The influence of particle size and concentration combined with pH on coagulation mechanisms

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ABSTRACT

In order to evaluate the influence of particle size and particle concentration on the coagulation process, two kinds of particle suspensions, nanoparticles and microparticles, were employed to investigate the effect of particle size on coagulation mechanisms with varying coagulation parameters. Results showed that it is easier for nanoparticles to cause self-aggregation because of Brownian motion, while interception and sedimentation are the mainly physical processes affecting particle transport for microparticles, so they are more stable and disperse more easily. The particle size distribution and particle concentration had distinct influence on the coagulation mechanisms. Under neutral conditions, as the amount of coagulant increased, the coagulation mechanism for nanoparticles changed from charge neutralization to sweep flocculation and the nanoparticles became destabilized, re-stabilized and again destabilized. For microparticles, although the coagulation mechanism was the same as that of nanoparticles, the increased rate of aluminum hydroxide precipitation exceeded the adsorption of incipiently formed soluble alum species, resulting in the disappearance of the re-stabilization zone. Under acidic conditions, Brownian motion dominates for nanoparticles at low particle concentrations, while sweep flocculation is predominant at high particle concentrations. As for microparticles, charge neutralization and sweep flocculation are the mechanisms for low and high particle concentrations respectively. Under alkaline condition, although the mechanisms for both nano- and microparticles are the same, the morphology of flocs and the kinetics of floc formation are different. At low particle concentrations, nanoparticles have larger growth rate and final size of flocs, while at high particle concentrations, nanoparticles have higher fractal dimension and recovery factors.

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Introduction

The existence of particles in water not only affects the sensory quality of water, but also leads to pollutant residue during water treatment. Most pollutants of concern to human health and environmental quality are associated with solid particles. For example, pathogens encapsulated within particles (particle-associated) are difficult to disinfect. The survival of coliform bacteria at moderate to high values of disinfectant dose has been attributed to incomplete penetration of chemical oxidants.
into suspended particles (Dietrich et al., 2007). Among the particulates, nanoparticles attract more and more attention because of their size and specific properties. Due to their large surface area and huge surface free energy, nanoparticles, as a vector on which hazardous compounds are concentrated, can easily absorb heavy metals, microorganisms and natural organic materials in water (Liu et al., 2012). Moreover, recent studies have discovered that nanoparticles could trigger metabolic disturbance in zebrafish larvae, induce cell damage in E. coli and influence the hemolytic activity of hemoglobin (Yu et al., 2017). Nanoparticles exist widely in water. Broadly speaking, most natural organic matters (NOMs) belong to nanoparticles in a sense, and are expected to be removed as much as possible since their presence can lead to drinking water quality issues, such as disinfection by-product (DBP) formation and microbial activity in distribution networks, and reduction in treatment efficiency (e.g., membrane separation) (Fabris et al., 2008; Su et al., 2017). In addition, nanoparticles also include some pathogens, such as enterovirus, of which the size is 22–39 nm and which can cause severe disease with high morbidity and mortality in children (Pham et al., 2018). The existence of nanoparticles in the natural environment can directly or indirectly affect human health and ecosystems. Therefore, the control of nanoparticles in traditional water treatment is vital.

Coagulation, as the most widely used traditional water treatment process, has not been clearly studied regarding nanoparticles’ coagulation behavior. Although the coagulation rate is considered to be independent of the particle size and concentration according to the classical Smoluchowski formula (Ludwig and Peschel, 1988), a previous study has found the rapid coagulation rate of nanoparticles to be inconsistent with the theoretical value. Higashitani et al. (2017) studied the rapid coagulation rates of a series of particle sizes of nanosilica, and the results clearly showed that the rapid coagulation rate was reduced by four orders of magnitude compared with the theoretical value when the particle size was smaller than 300 nm, while the rates were approximately equal to the theoretical value for particle sizes larger than 300 nm. In addition, Kobayashi et al. (2005) compared the aggregation behavior of 30, 50 and 80 nm silica, and found that silica particles of 30 and 50 nm size did not follow the DLVO theory, and a non-DLVO repulsive force was considered to exist in the small nanoparticle solution. These results all proved that compared with microparticles, nanoparticles have their own characteristics in the kinetics of coagulation. Moreover, Adachi et al. (1994) found that the initial number concentration of particles was also a factor that influenced the rapid coagulation rate. When the initial number concentration is larger than \(10^{12}/\text{cm}^3\), the value of the rapid coagulation rate was twice the theoretical value. This trend of rapid coagulation rate with particle concentration coincides with experimental observations.

Previous studies mainly focused on the kinetics of rapid coagulation using high concentrations of electrolytes. The difference of coagulation mechanisms between microparticles and nanoparticles is still unclear. Moreover, differences in aggregation rates, aggregate size and the morphology of flocs are still unavailable. This study aimed to evaluate the influence of particle size and particle concentration on the coagulation process for alum at different dosages and different pH. Floc properties, including size and fractal dimension before and after breakage, were investigated to explore the coagulation mechanisms. This basic study on the coagulation of nanoparticles and microparticles by alum would provide some necessary information for the enhancement of the efficiency of nanoparticle removal by coagulation.

### 1. Materials and methods

#### 1.1. Chemicals

Aluminum chloride hydrate (\(\text{AlCl}_3\cdot6\text{H}_2\text{O}\)) ‘alum’, sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium chloride (NaCl) and sodium bicarbonate (NaHCO₃) were all obtained from Sinopharm Chemical Reagent Co., Ltd., China. All the reagents used in this study were of analytical grade and Milli-Q water was used in all solutions.

#### 1.2. Preparation and characterization of silica suspension

Nano- and microsilica (Aladdin, China) were used as the model suspensions. 25 g of nanoparticles was dispersed in 5 L of deionized (DI) water in a high-speed blender. 4000 r/min for 10 min, the suspension was settled for 7 days. The top 4 L was decanted and retained. Its solid content was 1.6 g/L by gravimetry. 25 g of microparticles was dispersed in 5 L of DI water and magnetically stirred for 2 days. The size of nanoparticles and microparticles were measured by transmission electron microscopy (TEM, H-7500, Hachi, Japan) and dynamic light scattering (DLS, Zetasizer Nano ZS90, Malvern, UK). As shown in Fig. 1a, the microparticles were almost spherical, with diameter of 1–6 μm; while for nanoparticles, the size was about 200–600 nm in diameter with obvious agglomeration (Fig. 1b). Fig. 2 shows the particle size distributions of nanoparticle and microparticle systems as determined by the Nano ZS90. The size distribution of the nanoparticle system was 100–1000 nm, and the average size was 700 nm. The size distribution of the microparticle system was 1700–3500 nm, and the average size was 2800 nm. The zeta potentials of nanoparticles and microparticles were −21.9 and −45.5 mV, respectively, which confirmed that the stability of both systems was ensured by repulsive interactions.

The test solutions were prepared using DI water with addition of 5 mmol/L NaCl and 4 mmol/L NaHCO₃ to provide fixed concentrations of electrolyte and alkalinity, and the stock suspension was diluted in water to give a clay concentration of 10 or 1500 mg/L. The pH of the solution was adjusted to fixed values by pre-addition of 0.1 mol/L HCl and 0.1 mol/L NaOH. The experiments were conducted at ambient temperature.

#### 1.3. Jar test

Coagulation experiments were conducted in 500 mL glass beakers using a conventional Jar-test apparatus (MY 3000-6F, Wuhan Meiyu, China). Prior to the addition of alum, the target pH was adjusted with rapid mixing at 250 r/min for 30 sec.
Then alum was dosed, 2 min of rapid mixing at 200 r/min was applied, followed by 20 min of slow stirring at 40 r/min to generate flocs. After the growth of flocs, the flocs were exposed to 200 r/min for 5 min and then back to 40 r/min for 20 min to compare the shear properties of flocs in different conditions. The flocs were allowed to settle for 30 min, and the residual turbidity of the supernatant was measured using a 2100N Turbidimeter (Hach, USA). A small sample was taken immediately after 2 min rapid mixing for the determination of zeta potential (Zetasizer Nano ZS90, Malvern, UK).

1.4. Flocs fractal structural analysis

A laser diffraction instrument (Mastersizer 2000, Malvern, UK) operating with a He–Ne laser at a wavelength of 633 nm was used to determine the hydrodynamic diameter of the different samples. The principle of this monitoring technique has been described previously (Tang, 1999) and has been applied in many studies (Chekli et al., 2013; Xu et al., 2014, 2016; Yu et al., 2014). Essentially, this method follows the fact that the diffraction angle is inversely proportional to particle size, by application of Mie theory.

For independent aggregates, when light passes through the colloid, the aggregates scatter the light, and the total scattered light intensity \( I \) (cd) has a relationship with the scattering vector \( Q \) (V/m), as shown in Eq. (1). According to the formula, the fractal dimension \( D_f \) can be acquired through the slope of the plot \( I \) against \( Q \) on a log–log scale to reflect the density of flocs (Spicer et al., 1998). Furthermore, the floc strength and re-growth abilities have previously been compared by use of floc strength \( S_f \) and recovery factors \( R_f \). The calculation methods are as follows (Eqs. (2)–(3)) (Xiao et al., 2011).

\[
I \propto Q^{D_f} \tag{1}
\]

\[
S_f = \frac{d_2}{d_1} \tag{2}
\]

\[
R_f = \frac{d_3-d_2}{d_1-d_2} \tag{3}
\]

where \( d_1 \) (m) is the maximum diameter of flocs before breakage, \( d_2 \) (m) is the minimum diameter of flocs during breakage and \( d_3 \) (m) is the maximum diameter of flocs after re-growth.

2. Results and discussion

2.1. Effect of particle size on particle removal and coagulation mechanisms

Fig. 3 exhibits two particle systems with different particle sizes. The changes in turbidity removal rate and the variation of zeta potential with different concentrations of coagulant were compared. At the same particle concentration (1500 mg/L), the initial surface negative charge of nanoparticles was relatively lower. TEM images (Fig. 1a–b) showed that microparticles were more dispersed in water, while nanoparticles tended to be agglomerated. It was proposed that nanoparticles easily self-aggregated due to Brownian motion, resulting in the reduction of surface negative charge (O’Melia, 1980). Although the particle number of microparticles was lower than that of nanoparticles at the same particle concentration,
the surface negative charge of microparticles was higher. Therefore, the variation of the zeta potential of microparticles with the dosage of coagulant is the comprehensive embodiment of the particle number and surface charge of particles. As the concentration of coagulant increased, the zeta potential of the two systems also increased. Below 0.16 mmol/L dosage of alum, the zeta potential of nano- and microparticles was almost the same. Nevertheless, with the further increase of alum concentration, the zeta potential of nanoparticles was higher. There are probably two reasons for this phenomenon. One is that nanoparticles can collide with more highly charged hydrolysis products at the same stirring intensity due to their smaller size and stronger Brownian motion. The other one is that for microparticles, the dosage of coagulant is excessive, so its hydrolysis products are mainly amorphous precipitates rather than charged species. Consequently, the microparticles can be enmeshed by the mode “sweep flocculation.” As for nanoparticles, although the amorphous precipitates can also be formed under high alum concentration, the size is only several nanometers and the surface still has a relatively high positive charge, resulting in charge neutralization still playing a role. Details will be discussed later in the article.

Although both of the systems reached the maximum turbidity removal rate under 0.16 mmol/L alum dosage, the turbidity removal rate curves were different with the increase of alum dosage. For microparticles, the turbidity removal rate kept constant when the alum dosage was more than 0.16 mmol/L, while that of nanoparticles declined to zero. As can be seen in Fig. 3, both systems had the highest turbidity removal efficiency near the isoelectric point, indicating that under low coagulant dosage, charge neutralization plays a dominant role. As for nanoparticles, when the concentration of alum increases, the negative surface charges of particles are completely neutralized and reversed so that the turbidity removal rate declines to zero. As the alum concentration increases still further, especially around neutral pH, the main hydrolysis species of alum are transformed into amorphous precipitation (Duan and Gregory, 1998). This precipitation is relatively small in the early stage, probably a few nanometers in size, so the turbidity of the system is increased compared to raw water. Although the small colloid may further aggregate to form bigger flocs, it is insufficient to precipitate (for coagulant dosages more than 0.5 mmol/L). By contrast, for microparticles, re-stabilization does not occur because the increased rate of aluminum hydroxide precipitation may compete successfully with the adsorption of incipiently formed soluble alum(III) species (Stumm and O’Melia, 1968). It is easier to form bigger and heavier flocs by the sweep flocculation mechanism due to the large size of the particles. Consequently, the turbidity removal rate of microparticles remains higher.

### 2.2. Effect of pH on particle removal and coagulation mechanisms

Initial pH has an important effect on the surface charge of particles and the coagulation behaviors of Al-based coagulants (Zhang et al., 2015). Therefore, the influence of pH on zeta potential and turbidity removal rate for the two particle systems with different particle size was determined and is shown in Fig. 4. The coagulant dosage was 0.16 mmol/L, which was the optimum dosage determined in Section 2.1. In both systems, with pH variation, the zeta potential was negatively correlated with the turbidity removal rate, in that a significant decline of zeta potential corresponded to a high turbidity removal rate. Moreover, the zeta potential of both systems reached maximum under the condition of pH 6.

The isoelectric point of silica is about 2–3 (Sokolov et al., 2006), so as the pH increases from 5.5 to 8, the negative charge of silica increases as well. Nevertheless, the hydrolysis products of alum vary with aqueous pH. As pH increases, alum salts undergo hydrolysis, complexation, polymerization and precipitation processes. As shown by the hydrolysis pattern of alum with pH (Duan and Gregory, 2003; Stumm and O’Melia, 1968), when pH is below 3, Al3+ is the dominant hydrolysis species. Above pH 8, various monomeric species and polymeric species, such as Al(OH)3+, Al6(OH)153+, Al13(OH)405+ will form. Above pH 8, the concentration of both SiO2 were 1500 mg/L.

![Fig. 3 - Turbidity removal rate and Zeta potential of alum-silica flocs as a function of alum concentration at pH 7 (Concentration of both SiO2 were 1500 mg/L).](image1)

![Fig. 4 - Turbidity removal rate and Zeta potential of alum-silica flocs as a function of pH at 0.16 mmol/L of alum (Concentration of both SiO2 were 1500 mg/L).](image2)
aluminate anion $\text{Al(OH)}_3^-$ is the predominant hydrolysis product (Liu et al., 2012).

The variation of zeta potential under different pH conditions is the comprehensive embodiment of particle surface charge and the neutralization ability of the alum hydrolysis species. On the one hand, the surface charge of particles becomes more and more negative from pH 5 to 8. On the other hand, highly charged polymeric aluminum species (e.g., $\text{Al}_{13}$) form at pH 6, and as the pH further increases, the precipitation of alum occurs, which reduces its ability for neutralization. As a result, the zeta potential reached its peak at pH 6 and decreased gradually with the increment of pH.

At pH 7, the turbidity removal rate of both nano- and microparticles reached the maximum value. At this point, the zeta potential was close to zero, indicating that in neutral conditions, charge neutralization played a dominant role. However, when pH was greater than 7, the zeta potential decreased while the turbidity removal rate remained unchanged. Therefore, charge neutralization was not the dominant mechanism, because the optimized dosage for turbidity removal was inconsistent with the isoelectric point. According to the hydrolysis pattern of alum with pH, under the conditions of 0.16 mmol/L alum concentration at pH 8, the hydrolysis species of alum is mainly the precipitated amorphous aluminum hydroxide. Combined with the phenomenon of high turbidity removal rate, this indicates that sweep flocculation is the main mechanism under alkaline conditions.

As shown in Fig. 4, the effects of pH on zeta potential and turbidity removal rate for both systems were similar, so pH 6 and 8 were chosen to represent acidic and alkaline conditions for further studies.

### 2.3. Effect of particle concentration on particle removal and coagulation mechanisms

Some research showed that particle concentration could influence the aggregation rate, while others found the opposite results (Tourbin and Frances, 2009). Therefore, 10 and 1500 mg/L were chosen to represent low and high initial particle concentrations to determine the influence of the particle concentration for different particle size distributions.

As can be seen from Fig. 5a, under the condition of pH 6, the turbidity removal effect for both systems was not good whether for low or high particle concentrations, although the effect was more obvious for the nanoparticle system. With the increase of the particle concentration, the turbidity removal effect of the nanoparticle system was much worse than that of the microparticle system. As the concentration of nanoparticles increased, the turbidity removal rate decreased first and then increased, which is not in accordance with the change of zeta potential (Appendix A Fig. S1), indicating that charge neutralization was not dominant. The zeta potential stabilized at 30 mV for high particle concentrations, indicating that at the applied dosage of alum at pH 6, the solution should be supersaturated with respect to amorphous aluminum hydroxide precipitation. At the low concentration of alum, the precipitation forms gradually and is very slight. The surfaces of particles still have high positive charges, giving a low collision efficiency in the initial stage. When the precipitated hydroxide particles reach a certain size and number, sweep coagulation begins with the formation of small flocs, resulting in a slight rise in the turbidity removal rate (Wang and Gregory, 2002). However, for microparticles, the change of turbidity removal rate is broadly in line with the zeta potential data at low particle concentration, indicating that charge neutralization is the dominant mechanism. The charge on the surface reverses and microparticles are re-stabilized, so the removal of turbidity is poor. On increasing the concentration of microparticles, the turbidity removal rate slightly increased. On the one hand, high particle concentration increases the collision frequency of particles, which enhances coagulation. Compared with Brownian diffusion, as the main mechanism for nanoparticles, interception and sedimentation are the main mechanisms for microparticles. Therefore, at high particle concentration, the turbidity can be reduced by the sedimentation of the particles themselves. On the other hand, under the high concentration of alum, microparticles may promote growth sites on the aluminum hydroxide lattice, resulting in promotion of the nucleation of aluminum hydroxide (Duan and Gregory, 1998). As the concentration of particles increases, the particles can become

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**Fig. 5** – Turbidity removal rate as a function of the concentration of alum at low and high particle concentrations at pH 6 (a) and 8 (b).
emeshed by “sweep flocculation” in a flocculent mass of amorphous aluminum hydroxide, which improves the turbidity removal rate.

Under alkaline conditions (pH 8), the removal efficiency of turbidity was significantly increased when the particle concentration increased for both nano- and microparticle systems (Fig. 5b). Combined with the variation of zeta potential (Appendix A Fig. S2), this showed that under low particle concentrations, near the zeta potential of zero, the turbidity removal rate reached a maximum. With further increase of alum concentration, the particles acquired excess positive charge and became re-stabilized. The electrical repulsion between them resulted in a decline in the turbidity removal rate, which proved that charge neutralization played a dominant role at low particle concentrations. For the nanoparticle system, as the alum further increased, the primary amorphous precipitate was formed, which was only a few nanometers in size (Bottero et al., 1982), so the turbidity was increased slightly, resulting in a negative turbidity removal rate. Under the condition of high particle concentration, for both nanoparticle and microparticle systems, the optimal dosage of alum was 0.16 mmol/L, while the zeta potential at this dosage was ~10 mV, indicating that sweep flocculation was the main coagulation mechanism. According to the results, it could be found that particle size had slight effects on coagulation mechanisms under alkaline conditions.

There was a clear difference in turbidity removal rate between acidic and alkaline conditions. One reason is that the removal effect of particles is especially poor under acidic conditions. That is because the silica surface of SiOH is so hydrophilic that it forms a thick layer of adsorbed water molecules under acidic conditions, where short-range repulsion hinders particle collision. Under alkaline conditions, however, the deprotonation of SiOH reduces the effect of the bound water. On the other hand, the hydrolysis products of alum in acidic conditions are highly charged polymeric species with strong neutralization ability, so a small amount of alum is enough to re-stabilize the particles. The other reason is that the removal effect is especially poor for nanoparticles compared with microparticles under acidic conditions. It has been reported that the effect of the bound water on the coagulation will be reduced as the relative thickness of the adsorbed water to the particle size becomes small (Higashitani et al., 1990). Therefore, the repulsion effect of the adsorbed water layer on the surface of nanoparticles is more prominent due to its small particle size.

It is clear that particle concentration and particle size affect the coagulation mechanisms. Under acidic conditions, Brownian motion is predominant for nanoparticles at low particle concentrations, while with increasing particle concentration, the mechanism changes to sweep flocculation. For microparticles, charge neutralization and sweep flocculation are the dominant mechanisms for low and high particle concentrations, respectively. However, the particle size has slight effect on the coagulation mechanism under alkaline conditions. For both nano- and microparticles, the mechanism is charge neutralization for low particle concentrations and sweep flocculation for high particle concentrations.

2.4. The formation, breakage and re-growth of flocs

The characteristics of flocs strongly influence the efficiency of solid-liquid separation and water quality. Therefore, the growth of flocs was monitored online by dynamic light scattering and the size distribution, strength and fractal structure of flocs under different conditions were determined and compared.

Fig. 6a shows the online growth of flocs with different particle sizes and concentrations under the condition of pH 6. The optimum dosages of alum were chosen for each group of experiments. For nanoparticles, there was no flocculation growth curve at low particle concentration, which is lower than Malvern’s detection limit. Under high particle concentration, the amount of flocs increased significantly, but the size of the generated flocs was small, only 160 μm, which is not enough to generate settling, so the corresponding turbidity was not decreased. Combined with the characteristics of flocs (Table 1), it can be seen that the fractal dimension of generated flocs was about 2.2, which was higher than that of the microparticle system. It indicated the flocs formed by

![Fig. 6 – Formation, breakage and re-formation of aggregates by alum at pH 6 (a) and pH 8 (b).]
nanoparticles were relatively denser. This is because compared with microparticles, besides the effect of higher particle number, Brownian motion dominates due to the smaller size of nanoparticles, and the collision frequency is higher, resulting in denser morphology of flocs.

As for microparticles, it can be seen that under the mechanism of charge neutralization, the flocs are smaller and have higher strength factor and recovery factor at the low particle concentration. As reported, the fractal dimension is 1.8 for diffusion-limited colloid aggregation (DLCA) and 2.1 for reaction-limited colloid aggregation (RLCA) (Lin et al., 1989). Under high particle concentrations, the fractal dimension of generated flocs is 1.3, indicating that it is in the DLCA regime. In this regime, due to the lack of electrostatic repulsion between particles, they are transported by three mechanisms: Brownian diffusion, interception (a form of velocity gradient) and sedimentation (O’Melia, 1980). Because the particle size of microparticles is big, interception and sedimentation play a dominant role. Therefore, in the process of breakage, as the intensity of stirring increased, so did the particle collision frequency. As a result, at the later stage of coagulation, the size of flocs increased.

Fig. 6b shows the online growth of flocs with different particle sizes and concentrations under the condition of pH 8. It can be seen that the growth rate and final size of nanoparticle flocs are larger than those of microparticles under the condition of low particle concentration. The main reason for this phenomenon is that the surface charges of both nano- and microparticles are neutralized by alum, which means that this is in the diffusion-controlled regime. Nanoparticles have higher diffusion rate and larger particle number due to their smaller size, resulting in high particle collision frequency.

By contrast, at high particle concentration, the growth rate and final size in the nano- and microparticle systems are almost the same. As we discussed above, the mechanism for both systems is sweep flocculation. Compared with the large size of the amorphous aluminum hydroxide precipitates, the size of the particles themselves can be ignored. Nevertheless, the fractal dimension and the recovery factor of nanoparticles are both higher than those of microparticles. This is because nanoparticles have more chance to penetrate into the inner pores of large flocs due to their smaller size (Wang et al., 2011). Clearly, when increasing the particle concentration, no matter whether for the nano- or microparticle system, the growth rate and the final size of flocs are both increased, which is inconsistent with the Smoluchowski theory.

### Table 1 – Characteristics of flocs.

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<th>μSiO2</th>
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<th>μSiO2</th>
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**3. Conclusions**

Under neutral pH conditions, the initial negative charge on the surface of nanoparticles is lower due to self-agglomeration. For both nano- and microparticle systems, charge neutralization and sweep flocculation are the main mechanisms for low and high alum concentrations, respectively. However, for microparticles, the increased rate of aluminum hydroxide precipitation exceeds the adsorption of incipiently formed soluble alum species, resulting in the disappearance of the re-stabilization zone. The influence of the particle size distribution on particle removal and coagulation mechanisms is slight at different pH values. Particle size distribution and concentration have significant effects on coagulation mechanisms. Under acidic conditions, Brownian motion and sweep flocculation are predominant for low and high concentrations of nanoparticles. By contrast, charge neutralization and sweep flocculation are the main mechanisms respectively for low and high particle concentrations of microparticles. Under alkaline conditions, the coagulation mechanisms are only slightly affected by particle size. For both nano- or microparticle systems, charge neutralization is dominant for low particle concentrations, and sweep flocculation is the main mechanism for high particle concentrations. Under alkaline conditions, the growth rate and final size of nanoparticle flocs are larger than those of microparticle flocs at low particle concentrations. However, at high particle concentrations, the fractal dimension and recovery factor of nanoparticle flocs are higher than those of microparticle flocs. Whether in micro- or nanoparticle systems, improving the particle concentration leads to larger floc growth rate and final floc size.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2019.02.021.