Effects of Al_2O_3 and TiO_2 on the coagulation process by $\text{Al}_2(\text{SO}_4)_3$ (AS) and poly-aluminum chloride (PACl) in kaolin suspension

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ABSTRACT

More and more nanoparticles may be found in the aquatic environment. Effects of different nanoparticles (nano- Al_2O_3 and nano- TiO_2) on the coagulation process in kaolin suspension (with or without humic acid) were investigated. The results indicated that when the pH was 7.0 in kaolin suspension, the strength factor with the presence of TiO_2 increased from 28.79% to 48.69% and when the concentration of TiO_2 was larger than 1.6 mg/L, the strength factor decreased to 23.39%. The removal efficiencies for Al_2O_3 were 58.27%, 62.73% and 47.3% under pH 6.0, 7.0 or 8.5. The removal efficiencies for TiO_2 were 38.12%, 52.25% and 27.19%. When the concentration of DOC was 2.5 mg/L under pH 7.0, the recovery factor increased from 54.55% to 62.65% with increasing concentration of Al_2O_3 from 0.0 mg/L to 2.0 mg/L, and it increased from 54.55% to 67.74% for TiO_2 . PACl produced larger flocs, and this may be caused by higher charge neutralization ability and the electrostatic patch effect. The removal efficiency for TiO_2 decreased from 52.25% to 22.13% with increasing concentration of DOC from 0 mg/L to 7.5 mg/L. The removal efficiency for Al_2O_3 decreased from 62.73% to 32.12%.

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1. Introduction

With the development of nanotechnologies, more and more nanoparticles may be found in the aquatic environment [1]. Commercial TiO_2 powders have been widely used as a white pigment in the paint, and paper industries for their unique performance, such as outstanding refractive index, insolubility in alkaline and acidic solutions. TiO_2 is expected to continue to grow in the next decade, and may eventually substitute the bulk form [2]. Al_2O_3 is one of the most cost effective, strong and stiff materials in the family of engineering ceramics which has high corrosion resistance and good thermal properties. Considering the wide range of industrial applications of Al_2O_3 , their release into the environment and water would be inevitable [3]. Titanium dioxide could induce a significant reduction in mitochondrial dehydrogenase activity in human lymphocyte cells [4]. The negative size effect of NPs was clearly demonstrated by researchers who investigated various sizes of NP_5 [5,6]. Dissolved and surface-bound humic acid may affect the toxicity of TiO_2 nanoparticles [7].

Coagulation still is a widely applied process for removing particles and organic matter in Drinking Water Treatment Plant and it has played an important role in water treatment for decades [8,9]. Chuang et al. have applied poly-aluminum chloride (PACl) as the coagulant and cationic polyacrylamide as the flocculant to remove nanoparticles in the CMP wastewater [10]. But the effects

of nanoparticles on coagulation process were not investigated. In this study, we added nano- Al_2O_3 and nano- TiO_2 particles to kaolin solution to investigate the effects of nanoparticles on the coagulation process. The concentration of HA was also an important factor in the coagulation process [11–14]. The Al-based coagulants ($\text{Al}_2(\text{SO}_4)_3$ (AS) and PACl) were used as coagulants, and the floc size, fractal dimension and zeta potential were measured to understand the mechanism [15]. Generally, coagulation of colloids and particles by hydrolyzing coagulants is explained in terms of three distinct mechanisms: charge neutralization, bridging and sweep flocculation [16]. Yan et al. [17] demonstrated that the flocs formed by charge neutralization through a suppression of the electric double layer (EDL) had weak physical particle–particle bonds such as vander Waals force. Researchers also have found that flocs become more compact under exposure to increasing shear as they break at their weak points and rearrange into more stable and tight structure [18].

The breakage and re-growth of flocs has been studied by many researchers [14,19,20]. Flocs breakage and recovery should also be taken into consideration for overall process and have been the subject of in-depth research in recent years [21,22]. Yukselen and Gregory found that only limited re-growth of flocs occurred for alum and PACl, which indicated a significant irreversibility of flocs [23]. Some other researchers considered that the flocs formed by charge neutralization could be fully reformed. Some researchers have focused on the differences between breakage and re-growth nature of HA flocs coagulated with PACl.

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The major objective of this study is to investigate the effects of nanoparticles on the coagulation process under different coagulation conditions, including various solution pH values and the concentration of HA. The effects of ionic strength on coagulation process were also investigated. In order to better understand the mechanisms, two different nanoparticles were used. AS was used as coagulant, and PACI was used to compare with AS.

2. Materials and methods

2.1. Materials

The commercial humic acid (HA) was purchased from Sigma. The stock solution of HA was prepared by dissolving 1.0 g HA in 0.01 mol/L NaOH solution under continuous stirring for 24 h. After that, the solution was filtered through 0.45 μm membrane and stored in refrigerator for later use [24]. The final DOC of the prepared HA stock solution was 250 mg/L based on total organic carbon analysis.

Kaolin clay was used as the model suspension. 10 g kaolin was dispersed in 2 L of de-ionized water in a high-speed blender. In order to obtain full dispersion it was necessary to raise the pH of the suspension to about 7.5, which was achieved by adding 0.1 mol/L NaOH solution. After blending for 1 h, the suspension was allowed to stand for 3 h. Then the upper 1 L suspension was decanted. The stock suspension was diluted to give the suspensions in the coagulation process.

TiO₂ and Al₂O₃ particles were purchased from Beijing DK nanotechnology Co., Ltd. The nanoparticles were characterized by TEM. The images in Fig. 1 showed that the pure TiO₂ with a diameter of 40 nm, and the Al₂O₃ had a smaller diameter (30–40 nm). The two particles have different charges under the same pH values (Fig. S1). This may cause different effects on the characteristics of flocs. The iso-electric point (IEP) of Al₂O₃ was at pH 8.5, so the charges on the Al₂O₃ particles were positive in all experiment conditions. The iso-electric point of TiO₂ was at pH 4.8, and the charges on the TiO₂ particles were negative in all experiment conditions.

2.2. Water samples

Water samples used in this study were prepared by dissolving HA and kaolin stock solution, and added different concentration of TiO₂ and Al₂O₃ particles. All water samples were stirred for 12 h before the addition of coagulant. The water samples were added 5.0 mmol/L NaNO₃ and 4.0 mmol/L NaHCO₃ to provide ionic strength and alkalinity. Characteristics of water samples in kaolin suspension under pH 7.0 are summarized in Table 1.

The results in Table 1 indicated that the nanoparticles had significant effects on the kaolin particle size. Because the iso-electric point for Al₂O₃ is 8.5, it has positive charges under pH 7.0. The positive particles can be adsorbed on the negative surface of kaolin particles, and bridge the particles together. This effect is not significant for the negative charged TiO₂. Table 1 also showed that the turbidity increased more rapidly with increasing concentration of TiO₂ than Al₂O₃. When the concentration of Al₂O₃ was 1.2 mg/L, the zeta potential became positive (2.3 mv). The TiO₂ particles decreased the zeta potential from −30.1 mv to −49.5 mv with increasing the concentration.

In order to investigate the effects of HA on the coagulation process, we added different amounts of HA solution to the kaolin suspension, and the zeta potentials under different concentration of DOC (mg/L) were summarized in Fig. S2.

The addition of HA could significantly decrease the zeta potential from −30.1 mv to −47.8 mv with increasing concentration of DOC from 0 mg/L to 2.5 mg/L (Fig. S2). But when the concentration of DOC was larger than 2.5 mg/L, the concentration of DOC had no significant effects on the zeta potential. Researchers had showed that the presence of small concentration of DOC resulted in charge reversal at low pH and an increase negative net total particle charge at pH > IEP. The adsorption and zeta potential are consistent, since only the adsorbed HA is expected to affect zeta potential [13]. This trend was also existed when there were nanoparticles in the solution which was showed in Fig. S3.

The results in Fig. S3 indicated that the addition of HA solution could decrease the zeta potential of suspension at lower concentration (1.5 mg/L and 2.5 mg/L), but when the concentration of DOC exceeded 3.5 mg/L, the zeta potential was almost the same. As can be seen, HA causes the water samples with Al₂O₃ to under charge reversal. At high concentration of DOC, the particles undergo charge reversal and therefore particle stability is largely controlled by repulsive electrostatic interactions between adsorbed HA layers.

In order to investigate the interaction between nanoparticles and HA molecules, we investigated the zeta potential of HA solution (DOC 2.5 mg/L), HA (DOC 2.5 mg/L) + TiO₂ (2.0 mg/L) solution, HA (DOC 2.5 mg/L) + Al₂O₃ (2.0 mg/L) solution under different pH. The results in Fig. S4 indicated that the nature of TiO₂ particles was affected by pH [25–28]: the surface was positively charged in acid condition but negatively charged in basic condition. The positive charged TiO₂ surface hydroxyls were mainly TiOH₂⁺ and negative charged TiO₂ surface hydroxyls were TiO[−] in acidic and basic solution respectively [29]. The HA molecules became more negatively charged as pH value increased due to ionization of carboxylic and phenolic groups of HA. The dissociation of carboxylic groups usually takes place at pH > 4 whereas the phenolic groups undergo

Fig. 1. TEM images of TiO₂ and Al₂O₃ used in this study.

Table 1

Characteristics of water samples used in this study.

Concentration of nanoparticles (mg/L)	0.0	0.2	0.4	0.8	1.2	1.6	2.0
<i>Kaolin suspension</i>							
<i>Zeta potential (mV)</i>							
Al ₂ O ₃	−30.1	−20.1	−10.2	−8.1	2.3	10.2	13.5
TiO ₂	−30.1	−33.2	−38.7	−42.3	−45.4	−45.8	−49.5
<i>Turbidity (NTU)</i>							
Al ₂ O ₃	29.7	30.2	31.3	32.5	33.8	34.8	35.1
TiO ₂	29.7	33.8	36.3	40.2	50.7	55.2	66.3
<i>Particle size (μm)</i>							
Al ₂ O ₃	2.208	2.214	2.387	2.458	2.517	2.67	2.845
TiO ₂	2.208	2.248	2.257	2.261	2.247	2.25	2.26

dissociation at pH > 8. The zeta potential curve evidenced that the main factor that affected the adsorption extent was of electrostatic origin as agreed by many researchers. At pH < 5, negatively charged HA would adsorb on positively charged TiO₂ particles due to the electrostatic attraction. At pH > 5, both negatively charged HA and TiO₂ particles generated a strong electrostatic barrier which would inhibit the adsorption process. However HA adsorption did occur above PZC suggested that adsorption other than the electrostatic interaction between HA and TiO₂ particles must exist. The similar trend was also existed in HA and Al₂O₃ system. Researchers [30] observed that the surface of nanozero-valent iron (NZVI) used for groundwater remediation can be modified via coating with organic stabilizers. NOM is likely to coat TiO₂ nanoparticles discharged into the aquatic environment [31]. In addition, researchers [32,33] showed that anions increased the negative charge density adjacent to the mineral particle surface and could cause a shift in the position of the shear plane further away from the surface.

In order to investigate the effects of ionic strength, we adjusted the ionic strength to 0.5 mmol/L, 1.0 mmol/L, 3.0 mmol/L, 5.0 mmol/L, 7.0 mmol/L, 10.0 mmol/L, 20.0 mmol/L by adding different concentration of NaNO₃ and the alkalinity was also provided by 4.0 mmol/L NaHCO₃. Water samples were prepared by diluting from kaolin stock solution. The coagulation pH value was adjusted to 7.0 before the addition of coagulant. AS was used as coagulant.

2.3. Chemicals and coagulants

All reagents used were of analytical grade and de-ionized water was used in all solutions. The AS coagulant was prepared by dissolving a certain amount of Al₂(SO₄)₃·18H₂O to de-ionized water. PACl was diluted from commercial PACl. Initial alum speciation of coagulant was determined by the ferron method [34]. The results were summarized in Table 2.

2.4. Jar tests and removal efficiency for nanoparticles

Coagulation experiments were conducted in 500 ml beakers using conventional jar-test apparatus at room temperature. Samples were mixed at 250 r/min for 30 s, and they were mixed at 200 r/min for 90 s after coagulants addition to provide rapid mixing, and then the speed was reduced to 40 r/min for 10 min

to provide coagulation. After 30 min of settling, the supernatant from each jar test was withdraw from the beakers and analyzed for residual turbidity and the removal efficiency for nanoparticles.

Initially, coagulation experiments were performed to ascertain the optimum dosage for turbidity removal under different conditions. The initial pH of kaolin solution (29.7 mg/L) was adjusted at 7.0 by 0.1 mol/L HCl and 0.1 mol/L NaOH solutions. The residual turbidity and zeta potential for AS and PACl were comparatively investigated.

The kaolin particles used in this study were digested by microwave. The solutions were measured by an inductively coupled plasma mass spectrometer (ICP-MS, ICAP Q, Thermo Fischer). The different components are summarized in Table 3. The kaolin had Al and Ti elements. After the coagulation, the finished water was also digested. The removal efficiency for two nanoparticles can be measured through the ratio of SiO₂/Al₂O₃ and SiO₂/TiO₂. The concentration of nanoparticles used in this study was 2.0 mg/L for two nanoparticles. AS was used as coagulant, and the pH was adjusted to 6.0, 7.0 or 8.5.

2.5. Floc formation, breakage and re-growth

After 10 min of slow mixing period, the mixing speed was increased to 200 rpm for 5 min for breakage, followed by another slow mixing at 40 rpm for 10 min for flocs to reform. The dynamic floc sizes were measured using laser diffraction Mastersizer 2000. The suspension was monitored through optical unit of Mastersizer and back into the jar by a peristaltic pump. In order to investigate the effect of solution pH on floc breakage and re-growth, the pH values were adjusted to 6.0, 7.0 or 8.5. In addition, a series of jar tests were conducted to investigate the effect of concentration of TiO₂ or Al₂O₃ on floc strength and recovery ability.

2.6. Floc strength and recovery factors

Strength factor (S_f) and recovery factor (R_f) are well-established parameters for describing floc strength and recovery ability and can be calculated as follows [34]:

$$S_f = \frac{d_2}{d_1} \quad (1)$$

$$R_f = \frac{d_3 - d_2}{d_1 - d_2} \quad (2)$$

Table 2

Alum speciation of coagulant.

	Al _a (%)	Al _b (%)	Al _c (%)
AS	93.78	6.22	0
PACl	31.33	26.09	42.58

Table 3

Components of the kaolin particles used in this study.

Components	SiO ₂	Al ₂ O ₃	TiO ₂	CaO	Fe ₂ O ₃	MgO
Content (%)	55.18	42.19	0.24	0.27	0.97	0.21

The d_1 , d_2 , d_3 are the sizes of floc in the steady phase before breakage, after the breakage period and after the re-growth to another steady phase, respectively.

2.7. Fractal dimension

A brief description is given here of the widely used light scattering method for the determination of aggregate mass fractal dimension [24]. The technique involves measurement of light intensity I as a function of the scatter vector Q .

For independently scattering aggregates, the relationship among I , Q and the fractal dimension D_f can be represented by Eq. (3):

$$I \propto Q^{D_f} \quad (3)$$

The relationship shown in Eq. (3) indicates the determination of D_f , which can be given by the slope of $\log I$ versus $\log Q$ by fitting a straight line.

The floc growth rate was calculated by the slope of the rapid growth region, which was shown in Eq. (4):

$$\text{Growth rate} = \frac{\Delta \text{size}}{\Delta \text{time}} \quad (4)$$

3. Results and discussion

3.1. Dosage optimum

The residual turbidity and zeta potential for AS and PACl were comparatively investigated (Fig. S5). Results showed the variation of turbidity removal and zeta potential as a function of the coagulant dosage. It was found that when Al dosages ranged from 0.02 to 0.3 mmol/L calculated as Al, the turbidity removal increased gradually with the increase of coagulant dosage before reaching the optimum dosage. The optimum dosage for turbidities was at 0.1 mmol/L for two coagulants. It can be seen that as the coagulants dosages increased, zeta potential was gradually

Fig. 2. Floc size in the coagulant process under different conditions (kaolin suspension at pH = 6.0, 7.0 and 8.5).

elevated. Floc zeta potential under optimum condition was 1.2 mV for AS, and 4.5 mV for PACI.

3.2. Effects of nanoparticles on the coagulation process without HA

In this part, the water sample was diluted from the stock kaolin solution. The concentration of kaolin was 29.7 mg/L. The concentration of nanoparticles used in this study was from 0.0 mg/L to 2.0 mg/L for TiO_2 and Al_2O_3 particles in order to investigate the nanoparticles on the characteristics of flocs. The results of floc size under pH 6.0, 7.0 or 8.5 were summarized in Fig. 2. The floc size (μm) after growth period, floc growth rate ($\mu\text{m}/\text{min}$), strength factor, recovery factor and fractal dimension under pH 7.0 were summarized in Fig. 3. The characteristics of flocs formed under other two pH values are summarized in Table S1.

According to the results in Fig. 2A, floc size increased first, and decreased when the concentration of nanoparticles was high. The TiO_2 had little negative charges on the surface under pH 6.0, so the decrease of floc size happened at concentration of 2.0 mg/L. When Al_2O_3 particles were added to the suspension, the decrease happened at concentration of 1.6 mg/L (zeta potential 8.3 mV, Fig. 2B). From Fig. S1, the Al_2O_3 particles had more positive charges on the surface under pH 6.0, so when the concentration of Al_2O_3 was high, suspension was charge reversal.

The results of strength factor and recovery factor in Table S1 showed that when the concentration of TiO_2 was larger than 0.4 mg/L, the strength factor decreased from 31.14% to 25.00% under pH 6.0. The concentration of Al_2O_3 had no significant effects on the strength factor under pH 6.0. In the experiment condition, the

Al_2O_3 particles had positive charges, so the adsorption of Al coagulant was not significant. The bridging effects of Al_2O_3 were caused only by Al_2O_3 particles. The bridging force between Al_2O_3 particles and kaolin particles was smaller than the Al-species coagulant, so the concentration of Al_2O_3 particles had no significant effects on the strength factor. Licsko [35] showed that the hydrolysis of metal ions occurred immediately after contacting with water. The in situ formed Al_{13} was adsorbed on the TiO_2 particles (negative charges under pH 6.0), so the recovery force was formed by TiO_2 and Al-species coagulant adsorbed on the surface of TiO_2 particles. The amount adsorbed on the surface of TiO_2 increased with increasing the concentration of TiO_2 , so the recovery factor also increased. The results of recovery factor indicated that the addition of TiO_2 particles could increase the recovery factor from 34.49% to 54.27%. The recovery factor with addition of Al_2O_3 increased firstly from 34.49% to 53.68%, but it decreased to 34.09% when the concentration of Al_2O_3 was 2.0 mg/L. The zeta potential with 2.0 mg/L of Al_2O_3 particles was +20.0 mv, and the recovery factor decreased due to the repulsion force between particles.

The decrease of floc size happened at 1.2 mg/L for TiO_2 under pH 7.0. This trend also existed at pH 8.5, and the decrease happened at 0.8 mg/L. When the concentration of Al_2O_3 was larger than 1.6 mg/L, the floc size decreased due to charge reversal (zeta potential 18.75 mv) which was shown in Fig. 2D.

The results of strength factor and recovery factor in Fig. 3 indicated that zeta potential of flocs had significant effects on the strength and recovery factor. The strength factor in existence of TiO_2 increased from 28.79% to 48.69%, and when the concentration of TiO_2 was larger than 1.6 mg/L, the strength factor decreased to

Fig. 3. Under different concentration of nanoparticles without HA: comparison of floc growth rate and floc size with different HA concentration of nanoparticles (a) floc growth rate and floc size (b) strength factor and recovery factor and (c) fractal dimension.

23.39%. When the pH value was adjusted to 7.0, the positive charges on the Al_2O_3 particles decreased, so some Al hydrolyzed species could be adsorbed on the Al_2O_3 particles. The bridging effect between Al_2O_3 particles and kaolin particles was not only by the Al_2O_3 particles. The adsorption of Al hydrolyzed species increased with increasing the concentration of Al_2O_3 . The strength factor increased once there were Al_2O_3 particles in solution.

The floc sizes were the smallest in all three pH values (Fig. 2E and F), and the concentration of Al_2O_3 had no significant effects on the floc size. Because the addition of AS (0.1 mmol/L calculated as Al) at pH 8.5 made the solution negative in zeta potential, the floc size was smaller than other two pH values. The pH value was close to iso-electric point of Al_2O_3 , and the bridging effects of nanoparticles decreased.

The results of strength factor and recovery factor at pH 8.5 indicated that strength factor and recovery factor decreased when the concentration of TiO_2 was 1.2 mg/L. Because of zeta potential of water sample was close to 0 mV with 2.0 mg/L Al_2O_3 particles, the strength factor increased from 28.17% to 42.95%. Previous results indicated that pH had a significant effect on further transformation of PACl. In the acid region, Al_a decreases rapidly as pH is raised, and reaches a minimum in the near neutral pH region. Upon increase of pH to the alkaline region, Al_a species increase sharply

again. In contrast, a rapid increase of the Al_b species can be observed in the acidic pH region. The maximum of Al_b occurs in the near neutral pH conditions. In the alkaline portion, a rapid decrease occurs as pH is raised [36].

The results of fractal dimension in Fig. 3c indicated that the addition of nanoparticles decreased the fractal dimension. This was in agreement with previous study [37], and the larger flocs had smaller fractal dimension. When the concentration of TiO_2 was larger than 0.8 mg/L, the fractal dimension after re-growth was larger than fractal dimension after breakage. And the concentration for Al_2O_3 was 1.2 mg/L. These results indicated that the nanoparticles existed in solution could bridge the kaolin particles together, and the bridging effects increased with increasing the concentration of nanoparticles.

The removal efficiencies for Al_2O_3 were 58.27%, 62.73% and 47.3% under pH 6.0, 7.0 and 8.5, respectively. The removal efficiencies for TiO_2 were 38.12%, 52.25% and 27.19%. The iso-electric points for Al_2O_3 and TiO_2 were 8.5 and 4.8 respectively, and the Al_2O_3 particles would be adsorbed on kaolin particles because of different charges. The adsorption of TiO_2 was not significant. The removal efficiency for nanoparticles may be affected by two mechanisms: one is the adsorption of nanoparticles on kaolin surface; the other is the coagulation process. When the pH was adjusted

Fig. 4. Floc size in the coagulant process under different conditions (kaolin suspension + HA at pH = 6.0, 7.0 and 8.5).

to 8.5, the charges on Al_2O_3 particles were almost 0 mv. So the adsorption process was hindered, and the removal efficiency also decreased. When the pH was adjusted to 6.0, the removal efficiency also decreased because of the Al hydrolysis was hindered.

The effects of the ionic strength (Fig. S6) indicated that it had significant effects on the coagulation process. Floc size after growth increased from 212 μm to 350 μm in kaolin system with increasing ionic strength from 0.5 mmol/L to 5.0 mmol/L. An increase in the ionic strength leads to a corresponding higher growth rate for the flocs. However, increases in the ionic strength did not have a significant influence on the floc growth rate, when the ionic strength was larger than 5.0 mmol/L in kaolin system. The floc growth rate decreased because of charge reversal at larger ionic strength (20.0 mmol/L). The results of strength factor and recovery factor indicated that they increased with increasing ionic strength and zeta potential played a significant role. The strength factor and recovery factor increased with increasing the ionic strength, and decreased when the ionic strength was large. The addition of nanoparticles could significantly increase the recovery factor, and this increase was more significant when the ionic strength was larger than 5.0 mmol/L. This may be caused by the adsorption of Na^+ on the surface of nanoparticles.

The zeta potential generally increased with the increase of ionic strength. The increase in ionic strength resulted in compression of the EDL and therefore a decrease in the EDL repulsive energy. Our results clearly indicated that the addition of ionic strength reduced the repulsion force among the particles, so they could aggregate

and merge together to form larger flocs. Such a complex behavior is explained by the fact that the presence of salt is expected to influence two important parameters. The first one is related to the coagulation process at low salt concentration; to reduce the particle–particle repulsive force. The second one is related to the importance of the charge screening by increasing further the salt concentration. This effect is expected to increase the aggregation rate between the kaolin particles and nanoparticles.

3.3. Effects of nanoparticles on the coagulation process with HA (DOC 2.5 mg/L)

HA was abundant in soil and groundwater, and played important roles in both adsorption and electron transfer processes [38]. The physicochemical characteristics of NOM fractions may strongly alter the stability of inorganic colloids. Numerous studies have shown the stability impact of humic acids upon their sorption on inorganic colloids, predominantly through repulsive interactions due to the net negative surface charge development of the inorganic colloids [39,40]. Our study demonstrated that the hydrophobic nature of the HA molecules strongly influenced the aggregation of NPs, possibly through their conformation behavior in a particular solution condition. HA was prior to be adsorbed on the nanoparticles surface and form complex with functional groups, which occupied the active surface sites and hindered the contacts of Al.

Fig. 5. Under different concentration of nanoparticles with HA: comparison of floc growth rate and floc size with different concentration of nanoparticles (a) floc growth rate and floc size (b) strength factor and recovery factor and (c) fractal dimension.

According to the results of Figs. 2A–B and 4A–B the addition of HA decreased floc size formed in this study. The results in Table S2 indicated that the strength factor increased from 27.09% to 32.33% with increasing the concentration of TiO_2 from 0 mg/L to 1.2 mg/L under pH 6.0. The continuous increasing concentration of TiO_2 had no significant effects on the strength factor. This trend was also observed when using Al_2O_3 . The results of recovery factor indicated that the increasing concentration of nanoparticles could increase the recovery factor under pH 6.0. This may be caused by the bridging effects of nanoparticles with HA molecules. At acid condition, the TiO_2 particles had less negative charges and Al_2O_3 particles had positive charges, so the bridging effects existed. The results of Fig. 4A–D indicated that the floc size decreased with increasing pH values. Because Al_2O_3 particles had positive charges on the surface, it could complex with functional groups of HA. Although the TiO_2 particles had negative charges, the adsorption of HA on TiO_2 particles also existed. So the nanoparticles can bridge the particles of HA molecules together. The recovery factor increased from 54.55% to 62.65% with increasing concentration of Al_2O_3 from 0.0 mg/L to 2.0 mg/L, and it increased from 54.55% to 67.74% for TiO_2 (Fig. 5b).

The results in Fig. 4F indicated that the concentration of Al_2O_3 particles had no significant effects on the floc size formed in the coagulation process. This phenomenon was also observed in 3.2. According to the results in Table S2, the concentration of nanoparticles had no significant effects on the strength factors under pH 8.5. Recovery factor increased from 57.79% to 65.91% with increasing concentration of TiO_2 from 0.0 mg/L to 2.0 mg/L, and it increased from 57.79% to 62.7% for Al_2O_3 .

The results of fractal dimension in Fig. 5c indicated that the addition of nanoparticles increased the fractal dimension first, and when the concentration of TiO_2 was larger than 1.6 mg/L, the fractal dimension after breakage decreased from 2.78 to 2.62. The fractal dimension after breakage in the existence of Al_2O_3 increased from 2.58 to 2.81 with increasing the concentration of Al_2O_3 from 0.0 mg/L to 2.0 mg/L.

3.4. Effects of different coagulants on coagulation process under different concentration of HA

The floc sizes under different concentration of DOC are summarized in Figs. 6 and 7. The concentrations of TiO_2 and Al_2O_3 were 1.6 mg/L and 1.2 mg/L.

According to the results in Fig. 6, the increasing of DOC decreased the floc size in all pH values. When the concentration

Fig. 7. Floc size after growth under different concentration of DOC using PACI (a) TiO_2 and (b) Al_2O_3 .

of DOC was larger than 5.0 mg/L under pH 8.5, there was no floc formed in the coagulant process. Al_2O_3 particles had positive charges, and they were contributed to the growth of flocs under the same pH and coagulant dosage.

The results in Fig. 7 indicated that that PACI produced larger flocs. This may be caused by two mechanisms: one is the PACI has higher charge neutralization ability than AS; the other is the nanoparticles existed in the solution would adsorb Al_3 in the PACI solution, and the electrostatic patch effect was larger than using AS.

The results of different concentration of DOC on the removal efficiencies for nanoparticles (Fig. S7) indicated that HA molecules played a significant role in the removal of nanoparticles. The removal efficiency for TiO_2 decreased from 52.25% to 22.13% with increasing DOC from 0 mg/L to 7.5 mg/L. The removal efficiency for Al_2O_3 decreased from 62.73% to 32.12%. When there were HA molecules in the solution, the nanoparticles would adsorb HA molecules. The adsorption of nanoparticles on kaolin surface may be hindered. And there were still some HA molecules in the solution. The hydrolyzed Al species would react with particles and HA molecules, so the removal caused by coagulation process was also hindered.

4. Conclusion

Effects of different nanoparticles on the coagulation process were studied respectively. The floc size, flocs growth rate, strength factor, recovery factor and fractal dimension were comparatively investigated under different coagulation conditions. The removal efficiencies for two nanoparticles under different conditions were also investigated. The main conclusions from this work were listed as the following:

1. The zeta potential of flocs had significant effects on the strength and recovery factor in kaolin suspension. The strength factor with the presence of TiO_2 increased from 28.79% to 48.69%, and when the concentration of TiO_2 was larger than 1.6 mg/L, the strength factor decreased to 23.39% under pH 7.0. The removal efficiencies for Al_2O_3 were 58.27%, 62.73% and 47.3% under pH 6.0, 7.0 or 8.5. The removal efficiencies for TiO_2 were 38.12%, 52.25% and 27.19% respectively.
2. When the concentration of DOC was 2.5 mg/L under pH 7.0, the recovery factor increased from 54.55% to 62.65% with increasing concentration of Al_2O_3 from 0.0 mg/L to 2.0 mg/L, and it increased from 54.55% to 67.74% for TiO_2 . The concentration of Al_2O_3 particles had no significant effects on the floc size formed in the coagulation process under pH 8.5.

Fig. 6. Floc size after growth under different concentration of DOC using AS (a) TiO_2 and (b) Al_2O_3 .

3. The removal efficiency for TiO_2 decreased from 52.25% to 22.13% with increasing concentration of DOC from 0 mg/L to 7.5 mg/L. The removal efficiency for Al_2O_3 decreased from 62.73% to 32.12%.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2014.01.010>.

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