solids before coagulation text.

2.3. Coagulation test procedures

All coagulation experiments were conducted in 1.0 L plexiglass beakers by a conventional DC-506 laboratory stirrer jar-test apparatus. The synthetic test water (500 mL) was dosed with different coagulants. The synthetic test water was stirred rapidly at 120 rpm for 2 min during coagulant addition, followed by slow stirring at 40 rpm for 10 min and then 30 min of sedimentation. During the mixing period, HA aggregation was monitored using Photometric Dispersion Analyzer PDA 2000 (the Rank Brothers). Gregory [14] showed that the parameter of PDA would affect the results. In this study, the RMS gain was fixed at 20 and the DC gain fixed at 40, and the rate of flow through the PDA tubing was set at 20 mL/min. After sedimentation, supernatant samples were taken from a point 3 cm below the surface of the test water sample for analysis.

2.4. Analyses of PDA data

Particle aggregation in the coagulation step was monitored by Photometric Dispersion Analyzer PDA 2000 (the Rank Brothers). The size of flocs can be calculated by measuring the root mean square (RMS) value and direct current (DC) value of PDA 2000. Gregory [14] showed that the ratio of RMS to DC is directly proportional to the size of flocs. In this study, this ratio was denoted as FI.

Graphical representation of the data was provided by FI curves displaying the time dependent collection of FI values during the coagulation step [15]. The typical FI curve obtained from the experiments during this study is shown in Fig. 1. In Fig. 1, the initial growth region describes the stage where floc growth. The growth is noted as the linear portion of the region. The FI curve would reach a steady-state value immediately after the initial growth region. The steady-state region describes the balance between floc growth and breakage where the floc size distribution no longer changes with time [15].

In this study, two calculations were performed to analyze the data collected during the steady-state time interval. These calculations included a time-weighted average steady-state FI and a time-weighted variance of the steady-state FI.

The time-weighted average steady-state FI value was computed as

$$FI_A = \frac{\sum_{i=1}^{N}(FI_i \cdot time_i)}{\sum_{i=1}^{N} time_i} \tag{2}$$

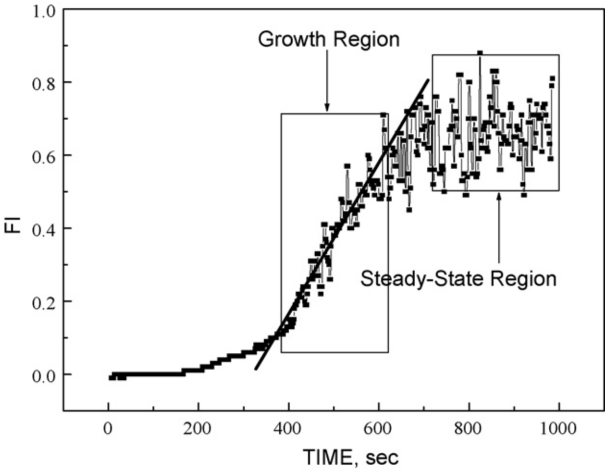

Fig. 1. FI distribution curve.

The time-weighted variance was calculated as

$$variance = \frac{\sqrt{\sum_{i=1}^{N}[(FI_i - FI_A)^2 \cdot time_i]/\sum_{i=1}^{N} time_i}}{FI_A} \times 100\% \qquad (3)$$

In Eqs. (2) and (3), FI_A is the time-weighted average steady-state FI value that represents the average size of flocs, FI_i is the FI value at *i* period, $time_i$ is the time of *i* period, *variance* is used to provide an indicator of the severity of breakup as well as a measure of floc size differences in steady-state region. It was thought that a smaller variance signified a tighter floc size distribution and an indication of a more homogeneous, dense, and less porous floc structure in the sampled reactor region.

3. Results and discussion

3.1. Coagulation optimization

Through jar testing procedures it was found that the highest HA removal efficiency was gotten at the same dosage when the same coagulation was used to treat HA water or HA–kaolin water. The optimum dosages of $AlCl_3$, PAC and Nano-PAC were 7 mg L^{-1}, 13 mg L^{-1}, and 8 mg L^{-1}, respectively. The highest HA removal efficiency was optimum pH was gotten at pH 6 for all tested coagulants. This pH value corresponds with the reported pH optimums for Al coagulants [16]. The highest HA removal efficiency were 90%, 93%, 95% in HA water, and 92%, 94%, 95% in HA–kaolin water for $AlCl_3$, PAC and Nano-PAC, respectively.

3.2. Effect of total hardness on coagulation performance and coagulation kinetics of HA water treatment

Fig. 2 shows HA removal efficiency of aluminum coagulations at different total hardness levels. The removal of HA by $AlCl_3$ and Nano-PAC is related to the total hardness. It was found that removal efficiency decreases with increasing total hardness. Removal efficiency of PAC was independent of the total hardness. For a given total hardness, HA removal efficiency of PAC is the highest and HA removal efficiency of $AlCl_3$ is the lowest.

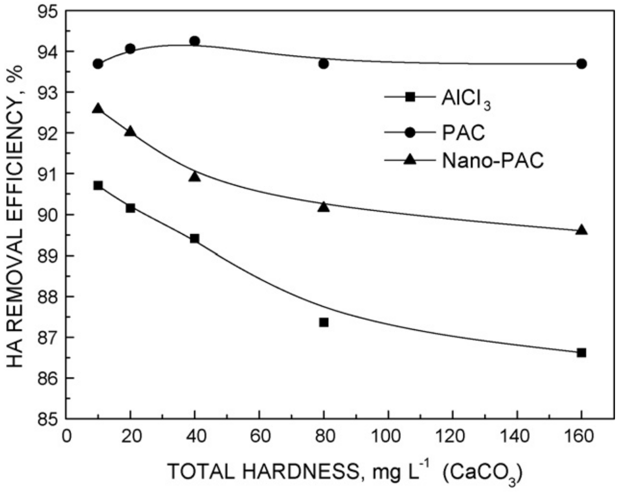

Fig. 2. Effect of total hardness on coagulation performance in HA water treatment.

Usually, water can be classified as very soft water (total hardness < 89 mg L^{-1} as $CaCO_3$), soft water (90 mg L^{-1} as $CaCO_3$ < total hardness < 159 mg L^{-1} as $CaCO_3$), medium hard water (160 mg L^{-1} as $CaCO_3$ < total hardness < 229 mg L^{-1} as $CaCO_3$), fairly hard water (230 mg L^{-1} as $CaCO_3$ < total hardness < 339 mg L^{-1} as $CaCO_3$), hard water (340 mg L^{-1} as $CaCO_3$ < total hardness < 534 mg L^{-1} as $CaCO_3$) and very hard water (total hardness > 535 mg L^{-1} as $CaCO_3$) according to total hardness. In this study, HA removal efficiency was investigated in very soft water and medium hard water, because HA exists in surface water whose total hardness is lower 200 mg L^{-1} as $CaCO_3$. The coagulation kinetics at total hardness = 10 mg L^{-1} and 160 mg L^{-1} as $CaCO_3$ are shown in Fig. 3. At 10 mg L^{-1} as $CaCO_3$ total hardness, the flocs formed by Nano-PAC were much larger than those formed by $AlCl_3$ and PAC. However, *variance* of the flocs

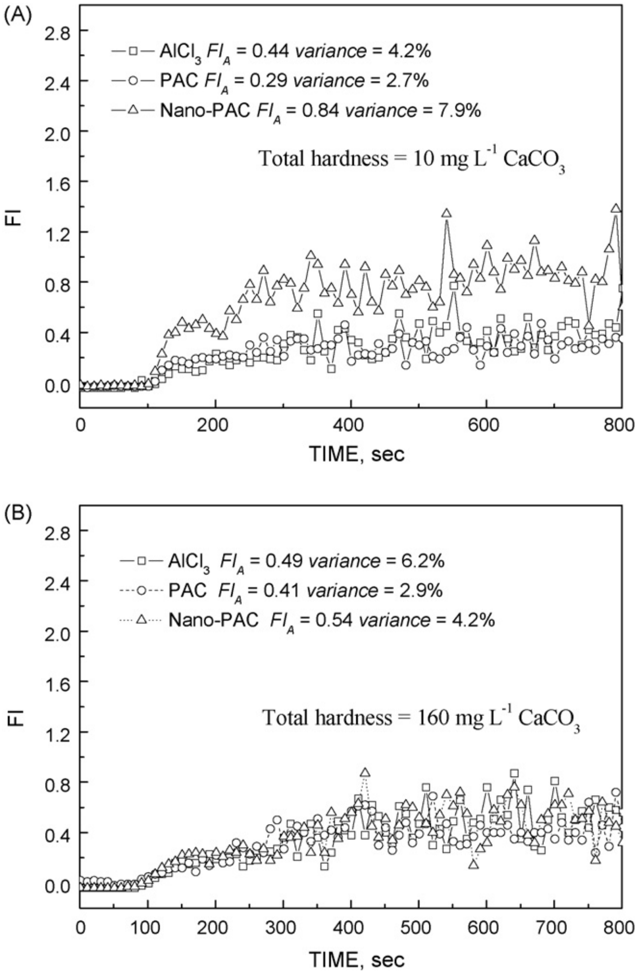

Fig. 3. Effect of total hardness on coagulation kinetics in HA water treatment.

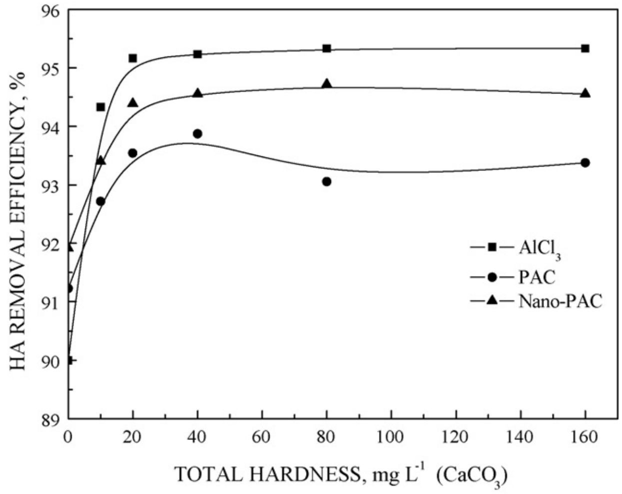

Fig. 4. Effect of total hardness on coagulation performance in HA–kaoline water treatment.

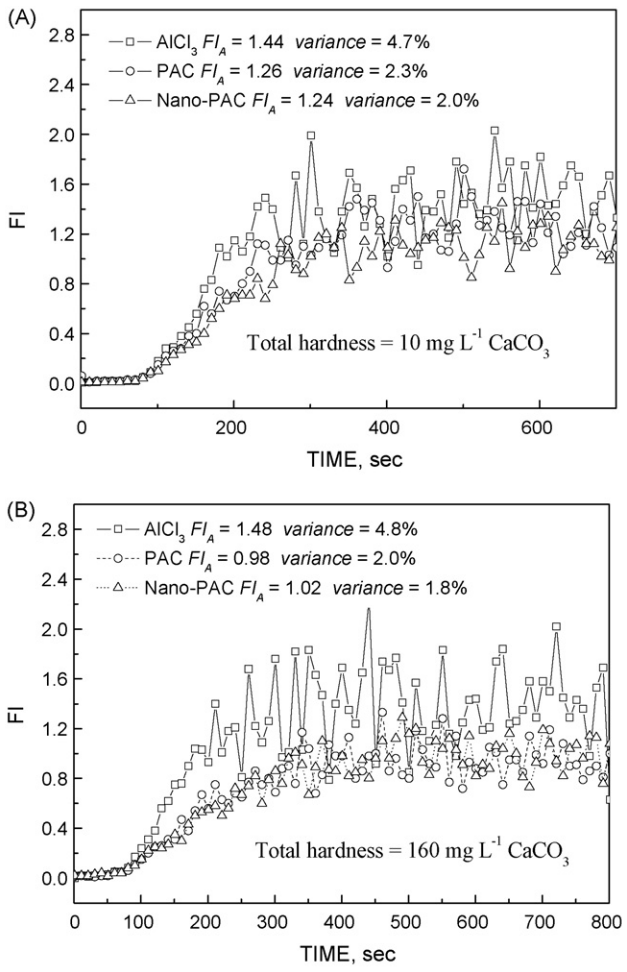

Fig. 5. Effect of total hardness on coagulation kinetics in HA–kaoline water treatment.

formed by Nano-PAC is larger than others. It was thought that a larger variance signified a wider floc size distribution and an indication of a less homogeneous, dense and more porous floc structure in the sampled reactor region [17]. This indicated that although the floc size in Nano-PAC treatment was the largest, the flocs were loose and weak at total hardness 10 mg L^{-1} as $CaCO_3$. This may be the reason for the lower efficiency of Nano-PAC. The size of flocs formed by $AlCl_3$ and PAC were similar, but the FI_A *variance* of PAC was about half that of $AlCl_3$. Therefore, the efficiency of PAC was higher than that of $AlCl_3$.

When total hardness increased to 160 mg L^{-1} as $CaCO_3$, the sizes of flocs formed by different aluminum coagulants were similar. Compared to Fig. 3a, it can be found that FI_A of the tested coagulants was about 0.5 at total hardness 160 mg L^{-1} as $CaCO_3$ and similar to that of $AlCl_3$ and PAC at total hardness 10 mg L^{-1} as $CaCO_3$. However, the *variance* of $AlCl_3$ at total hardness 160 mg L^{-1} as $CaCO_3$ was larger than that at total hardness 10 mg L^{-1} as $CaCO_3$. This means that the flocs formed by $AlCl_3$ are more loose and porous when the total hardness increases, which would lead to worse settling ability of flocs at high total hardness. Therefore, the efficiency of $AlCl_3$ decreases with increasing total hardness. When total hardness increases from 10 mg L^{-1} as $CaCO_3$ to 160 mg L^{-1} as $CaCO_3$, FI_A and the *variance* of PAC increases from 0.49 to 0.51 and from 2.7 to 2.9, respectively. It was not significant enough to affect the coagulation performance of PAC. The efficiency of PAC is steady with increase in total hardness. For Nano-PAC, although the *variance* decreases from 5.9 to 4.2, FI_A decrease from 0.84 to 0.54 when total hardness increases to 160 mg L^{-1} as $CaCO_3$. Thus, HA removal efficiency by Nano-PAC also decreases with increasing total hardness.

3.3. *Effect of total hardness on coagulation performance and coagulation kinetics of HA–kaolin water treatment*

Fig. 4 shows the influence of total hardness on the coagulation efficiency of HA–kaolin water. The influence of total hardness was similar for all tested coagulants. The coagulation efficiency increased with increasing total hardness. When total hardness was above 20 mg L^{-1} as $CaCO_3$, there was a negligible increase in coagulation efficiency. As total hardness exceeds 10 mg L^{-1} as $CaCO_3$, the coagulation efficiency increased in the following order: $AlCl_3$ > Nano-PAC > PAC.

Compared with Fig. 2, the effect of total hardness on coagulation performance of HA water is different from that of HA–kaolin water. This is due to the characteristics of HA. HA is composed of carboxyl group, phenolic hydroxyl group, carbonyl group and amino group ect. Among them, the carboxyl group and phenolic hydroxyl group are the acidic functional groups of HA. Typically, these acidic functional groups of HA are deprotonated in neutral or acidic environment, and the deprotonated acidic functional groups can interact with metal ions and metal hydrated oxide by the reactions such as ion exchange [18]. This indicates that HA not only reacts with inorganic coagulants to form complex but also reacts with metal ion in water [19]. On one hand, this characteristic would lead to competition for the active groups between inorganic coagulants and metal ion, on the other hand, the negative charge on HA surface would decrease by binding some metal ion with the positive charge.

In HA water HA is removed by reacting with aluminum coagulants to form the complex mater, which deposits easily from water. Since a competition between Al(III) and Ca^{2+} leads to decreasing the reaction between HA and Al(III), the coagulation efficiency decreases with increasing total hardness in HA water treatment. However, in HA–kaolin water HA can be adsorbed on the surface of kaolin to form HA–kaolin complex. This HA–kaolin complex is removed mainly by charge neutralization and sweeping of coagulants, which is major coagulation mechanism. Because the negative charge of HA–kaolin complex drops by binding Ca^{2+}, it is easier to remove the HA–kaolin complex for HA–kaolin water with high total hardness. Thus, the coagulation efficiency increases with increasing total hardness in HA–kaolin water treatment.

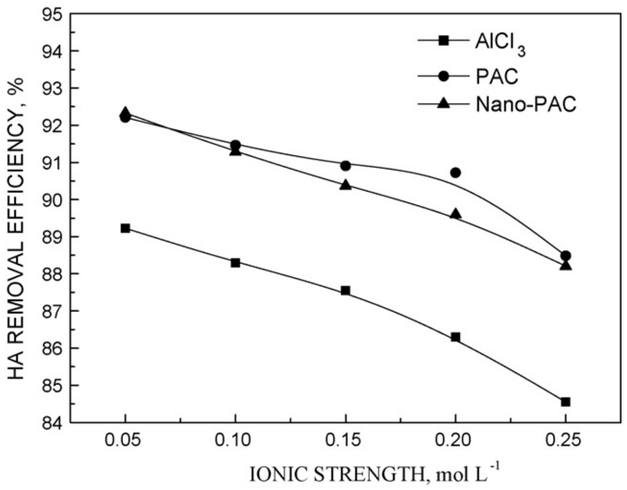

Fig. 6. Effect of ionic strength on coagulation performance in HA water treatment.

Fig. 5 shows the coagulation kinetics of HA–kaolin water at different total hardness levels. Although the *variance* of $AlCl_3$ is larger than that of PAC and Nano-PAC, the floc size of $AlCl_3$ is the largest (higher than 1.4). Thus, the efficiency of $AlCl_3$ is the highest when total hardness ranges from 10 mg L^{-1} as $CaCO_3$ to 160 mg L^{-1} as $CaCO_3$. The flocs formed by PAC were similar to those formed by Nano-PAC, while the *variance* of PAC is larger than Nano-PAC. Therefore, the efficiency of PAC is the lowest for the HA–kaolin. Compared with HA water, one distinct difference should be noted: for a given coagulant the floc size in HA–kaolin water is larger than that in HA water, and the *variance* in HA–kaolin water is smaller than in HA water. It shows that kaolin in water is favorable to HA removal by coagulation.

HA are more readily adsorbed on the precipitate rather than the hydroxide [20]. Moreover, the particle could readily adsorb HA [18]. Lin found that the presence of HA in kaolin suspension did not change the structure of flocs nor decrease the strength of the formed flocs. This indicates that when kaolin is added to HA water, the coagulation process of kaolin determines the coagulation kinetics of removing HA. Kaolin is removed by bridging and charge neutralization, while HA is removed by complexation. The strength of flocs formed by bridging and charge neutralization is higher than those formed by complex. For a given shear force, the floc size increases with increasing the floc strength [21]. Therefore, the flocs in HA–kaolin water treatment are larger than those in HA water treatment.

3.4. *Effect of ionic strength on coagulation performance and coagulation kinetics of HA water treatment*

Inevitably there are various inorganic ions in natural water that affect the coagulation performance of aluminum salts. In this study, ionic strength was used to investigate the effect of inorganic ions on HA removal efficiency, and the results were shown in Fig. 6. The removal of HA is related to ionic strength of solution, and the ionic-variation trends were similar for all the coagulants. The removal efficiency decreased with increasing ionic strength for $AlCl_3$, PAC and Nano-PAC. When ionic strength exceeded 0.05 mol L^{-1}, the removal efficiency of PAC was the highest, and the removal efficiency of $AlCl_3$ was the lowest.

The coagulation kinetics of aluminum coagulants in HA water treatment are shown in Fig. 7. For a given ionic strength, $AlCl_3$, PAC and Nano-PAC yielded flocs with similar size and different *variance*. For example, the *variance* of $AlCl_3$ is 24.4, while the *variance* of Nano-PAC is only 1.43. This indicates Nano-PAC yields more dense flocs than other aluminum salts, which is convenient to removing HA from water. This is one reason for the higher efficiency of Nano-PAC.

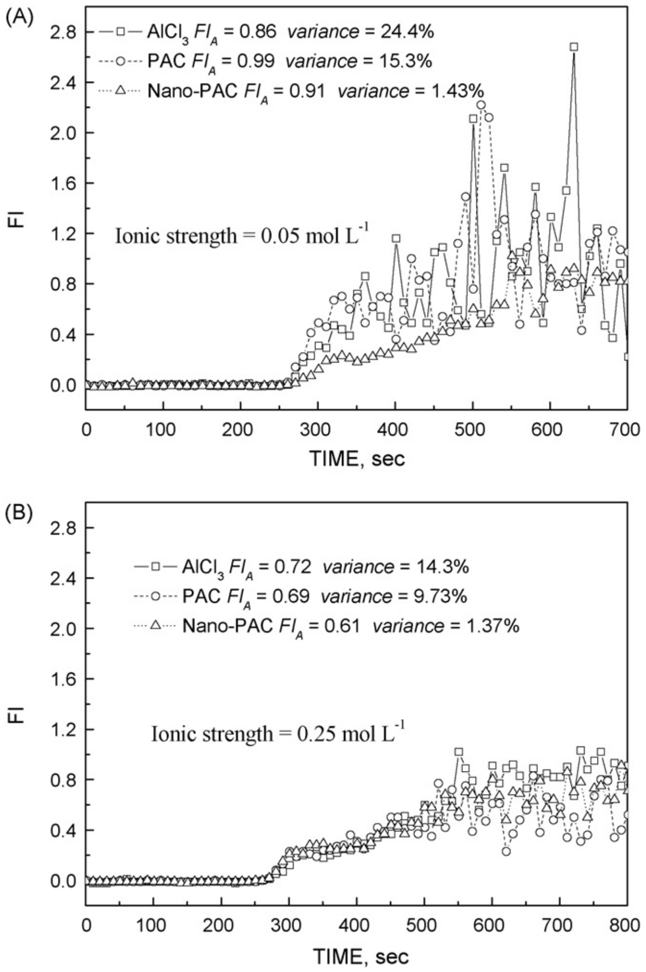

Fig. 7. Effect of ionic strength on coagulation kinetics in HA water treatment.

3.5. *Effect of ionic strength on coagulation performance and coagulation kinetics of HA–kaoline water treatment*

Fig. 8 shows the effect of ionic strength on HA removal efficiency in HA–kaolin water treatment. For the tested coagulants, HA removal efficiency decreases with increasing ionic strength, which is in agreement with the results in HA water treatment. According to ionic strength effect, effective concentration of ion would decrease with increasing ionic strength because ion activity decreases [22]. Aluminum salts remove HA by various charged hydrolysis products, and the activity of these hydrolysis products would decrease with increasing ionic strength of the water. Therefore, HA removal efficiency of aluminum salts decreases with increasing ionic strength in HA water treatment and HA–kaolin treatment.

For given ionic strength HA removal efficiency of $AlCl_3$ was the highest, and for Nano-PAC was the lowest. The active aluminum species in $AlCl_3$, PAC and Nano-PAC are different from each other. $AlCl_3$ coagulates contamination mainly by Al_{mono}, and PAC removes contamination by the mix of various Al species. Nano-PAC depends on the Al_{13} species. Among these species, the charge of Al_{13} is the highest. Since ionic strength only influence the activity of charged ion according to ionic strength effect, Al_{13} with the highest charge would lose more activity than other aluminum species

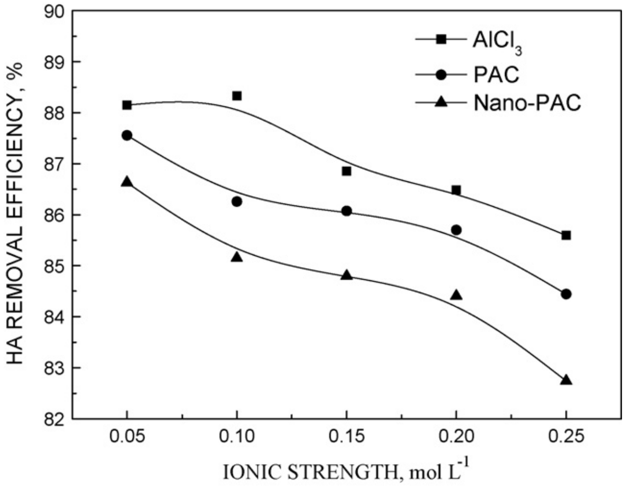

Fig. 8. Effect of ionic strength on coagulation performance in HA–kaoline water treatment.

with increasing ionic strength. This may be the reason for the lowest efficiency of Nano-PAC. Compared to Fig. 6, it can be found that the performance of different aluminum salts is different for treating HA water and HA–kaolin water. The efficiency of Nano-PAC in HA water treatment is higher than $AlCl_3$, while in HA–kaolin water treatment, the efficiency of Nano-PAC is the lowest.

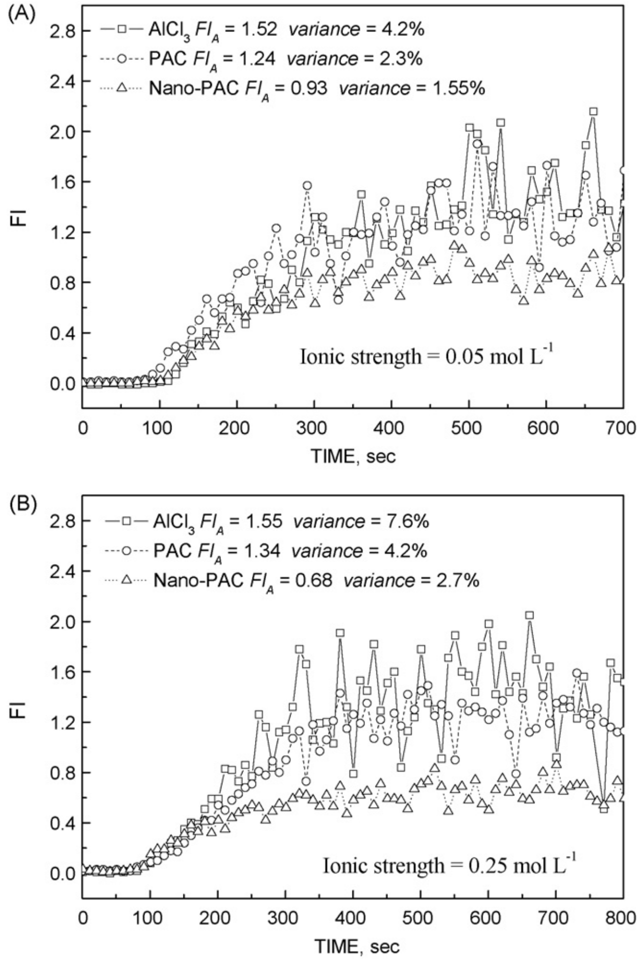

Fig. 9. Effect of ionic strength on coagulation kinetics in HA–kaoline water treatment.

Fig. 9 shows the coagulation kinetics of HA–kaolin water at different ionic strength. Although the floc size of $AlCl_3$ and PAC is constant when ionic strength increased from 0.05 mol L^{-1} to 0.25 mol L^{-1}, the *variance* of $AlCl_3$ and PAC increased from 4.2 to 7.6 and from 2.3 to 4.18, respectively. Therefore, HA removal efficiency decreases due to decrease of settlement ability of flocs when ionic strength increases. For Nano-PAC, the floc size decreased from 0.93 to 0.68 and the *variance* increased from 1.55 to 2.71. Thus, HA removal efficiency of Nano-PAC decreases when ionic strength increases. Compared to Fig. 7, the flocs formed in HA–kaolin water are more dense than that in HA water, which is in agreement with the results in HA water treatment.

4. Conclusions

(1) For treating HA water the efficiency of PAC is the highest, and HA removal efficiency of $AlCl_3$ is the lowest. The efficiency of aluminum salts decreases with increasing total hardness or ionic strength, while the removal efficiency for PAC is independent of the total hardness. When total hardness increases from 10 as $CaCO_3$ to 160 mg L^{-1} as $CaCO_3$, $AlCl_3$ yields more loose flocs, while the properties of flocs formed by PAC remain constant. Nano-PAC yields the smallest and densest flocs. When ionic strength increases from 0.05 mol L^{-1} to 0.25 mol L^{-1}, the floc size and the variance decrease for the tested aluminum salts.

(2) The order is as follows of the coagulation efficiency in HA–kaolin water with different total hardness and different ionic strength: $AlCl_3$ > Nano-PAC > PAC and $AlCl_3$ > PAC > Nano-PAC, respectively. The coagulation efficiency increases with increasing total hardness or decreasing ionic strength. When total hardness increases from 10 mg L^{-1} to 160 mg L^{-1} as $CaCO_3$, or ionic strength increases from 0.05 mol L^{-1} to 0.25 mol L^{-1}, $AlCl_3$ and PAC yield more loose flocs, and the flocs formed by Nano-PAC is larger and looser.

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