Effects of different coagulants in treatment of TiO₂–humic acid (HA) water and the aggregate characterization in different coagulation conditions

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HIGHLIGHTS

- Coagulation behaviors by PACl and nano-Al₁₃ displayed less variation.
- Nano-Al₁₃ produced larger flocs under smaller dosage.
- Fractal dimension formed by nano-Al₁₃ and PACl was larger.
- Strength factor increased with increasing the coagulant dosage using AS.

GRAPHICAL ABSTRACT

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ABSTRACT

Effects of coagulant dosage and solution pH on the coagulation behavior of nano-Al₁₃ were studied with respect to the treatment of TiO₂–humic acid water. Polyaluminum chloride (PACl) or AS (Al₂(SO₄)₃) and Al₂O₃ (100 mg/L) + AS were used to compare with nano-Al₁₃. The floc size, strength factor and fractal dimension under different coagulation conditions were investigated. The results indicated that hydrophobic NOM with larger molecular weight could be easily removed by the four coagulants. The strength factor increased with increasing the coagulant dosage for AS under all coagulation pH values. The results using PACl and nano-Al₁₃ as coagulants indicated that the coagulant dosage had no significant effects on the strength factors. The addition of Al₂O₃ could significantly increase the floc size, and the fractal dimension after breakage was larger than using AS. Nano-Al₁₃ had highest charge neutralization ability, so when the dosage was high, the removal efficiency decreased due to charge reversal. The results of the coagulation performances under three coagulation pH values indicated that nano-Al₁₃ could re-stabilize the particles under pH 6.0 at 0.2 mmol/L calculated as Al. The recovery factors using Al₂O₃ + AS as coagulant were smaller than using AS, and this may be caused by the adsorption of HA molecules on nano-Al₂O₃ particles. The HA molecules in the solution could bridge the nano-particles together through bridging effects. The Al₂O₃ particles had positive charges on the surface under pH 6.0, and it could bridge the particles together.

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1. Introduction

With the development of nanotechnologies, more and more nano-particles may be found in the aquatic environment [1]. The potential hazards of nano-particles are still unknown, even if there are lots of researches on the hazards relevant to humans [2]. In fact, the very large surface area of ultra-small particles can result in the direct generation of harmful oxy radicals: these can cause cell injury

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by attacking DNA, proteins, and membranes [1]. Today, nano-TiO₂ particles have already been produced in very large quantities. TiO₂ are commonly used as white pigment due to its brightness and very high refractive index. TiO₂ is a photo-catalyst under UV light. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals [3]. The application of nano-Al₂O₃ as adsorbents has come up as an interesting area of research because of their high removal efficiency [4]. A previous study also indicated that in many cases the adsorption capacities remained almost the same after regeneration. However, there are not many researches on the effects of nano-Al₂O₃ particles on coagulation performance. In the present study, nano-Al₂O₃ particles (100 mg/L) were mixed with AS solution to investigate its effects on coagulation performance. HA has been shown to be reactive with a variety of oxidants and disinfectants that are used in the purification of drinking water [5]. The adsorption of HA onto minerals was not clearly defined by many researchers due to the nature of the adsorbent surface [6]. Various mechanisms which had been proposed to explained the interaction between HA and minerals such as electrostatic interaction, hydrophobic interaction.

Coagulation has played an important role in the water treatment plant [7,8]. Charge neutralization is thought to occur in the region where aluminum hydroxide precipitation is minimal and cationic aluminum interacts electro-statically with anionic NOM to form insoluble products; and destabilization by bridging happens when segment of a polymer chain is absorbed on more than one particle, thereby linking the particles together; while surface adsorption of NOM could play an important role in the regions where the concentration of coagulant was high enough to cause rapid precipitation of Al(OH)₃ [9].

Polyaluminum chloride (PACl) is widely used as the coagulant [10]. Although there is increasing interest in the research of coagulants with PACl, the effect of nano-Al₁₃ on the treatment of TiO₂-HA water has not been fully studied. The characteristics of flocs, including size, strength and fractal dimension, could significantly affect the efficiency of separation and purification operation in treatment works. Additionally, previous studies showed that the floc shapes affected the behaviors of aggregated particles, particularly with regard to collision efficiency and settling rates. Jarvis et al. also demonstrated that smaller particles in raw water would pose a challenge to the solid/liquids separation processes if the pre-formed flocs tend to be broken by increasing in shear rate [11].

However, nano-particles that are different from classical solid particles by their size and specific properties due to their high surface area over volume ratio could be responsible for a lower removal efficiency in the coagulation process. Although cationic surfactants and cationic polymers may be more effective for coagulation of nano-particles, their possible steric effects besides the neutralization enhanced the complication of the basic research [12].

The overall objective of this research was (1) To investigate the effects of nano-Al₁₃ on the coagulation process. (2) To investigate the changes of floc size under an enhanced shear. (3) To investigate floc strength and fractal properties. (4) To investigate the effects of nano-Al₂O₃ on the coagulation process. AS and PACl were used for the purpose of comparison.

2. Materials and methods

2.1. Water samples used in this study

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. The stability of these

Table 1
Characteristics of water samples.

Characteristics	pH	Turbidity (NTU)	UV ₂₅₄	DOC (mg/L)
Value	8.90	73.5	0.320	2.55

manufactured nano-TiO₂ suspensions was obtained through the addition of NaOH (0.01 mol/L) which generated anionic on nano-TiO₂ surface. The suspensions were stirred for 6 h for better disperse. Particles would thus repel each other, and provide a good stability. Water samples were prepared by diluting TiO₂ stock suspension and HA stock solution. Water samples were stirred for 12 h to achieve the adsorption equipment. The concentration of TiO₂ was 5.0 mg/L, and the DOC was 2.55 mg/L. The water samples were added 5.0 mM NaNO₃ and 4.0 mM NaHCO₃. The pH of the water sample was adjusted to varied pH values by addition of 0.1 mol/L HCl and 0.1 mol/L NaOH before the addition of coagulant. The zeta potentials of water sample were measured by Zetasizer 2000 (Malvern Instrument). PH was measured at room temperature with a pH-meter. Turbidity was measured with a turbidity meter. The results are summarized in Table 1. The two particles used in this study were purchased from Beijing DK nanotechnology Co. LTD.

2.2. Coagulants preparation and characterization

All the reagents used in this study were of analytical grade and de-ionized water was used in all solutions. AS was prepared by directly dissolving Al₂(SO₄)₃ · 18H₂O into de-ionized water. PACl was prepared by diluting from commercial PACl. The new coagulant was prepared by adding nano-Al₂O₃ particles (100 mg/L) to the AS solution, and the coagulant was used after the adsorption equilibrium. The nano-Al₁₃ was prepared by SO₄²⁻/Ba²⁺ displacement method from the stock PACl solution as shown in ref. [13]. The Al species distributions were measured by Ferron method as described in ref. [10]. The total Al concentration (Al_T) was determined by ICP-OES, and the species distributions of four coagulants are summarized in Table 2.

2.3. Jar tests

Jar tests were performed on a jar test apparatus with 500 mL glass beakers. The coagulation process was started with a rapid mixing at 200 rpm for 1.5 min after the addition of coagulant, followed by a mixing at 40 rpm for 10 min and the 30 min of settlement. After the settlement, samples were collected from about 2 cm below the solution surface for subsequent measurements, including residual turbidity, DOC, UV₂₅₄. All experiments were conducted at room temperature and coagulant dosages used in this study were calculated as Al. The experiments were conducted for three times.

2.4. Floc breakage, floc re-growth and floc fractal structure analysis

One of the simplest quantitative evaluations for floc strength is the calculation of a floc strength factor [9]. A larger strength factor implies flocs that are better able to withstand shear and thus should be considered stronger than those with lower factors. The strength

Table 2
Al species distribution of four coagulants used in this study.

Coagulants	Al _a	Al _b	Al _c
AS	98.3%	1.7%	0
PACl	31.33%	16.09%	52.58%
Nano-Al ₁₃	5.9%	92.3%	1.8%
Nano-Al ₂ O ₃ + AS	94.12%	3.42%	2.46%

Fig. 1. TEM images of Al_2O_3 particles used in this study.

factor (S_f) and recovery factor (R_f) are calculated as described before [14,9]. The floc growth rate, fractal dimension and shear based floc strength were calculated as described in former studies [15–20]. In order to investigate the characteristics of flocs formed in the coagulant process under different coagulant dosage, three coagulant dosages (0.1 mmol/L, 0.15 mmol/L, 0.2 mmol/L calculated as Al) for AS, PACl, nano- Al_{13} and nano- Al_2O_3 + AS were applied, and the strength factor and the recovery factor were also calculated. The solution pH was adjusted to three pH values (6.0, 7.0, 8.0). The flocs after growth were exposed to 200 rpm for 5.0 min for breakage, and then the shear rate was decreased to 40 rpm for 10 min for the re-growth. The sizes under different coagulation conditions for the four coagulants were summarized in Figs. 4–7.

2.5. Characteristics of Al_2O_3 particles used in this study

2.5.1. TEM images for Al_2O_3 particles

The TEM images for Al_2O_3 particles were shown in Fig. 1.

2.5.2. Iso-electric point (IEP) and ATR-FTIR spectrum for Al_2O_3 particles and Al_2O_3 particles after adsorption of Al^{3+}

Iso-electric points of two nano-particles were achieved under different pH values, and the results were summarized

Fig. 2. Iso-electric point (IEP) for Al_2O_3 particles and Al_2O_3 particles after adsorption of Al^{3+} .

Fig. 3. ATR-FTIR spectrum for Al_2O_3 particles and Al_2O_3 particles after adsorption of Al^{3+} .

in Fig. 2. Al_2O_3 suspension and Al_2O_3 mixed with AS were measured by ATR-FTIR, and the results were summarized in Fig. 3.

2.6. Effects of coagulant dosage on coagulation performance

The water sample was adjusted to pH 7.0 to investigate effects of coagulant dosage on coagulation performance, and residual turbidity and residual DOC after sedimentation with the dosage ranging from 0.02 mmol/L to 0.4 mmol/L calculated as Al were also investigated. The results were summarized in Fig. S1.

2.7. Effects of coagulation pH on coagulation performance

Coagulation pH has important effects on transformation of Al species [21]. It is claimed that the monomeric Al could hydrolyze to form Al_6 at neutral and slightly alkaline pH. The effects of initial pH on coagulation behaviors by the four different of Al coagulants were investigated in the pH range of 4.0–9.0. The coagulant dosage was 0.12 mmol/L calculated as Al for all coagulants. The results are summarized in Fig. S2.

3. Results and discussion

3.1. Characteristics of Al_2O_3 particles used in this study

The results in Fig. 1 indicated that the Al_2O_3 particles had a 20–30 nm diameter.

3.2. Iso-electric point (IEP) and ATR-FTIR spectrum for Al_2O_3 particles and Al_2O_3 particles after adsorption of Al^{3+}

The results in Fig. 2 showed that the iso-electric point for Al_2O_3 was between pH 8.0 and pH 9.0, so the Al_2O_3 particles always had positive charges in the experiment process. When the Al^{3+} was adsorbed on nano-particles, the iso-electric point was decreased to 6.8. The spectrum in Fig. 3 displayed two characteristics broad centered at 3480 cm^{-1} and 1620 cm^{-1} , which were referred to the stretching and bending modes of vibrations for physical adsorbed water and hydroxyl group existed on the oxide surfaces. The bands at 400 cm^{-1} to 1000 cm^{-1} were the Al-O vibration. After the

Fig. 4. Floc size and fractal dimension in different coagulation condition using AS.

adsorption, the bands were shifted from 521 cm^{-1} to 728 cm^{-1} , which indicated that the Al-O active decreased, and this may be caused by adsorption of Al^{3+} . The bands at 1620 cm^{-1} were shifted to 1684 cm^{-1} after the adsorption.

3.3. Effects of coagulant dosage on coagulation performance

The results in Fig. 4 indicated that DOC was removed more efficiently by nano- Al_{13} . Some researchers believed that the high

Fig. 5. Floc size and fractal dimension in different coagulation condition using PACl.

Fig. 6. Floc size and fractal dimension in different coagulation condition using nano- Al_{13} .

Fig. 7. Floc size and fractal dimension in different coagulation condition using nano- $\text{Al}_2\text{O}_3 + \text{AS}$.

neutralization ability of Al_{13} species contributed to the effective removal of DOC [22]. The residual DOC decreased with increasing the dosage of AS and PACI. The Al -NOM flocs could be adsorbed by further hydrolyzed and polymerized Al precipitates, and elevated coagulant concentration would be in favor of collision frequency and efficiency. When nano- Al_{13} was used as coagulants, removal efficiencies for DOC and turbidity were decreased when the dosage was high. This may be caused by highest charge ability of nano- Al_{13} . The removal efficiency for UV_{254} , which was essentially attributed to the presence of aromatic compounds, presented a continuous increase with increasing dosage using AS, PACI and nano- Al_2O_3 + AS. Al_6 could remove large and hydrophobic organic matters more easily at lower dosage due to its higher positive charge per molecule [9]. When nano- Al_{13} was used as coagulants, the charge reversal caused by highest charge ability of nano- Al_{13} caused the UV_{254} increasing when the dosage was larger than 0.2 mmol/L. The results of SUVA indicated that the large hydrophobic compounds were more easily removed. Nano- Al_{13} was more efficiently to remove large hydrophobic compounds and high dosage was more favorable for the removal of larger hydrophobic compounds. PACI and nano- Al_{13} produced larger SUVA in effluent at higher dosage, indicating that they removed larger proportion of low MW fractions of organic matter. The results showed that the addition of nano- Al_2O_3 particles could increase the removal efficiency of large MW organic matters. The results in Fig. S2 indicated that nano- Al_{13} had highest removal efficiency at lower dosage due to its highest charge neutralization ability. The addition of nano- Al_2O_3 could increase the turbidity and DOC removal efficiency.

3.4. Effects of coagulation pH on coagulation performance

The residual turbidity decreased sharply with increasing pH at acid pH and reached the lowest at around neutral pH condition. The coagulation performance for nano- Al_{13} was less affected by pH values, and this may be caused by the stability of Al species in nano- Al_{13} solution. The addition of nano- Al_2O_3 could increase the turbidity removal efficiency than using AS. The turbidity removal efficiency was highest for PACI at pH 6.0, and it reached the highest point at pH 7.0 for AS and AS + nano- Al_2O_3 . The maximum DOC removal efficiency was at 6.0 for AS, PACI and nano- Al_2O_3 + AS. The abrupt increase in DOC removal efficiency at pH 4.0–6.0 could be ascribed to the adsorption of NOM onto hydrolysis products Al_6 . DOC removal efficiency decreased with increasing pH especially for AS. When the pH value was larger than 7.0, the removal efficiency for DOC using nano- Al_{13} was decreased. This result indicated that nano- Al_{13} removed DOC more efficiency at acid region. The addition of nano- Al_2O_3 could increase the removal efficiency of DOC under the same coagulation condition, and the removal efficiency was less affected by coagulation pH compared to AS. This was caused by the adsorption capacity of nano- Al_2O_3 particles which was shown in Figs. 2 and 3. The Al^{3+} adsorbed on Al_2O_3 particle surface was less affected by the solution pH. The removal efficiency of UV_{254} increased first and then decreased when the pH was high. The highest removal efficiency was reached at neutral pH conditions. Nano- Al_{13} had a more stable UV_{254} removal across the pH range investigated.

The results of residual SUVA showed that the SUVA value decreased firstly and increased when the pH was high. The hydrophobic NOM was most inclined to be removed by nano- Al_{13} , so the SUVA value using nano- Al_{13} was lower than using other three coagulants. It could be seen that the SUVA in coagulated water at acidic pH was obviously larger than that at the higher pH region, indicating that the organic matter with lower SUVA was easier to be removed at acid pH condition. It also indicated that part of the organic matter with lower molecular weight and hydrophilic was favored to be removed at acidic pH condition because nano-particle

and Al_{13} could adsorb them and made it more hydrophobic to be removed. The results in Fig. S2 indicated that the coagulation performance of nano- Al_{13} was less affected by solution pH, and the addition of nano- Al_2O_3 could increase the adaption ability for pH. Al ions are bond into the organic molecules and therefore are no longer active in the coagulation process. As mentioned above, HA molecules contained many functional groups [23], such as $-\text{OH}$, $-\text{COOH}$, $-\text{SH}$ etc., which were able to possess charge under certain pH conditions. The surface charge of HA molecules was the source of their reactivity towards their surroundings, and led to electrostatic interactions. The highest coagulation efficiency was reached at pH 6.0 for AS, PACI and nano- Al_2O_3 + AS, where the electrostatic interactions between negatively charged acid functional groups of HA and positively charged Al -polymers were enabled. These attractive interactions resulted in gradual neutralization of HA surface charges and consequently allowed the formation of uncharged micro-aggregates. When the pH was at basic region, the adsorption of HA molecules on the surface of colloidal may also be very important. The interaction proceeded mainly in accordance with the electrostatic patch model postulated by Gregory [24]. According to this theory, negatively charged HA molecules attached themselves to the positively charged colloidal particles of Al -hydroxides. These reactions resulted in the development of negatively charged areas on the surface of Al colloidal particles. When so charged particles colloid with each other, a simultaneous attachment of oppositely charged areas to the surface of particles occurred. Besides the electrostatic patch model, adsorption may also be explained by the formation of hydrogen bonds between functional groups of HA and Al -oxide-hydroxides [25].

3.5. Characteristics of flocs formed under different pH values

The results of floc size in Fig. 4 indicated that the floc size after growth period increased from 300 μm to 450 μm with increasing dosage of AS from 0.1 mmol/L to 0.2 mmol/L. The results of fractal dimension in Fig. 4 indicated that the fractal dimension of flocs after breakage decreased with increasing the pH value under the same coagulant dosage. When the dosage was 0.1 mmol/L under pH 8.0, there were no significant flocs formed in the coagulation progress. The fractal dimensions of flocs after re-growth were smaller than fractal dimension of flocs after breakage. These results were in accordance with the former study, and the smaller flocs had the larger fractal dimension. The strength factor and recovery factor (Table S1) indicated that the strength factor increased with increasing the coagulant dosage using AS, and the recovery factor had reverse trend. These results maybe caused by the decreasing concentration of HA molecules in the solution. Two possible mechanisms of HA binding to nano-particles had been suggested: HA molecules could be attached to the surface by chemical cross-linking reagents, or they could spontaneously assemble because of the electrostatic forces. The interaction of the HA with a colloid surface involved these two possibilities, and the electrostatic interaction would be an important effects in the re-growth period.

The results described in Figs. 4 and 5 indicated that PACI had larger charge neutralization ability than AS, and flocs formed at acid region had larger floc size. The results in Table S2 indicated that PACI had larger strength factor and smaller recovery factor. The results of floc dimension after breakage by AS and PACI at dosage (0.2 mmol/L) was in the hierarchy: pH 6.0 > pH 7.0 > pH 8.0.

The results of coagulation performance using nano- Al_{13} (Fig. 6) indicated that nano- Al_{13} could produce larger flocs under the same coagulant dosage. But at acid condition (pH 6.0), when the dosage was 0.2 mmol/L, there was no significant flocs formed. This may be caused by the charge reversal of nano- Al_{13} (zeta potential = 25 mV). Nano- Al_{13} could produce the biggest fractal dimension. The dosage of nano- Al_{13} and solution pH had no significant effects on

Fig. 8. Growth rate under different different coagulation conditions using four coagulants (a: pH 6.0; b: pH 7.0; c: pH 8.0).

fractal dimension. This could be explained by the stable Al species in nano-Al₁₃ solution. For nano-Al₁₃ and PACl which at low dosage (0.15 mmol/L), the fractal dimension after breakage was as following: pH 7.0 > pH 8.0 > pH 6.0.

The results in Fig. 7 indicated that the addition of nano-Al₂O₃ particles could significantly increase the floc size compared with AS. When the coagulant dosage was 0.1 mmol/L at pH 8.0, the floc size formed by AS had no difference with initial particles (zeta potential = −18 mV). When nano-Al₂O₃ + AS was used, there were flocs formed under pH 8.0. So the addition of nano-Al₂O₃ could increase the adaption ability to pH variation and charge neutralization ability. In the nano-Al₂O₃ + AS solution, the nano-Al₂O₃ could be regarded as sorbent. Most of atoms on the surface of the nano-particles were unsaturated and could easily bind with other atoms. When we added nano-Al₂O₃ particles to AS solution, the OH[−] on the surface of nano-Al₂O₃ provides the ability of binding Al³⁺. The binding Al³⁺ is less affected by solution pH. When the coagulation pH was 8.0, the nano-Al₂O₃ + AS could produce larger flocs than AS. The results in Figs. 4 and 7 indicated that the addition of nano-Al₂O₃ particles significantly increased the fractal dimension. This may be caused by the bridging effects of nano-Al₂O₃ particles. When nano-Al₂O₃ + AS was used as coagulant, the fractal dimension increased with decreasing the coagulation pH.

When the coagulant dosage was high (0.2 mmol/L), the flocs formed by AS had larger strength factors than formed by PACl and nano-Al₁₃. The strength factor in acid condition was smaller than at neutral condition and alkaline condition for all four coagulants. The strength factors using Al₂O₃ + AS (0.2 mmol/L) were smaller than using AS. The nano-Al₂O₃ particles could bridge the small flocs together, but the bridging point was easy to be broken in the breakage period.

For all four coagulants, the recovery factor increased with increasing the pH values. The more hydrogen bonds formed between COOH groups of HA and OH groups or bonded water

molecules on oxide surfaces, the less amounts of COOH groups of HA remained. When the charges of HA molecules and oxide particles had the same sign, electrostatic repulsion between the two surfaces reduced the density of the HA layer covering on an oxide surface. When the charge of HA molecules and oxide particles had opposite signs, electrostatic attraction weakened the structure stability of HA molecules, resulting in a less compact HA layer covering oxide surfaces. The adsorption ability increased with decreasing the pH values from 8.0 to 6.0. This may be the reason why the recovery factor increased with increasing the pH value.

Fig. 9. The log-log curves of stable floc size decreasing with rotary rate under three coagulation pH.

Fig. 10. Floc size, strength factor and recovery factor under different coagulation conditions.

The results of floc growth rate were summarized in Fig. 8. The results indicated that the floc growth rate decreased with increasing pH from 6.0 to 8.0 at the same dosage of coagulant. The addition of Al_2O_3 particles could increase the floc growth rate.

3.6. Empirical shear-based floc strength

The results in Fig. 8 indicated that the floc strength decreased with increasing pH values. Larger flocs were more exposed to micro scale energy-dissipating eddies that gave rise to floc breakage, while smaller flocs were more likely to become entrained within these eddies rather than being broken by them. The floc size decreased with increasing pH values for two coagulants. The results of decreasing slope in Fig. 9 revealed that the strength factor of flocs formed under the same coagulant dosage increased with increasing the coagulation pH. These results are consistent with results in Tables S1 and S3.

3.7. The adsorption of HA on Al_2O_3 and TiO_2 particles

The results in Fig. S3 indicated that the adsorbed HA concentration onto nano-particles versus the equilibration contact time. Initially HA adsorption was relatively fast: 95% and 87% of the maximum HA adsorption for Al_2O_3 and TiO_2 after 30 min, respectively. So the adsorption time was adjusted for 12 h for the equilibrium of adsorption for HA on nano-particles in this study.

3.7.1. Effects of concentration of nano-particles on the adsorption process of HA

The results in Fig. S4 indicated that the adsorption of HA increased with increasing the concentration of nano-particles. In Section 3.8, when the Al_2O_3 particles were added firstly, the

recovery factor decreased with increasing the concentration of Al_2O_3 particles. The concentration of HA molecules decreased with increasing the concentration of nano- Al_2O_3 , so the bridging effects caused by HA molecules decreased.

3.7.2. Effects of solution pH on the adsorption process of HA

The results (Fig. S5) indicated that the amount of HA molecules adsorbed on TiO_2 and Al_2O_3 particles decreased with increasing pH values. The nature of TiO_2 particles was affected by pH condition [26–29]: the surface was positively charged in acid condition but negatively charged in basic condition. The positive charged TiO_2 surface hydroxyls were mainly TiOH_2^+ and negative charged TiO_2 surface hydroxyls were TiO^- in acidic and basic solution respectively [30]. 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 occurred at $\text{pH} > 4.0$ whereas the phenolic groups undergo dissociation at $\text{pH} > 8.0$. At $\text{pH} < 5.0$, negatively charged HA would adsorb on positively charged TiO_2 particles due to the electrostatic attraction. At $\text{pH} > 5.0$, both negatively charged HA and TiO_2 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 molecules and TiO_2 particles must exist.

3.8. The second addition of coagulant and nano-particles on the re-growth of flocs

The results of floc size in Fig. 10 showed that the addition of Al_2O_3 particles had no significant effects on the strength factors and floc size after breakage under pH 6.0 and the bridging effects of Al_2O_3 particles were smaller compared to Al-based coagulant. The

Fig. 11. Floc size in the coagulation process with previous and simultaneous addition of Al₂O₃ (AS(1): Al₂O₃ (100 mg/L) + AS; AS(2): Al₂O₃ (200 mg/L) + AS; AS(3): Al₂O₃ (400 mg/L) + AS).

results of recovery factor and floc size after re-growth indicated that they increased with increasing the concentration of Al₂O₃. Because the Al₂O₃ particles had positive charges on the surface under pH 6.0, so it could bridge the particles together after the addition. The

trends of floc size under pH 7.0 were as the same when the coagulation pH was 6.0. The charges on the surface of Al₂O₃ particles decreased with increasing pH value from 6.0 to 7.0. The Al₂O₃ particles had no charges on the surface under pH 8.5, so the bridging

Fig. 12. Mechanism in the coagulation process.

effects were smallest under pH 8.0. The adsorption of HA caused by electrostatic attraction was smaller than other two pH values, so the more HA molecules remaining in the solution would cause the increasing of recovery factor.

3.9. Effects of previous addition and simultaneous addition of nano- Al_2O_3 on characteristics of flocs

The results in Fig. 11 indicated that the increase concentration of Al_2O_3 in AS solution could increase the floc size under pH 6.0. The floc size formed in the condition of the previous addition of Al_2O_3 was smaller than the floc size formed by the simultaneous addition. When the solution pH was 6.0, the Al_2O_3 particles had the largest positive charges. Al_2O_3 particles without adsorption of Al^{3+} would cause charge reversal. The results for pH 6.0 and pH 7.0 showed that the floc size decreased when the concentration of Al_2O_3 was 0.8 mg/L. Al_2O_3 particles had positive charges on the surface when the solution pH value was 6.0, and the charges decreased with increasing the solution pH. When the solution pH was adjusted to 8.0, which was near the iso-electric point of Al_2O_3 , the concentration of Al_2O_3 had no significant effects on the floc size. The results indicated that the charges on the nano-particles affected the bridging effects.

3.10. The mechanism of using four coagulants in the coagulation process

The results presented in this paper revealed that the coagulation process was determined by the application conditions, such as the coagulant dosage or coagulation pH. The mechanism of coagulation process in this study could be summarized in Fig. 12.

The results in Fig. 12 indicated that the Al_{13} which had higher positive charges would bridge more particles together, and the floc size was larger than using PACl and AS as coagulants. When the Al_2O_3 particles were added to the solution, it would adsorb Al on its surface.

4. Conclusions

A series of experiments were developed to investigate the coagulation behavior of four coagulants as well as floc properties. The main conclusions from this work were listed as follows:

- (1) Nano- Al_{13} displayed less variation in coagulation behavior with pH changes due to its stable structure. The particles would be re-stabilized when the dosage of nano- Al_{13} was high (0.2 mmol/L calculated as Al).
- (2) Nano- Al_{13} could produce larger flocs at low dosage, and floc size formed under acid region was larger than at neutral or alkaline region.
- (3) The fractal dimension of flocs formed by nano- Al_{13} and PACl was larger than using AS. The addition of nano- Al_2O_3 could increase the fractal dimension.
- (4) The strength factor increased with increasing coagulant dosage using AS. When the coagulant dosage was high (0.2 mmol/L), the flocs formed by AS had larger strength factors than formed by PACl and nano- Al_{13} . The strength factor in acid condition was smaller than at neutral condition and alkaline condition for all coagulants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2014.01.028>.

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