

# Stability and sedimentation of silver nanoparticles in the presence of monovalent, divalent and trivalent electrolyte solutions

Shao-Feng Chen and Hongyin Zhang

## ABSTRACT

The present study seeks to elucidate the effect of different electrolytes on the stability of citrate-coated silver nanoparticles synthesized by the reduction of the  $\text{Ag}(\text{NH}_3)_2^+$  complex via Tollens' method. Time-resolved dynamic light scattering technique was used to measure the aggregation behavior of the nanoparticles over a range of electrolyte ( $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$ ) concentrations. From the aggregation kinetic data, the critical coagulation concentration values were calculated as 0.11,  $1.7 \times 10^{-3}$ , and  $5.06 \times 10^{-6}$  M for  $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$ , respectively. Supernatant of the nanoparticle suspension in presence of the three electrolytes was collected and measured using inductively coupled plasma mass spectrometry to quantify the sedimentation. It was found that the silver nanoparticle aggregates settled rapidly in the slow aggregation and fast aggregation regimes. Their sedimentation followed a nanoparticle size-dependent manner.

**Key words** | aggregation, sedimentation, silver nanoparticles, stability

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## INTRODUCTION

Silver nanoparticles (AgNPs) are widely used in many consumer products with applications in clothing, medical devices, cosmetics and other products due to their antimicrobial effect (Greulich *et al.* 2012). The extensive applications of AgNPs result in their inevitable release into the environment (Colvin 2003; Li *et al.* 2010). One of the likely routes include their release into natural aquatic systems, which results in their possible introduction into drinking water treatment facilities, or the nanoparticles can be drained into sewer systems and finally into wastewater treatment facilities (Colvin 2003). However, the stability and fate of AgNPs are still not well understood. Numerous previous studies have demonstrated that the stability of AgNPs is closely related to their toxicity (Choi *et al.* 2009; Gao *et al.* 2009; Brar *et al.* 2010; Zook *et al.* 2011). Recent investigations have shown that small dispersed nanoparticles are more toxic than larger nanoparticle aggregates (Bae *et al.* 2010; Zook *et al.* 2011). Therefore, it is important to study and quantify the aggregation behavior of AgNPs to predict the fate of AgNPs in different aqueous media.

Prior studies have focused on studying the effect of monovalent and divalent electrolytes on the aggregation behavior of AgNPs (Li *et al.* 2010, 2012; Huynh & Chen 2011; Chen & Zhang 2012; Zhang *et al.* 2012; Baalousha *et al.* 2013; Chen & Zhang 2013). It has been widely reported that divalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  have much higher destabilizing effect on AgNPs than monovalent cations (Li *et al.* 2010, 2012; Huynh & Chen 2011). The destabilizing effect of the electrolytes is quantified as the critical coagulation concentration (CCC). It represents the minimum amount of electrolyte required to completely destabilize the suspension. Previous studies reported the CCCs of  $\text{Ca}^{2+}$  are 2.0, 2.1, and 4.9 mM for bare AgNPs, AgNPs stabilized with sodium citrate, and AgNPs stabilized with pyrovinylypyrrolidone, respectively, while the CCCs of  $\text{Na}^+$  are 40.0, 47.6, and 111.5 mM for the respective AgNPs. The classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory of colloidal stability can satisfactorily explain the aggregation behavior of the AgNPs in the presence of various electrolytes in the above-mentioned studies. However, none of the above-mentioned

studies has uncovered the influence of trivalent cations such as  $\text{Al}^{3+}$  on the aggregation behavior of AgNPs.  $\text{Al}^{3+}$  cation is a commonly used conventional multivalent metal ion in water and wastewater treatment facilities for coagulation purposes. As one of the likely routes include the release of AgNPs into water and wastewater treatment facilities, it is of great interest to investigate the destabilizing effect of  $\text{Al}^{3+}$  on the AgNPs. To the authors' knowledge, this study is the first to investigate the aggregation behavior of AgNPs in the presence of  $\text{Al}^{3+}$  cation. This is also the first study investigating and comparing the sedimentation of AgNPs in monovalent, divalent, and trivalent cationic solutions.

The objective of this study is to compare the effect of monovalent ( $\text{Na}^+$ ), divalent ( $\text{Ca}^{2+}$ ), and trivalent ( $\text{Al}^{3+}$ ) cations on the stability of AgNPs that were synthesized via reduction of  $\text{Ag}(\text{NH}_3)_2^+$  using maltose and stabilized with sodium citrate. Time-resolved dynamic light scattering (DLS) technique was used to measure the aggregation kinetics of the AgNPs over a range of electrolyte concentrations. CCCs were calculated based on the aggregation kinetic data. In addition, sedimentation of AgNPs was also studied by measuring concentration of total silver from the supernatant of AgNP suspension in the presence of the three electrolytes.

## EXPERIMENTAL

### Synthesis of AgNPs

Citrate-stabilized AgNPs were synthesized via Tollens' method according to previously described procedure (Kvitek *et al.* 2008). In brief, ammonia (5 mM) was added slowly into  $\text{AgNO}_3$  (10 mM) solution to form an  $\text{Ag}(\text{NH}_3)_2^+$  complex. Then, a mixture of reducing sugar (1 mM D-maltose) and stabilizing agent (1 mM sodium citrate) was added to the  $\text{Ag}(\text{NH}_3)_2^+$  solution under vigorous stirring to reduce the  $\text{Ag}(\text{NH}_3)_2^+$  complex to AgNPs. Sodium citrate was used as stabilizing agent because it was extensively used in previous studies and allows us to compare results (Kvitek *et al.* 2008; Huynh & Chen 2011; Baalousha *et al.* 2013). During the synthetic process, NaOH was added to adjust the pH in the reaction system to about 11.5. The obtained AgNPs were cleaned in an ultrafiltration cell with 3,000 molecular weight cut-off membrane (Amicon) using deionized (DI) water until the pH reached 7. AgNPs were further characterized by UV-Vis spectrometry (Evolution 60S, Thermo Scientific) and DLS with a Malvern zetasizer, Nano ZS (Malvern, UK).

### Zeta potential measurement

The zeta potential of the AgNPs was measured at a temperature of 25 °C in NaCl,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$  solutions with concentrations range from  $10^{-7}$ – $10^0$  M using a zetasizer.

### Aggregation kinetics

The Malvern zetasizer was used to measure the aggregation kinetics of AgNPs. AgNP suspension was firstly introduced into an acrylic cuvette. A predetermined amount of electrolyte solution was added into the cuvette to achieve the desired electrolyte concentration. The cuvette was then hand-shaken and quickly inserted into the zetasizer. Particle size of AgNPs was recorded over 500 s at a time interval of 10 s. The aggregation rate ( $k$ ) of AgNPs can be determined by fitting the recorded experimental data using a linear least-squares regression (the slope: particle size versus time). The aggregation rate is directly proportional to the rate of change in particle size (Chen *et al.* 2006; Li & Huang 2010; Li *et al.* 2010):

$$k \propto \frac{dr}{dt}$$

where  $k$  is the aggregation rate;  $r$  is the particle size of AgNPs;  $t$  is the elapsed time of the experiment.

When repulsion forces present between AgNPs are strong, the degree of aggregation will be low, which is termed as slow aggregation. When the electrolyte concentration is increased to a certain threshold concentration, the aggregation of AgNPs falls into the fast aggregation regime, where the aggregation energy barriers are completely removed and the aggregation rate is independent of the increasing electrolyte concentrations. When the AgNPs in the electrolyte solution begin to form aggregates, each collision between nanoparticles will form larger nanoparticle aggregates. The possibility of successful collisions is defined as the attachment efficiency. It can be determined according to the following equation:

$$\alpha = \frac{k_{\text{slow}}}{k_{\text{fast}}}$$

where  $\alpha$  is the attachment efficiency of AgNPs, and  $k_{\text{fast}}$  represents the aggregation rate under the fast aggregation regime when the electrolyte concentration is equal to or above CCC. It is calculated by averaging the aggregation rates under electrolyte concentrations in the fast aggregation

regime. A good example showing the fast aggregation regime is shown in Figure 2(a), where the aggregation rates of AgNPs in  $\text{AlCl}_3$  solution become constant above  $5.06 \times 10^{-6} \text{ M}$  of  $\text{AlCl}_3$ .  $k_{\text{slow}}$  represents the aggregation rate under the slow aggregation regime when the electrolyte concentration is below CCC (aggregation rates below  $5.06 \times 10^{-6} \text{ M}$   $\text{AlCl}_3$  concentration) (Li & Huang 2010; Li *et al.* 2010; Baalousha *et al.* 2013). The attachment efficiencies were calculated by dividing the  $k_{\text{slow}}$  in the slow aggregation regime by the averaged  $k_{\text{fast}}$  values in the fast aggregation regime (Li *et al.* 2010). The calculated attachment efficiencies under slow and fast aggregation regimes were then fitted by a least-square linear regression and the intersections yield the CCC values (Baalousha *et al.* 2013).

### Sedimentation of AgNPs

The sedimentation study was conducted by monitoring the AgNP concentration (as total silver) in the supernatant of the nanosuspension as a function of time using inductively coupled plasma mass spectrometry (Element 2 series, Thermo Scientific). All measurements were made at  $25^\circ \text{C}$  in square cuvettes with duration of 24 h.

## RESULTS AND DISCUSSION

### Characterization of AgNPs

Average particle size and zeta potential of the AgNP suspension in DI water were found to be 42.2 nm and  $-36.9 \text{ mV}$ , respectively. The negative zeta potential is attributed to the adsorption of the citrate on the surface of AgNPs.

### Zeta potential of AgNPs in different electrolyte solutions

Figure 1 presents the zeta potentials of the citrate-stabilized AgNPs measured over a range of NaCl,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$  concentrations. Zeta potential is related to the electrostatic stability of the colloidal systems. Its value represents the degree of electrostatic repulsion between charged particles in a colloidal suspension. The result showed that AgNPs were negatively charged across all the conditions. Zeta potentials of AgNPs became less negative with increasing electrolyte concentrations due to the neutralization of the negative charges of AgNPs by the cations present in the electrolyte. Similar trends were observed in the literature (Li *et al.* 2010, 2012; Huynh & Chen 2011; Thio *et al.* 2012). Figure 1 also

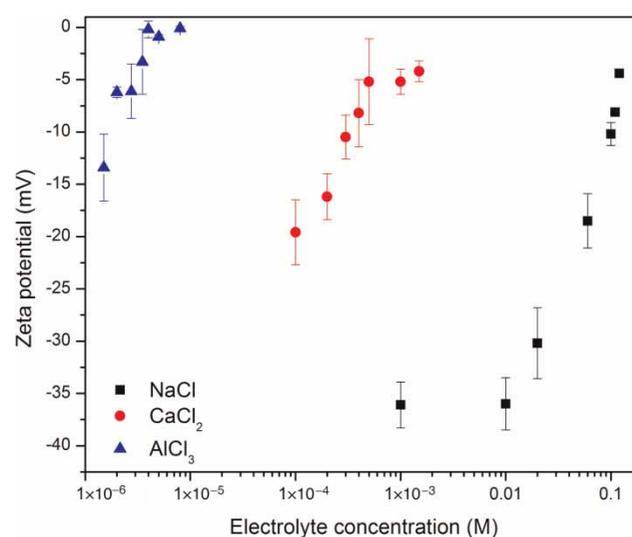


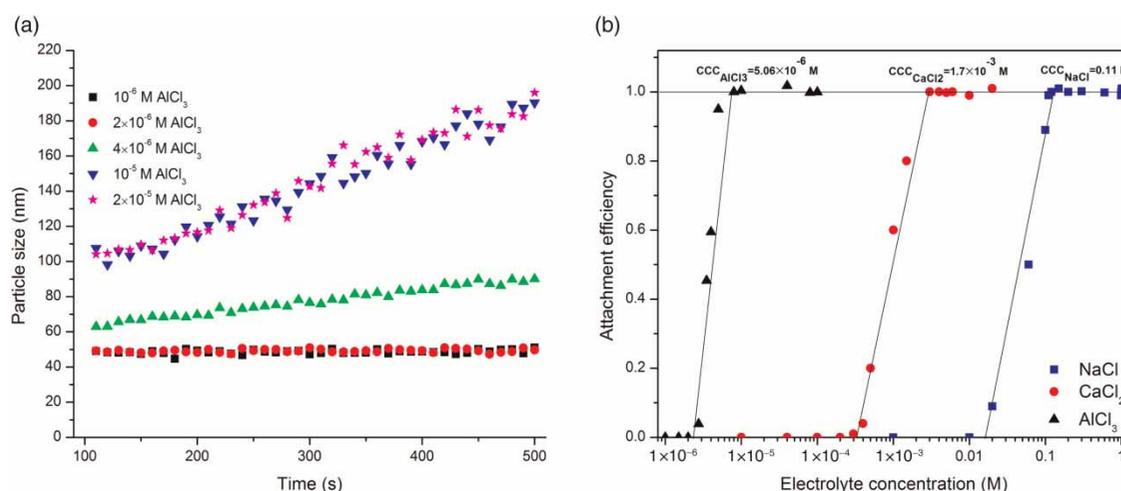
Figure 1 | Zeta potentials of AgNPs in the presence of NaCl,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$  solutions (AgNP concentration: 1 mg/L; temperature:  $25^\circ \text{C}$ ).

shows that zeta potentials of AgNPs in the presence of  $\text{CaCl}_2$  and  $\text{AlCl}_3$  are less negative than NaCl, which is because multivalent cations, especially  $\text{Al}^{3+}$ , could more effectively neutralize the negative charges of AgNPs (Li *et al.* 2010, 2012; Thio *et al.* 2012; Baalousha *et al.* 2013).

### Aggregation behavior of AgNPs in the presence of various electrolytes

The representative aggregation profile of citrate-stabilized AgNPs in the presence of  $\text{AlCl}_3$  is presented in Figure 2(a). The increase in electrolyte concentration results in a corresponding increase in the aggregation rates until the CCC is reached. Above the CCC, the aggregation rates do not increase any further. This aggregation behavior of AgNPs in the electrolyte solutions follows the DLVO-type behavior. The observed aggregation behavior of citrate-coated AgNPs agrees well with other published literature using the same citrate-stabilized AgNPs (Huynh & Chen 2011; Baalousha *et al.* 2013).

The attachment efficiencies  $\alpha$  (Figure 2(b)) were calculated from the aggregation rates of AgNPs as a function of electrolyte concentrations. The calculated attachment efficiencies under slow and fast aggregation regimes ( $\alpha = 1$ ) were then fitted by a least-square linear regression and the intersections yield the CCC values (Li & Huang 2010; Baalousha *et al.* 2013). The typical attachment efficiency profile consistent with DLVO colloidal theory was observed. Within the slow aggregation regime ( $\alpha < 1$ ), the stability of the AgNPs decreased with increasing electrolyte



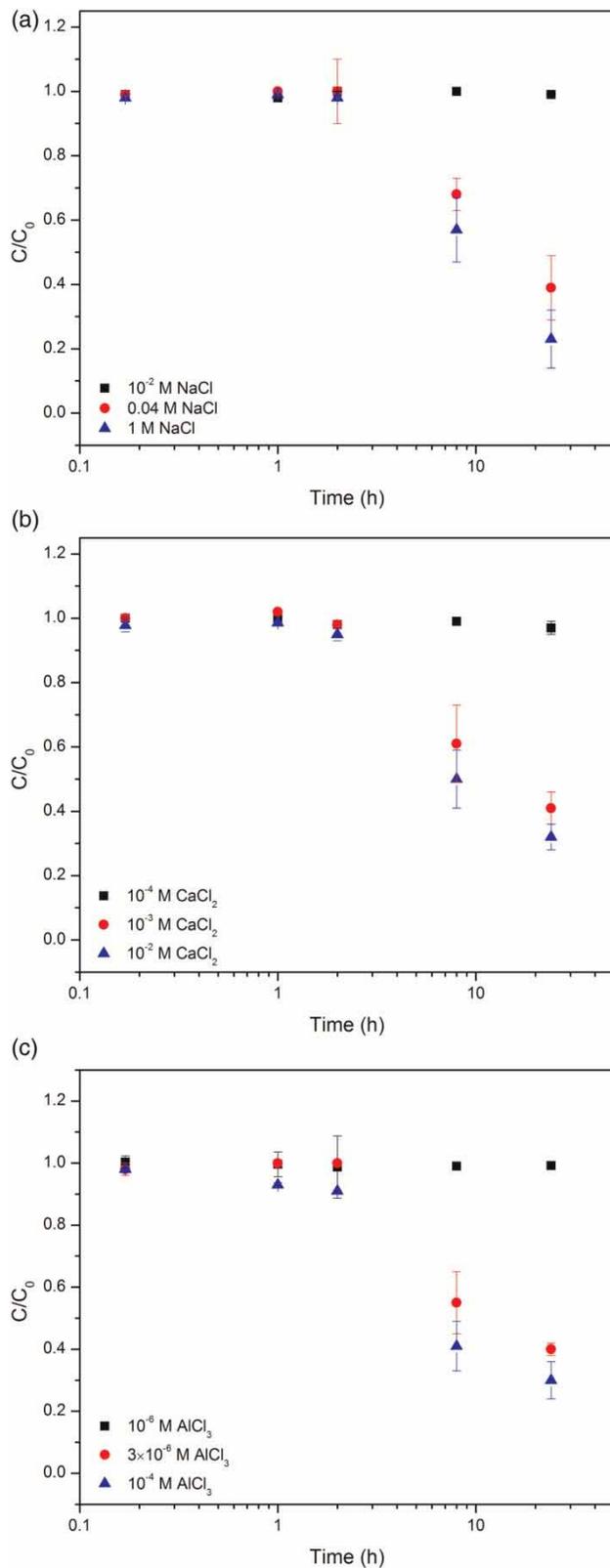
**Figure 2** | Representative aggregation kinetics of AgNPs in  $\text{AlCl}_3$  solution (a) and attachment efficiency of AgNPs as a function of electrolyte concentrations (b) (AgNP concentration: 1 mg/L; temperature: 25 °C).

concentrations. Increasing electrolyte concentrations can result in an increase in the aggregation rate by lowering the electrostatic energy barrier between the negatively charged AgNPs. The CCCs of AgNPs in the presence of NaCl,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$  were calculated as 0.11,  $1.7 \times 10^{-3}$ , and  $5.06 \times 10^{-6}$  M, respectively. The CCC measurements are consistent with the Schulze–Hardy rule, which indicates that the CCC of a colloidal system is extremely sensitive to valence of the counterions present in the colloidal system. However, the theoretical ratio of CCC for the three electrolytes is  $\text{CCC}_{\text{NaCl}}:\text{CCC}_{\text{CaCl}_2}:\text{CCC}_{\text{AlCl}_3} = 1/1^6:1/2^6:1/3^6 = 730:11.4:1$  indicated by the Schulze–Hardy rule, while the ratio of the CCCs obtained in our experiment was  $\text{CCC}_{\text{NaCl}}:\text{CCC}_{\text{CaCl}_2}:\text{CCC}_{\text{AlCl}_3} = 21739:336:1$ . It should be noted that the Schulze–Hardy rule applies well to symmetrical electrolytes such as NaCl. However, it may not apply to asymmetrical electrolytes such as  $\text{CaCl}_2$  and  $\text{AlCl}_3$  (Hunter 2001; Mylon *et al.* 2004). In addition, the difference between the experimental data and the theoretical CCCs might be due to the interaction between the multivalent cations ( $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ ) and the citrate molecules coated on the AgNPs. The interaction can lower the energy barrier against aggregation, which could facilitate the aggregation process.

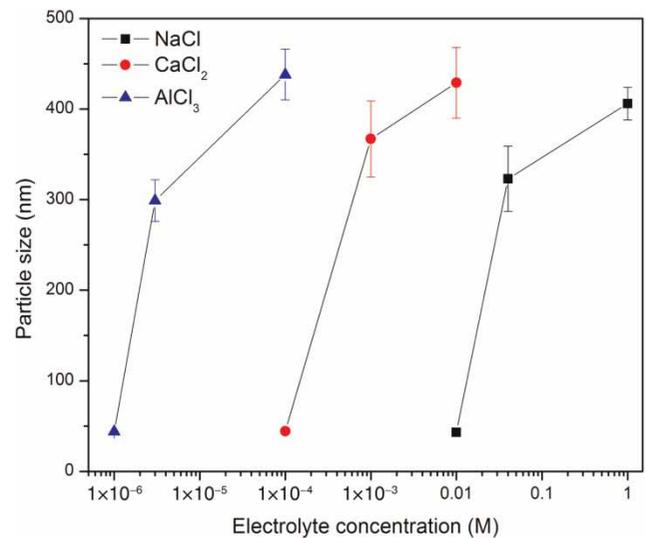
### Sedimentation profile of AgNPs in the presence of various electrolytes

Figure 3 presents the sedimentation profile of AgNPs in the presence of NaCl,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$  electrolyte solution. The three chosen concentrations of each electrolyte, from low to high, represent the electrolyte concentrations that

induce no aggregation ( $\ll \text{CCC}$ ), slow aggregation ( $< \text{CCC}$ ), and fast aggregation ( $\geq \text{CCC}$ ).  $C/C_0$  represents the AgNP concentration (as total silver) in the supernatant after sedimentation ( $C$ ) normalized with the initial AgNP concentration ( $C_0$ ). No sedimentation was observed using the lowest electrolyte concentrations for each salt. However, increasing electrolyte concentrations results in faster sedimentation of AgNPs. The observation agrees well with previous data (Elimelech *et al.* 1995; Tiraferri *et al.* 2008; Allouni *et al.* 2009; Stebounova *et al.* 2010). This might be attributed to the changes in particle size of AgNPs due to the nanoparticle aggregation. Previous studies have proposed that large nanoparticle aggregates may settle down faster than dispersed nanoparticles (Tiraferri *et al.* 2008; Stebounova *et al.* 2010). Therefore, in this study, particle size of AgNPs was measured using the same electrolyte concentrations and experimental duration (24 h) as used in the sedimentation experiment (Figure 4). Figure 4 shows that the particle size of AgNPs increases with increasing electrolyte concentrations. Figures 3 and 4 show that sedimentation of AgNPs is particle-size dependent. Similarly, Stebounova *et al.* (2010) showed that the sedimentation rate of AgNPs is faster in ALF solution (artificial lysosomal fluid) than in Gamle's solution (artificial interstitial fluid) due to the formation of larger nanoparticle aggregates (Stebounova *et al.* 2010). Tiraferri *et al.* (2008) also reported that the sedimentation rate is highly dependent on the nanoparticle sizes, and the experimental data of the sedimentation kinetics were fitted using an exponential decay curve which positively correlated sedimentation rate with particle size of nanoparticle aggregates (Tiraferri *et al.* 2008).



**Figure 3** | Sedimentation of AgNPs in the presence of NaCl (a), CaCl<sub>2</sub> (b), and AlCl<sub>3</sub> (c) over a range of electrolyte concentrations (initial AgNP concentration: 1 mg/L; duration: 24 h; temperature: 25 °C).



**Figure 4** | Particle size of AgNPs in the presence of NaCl, CaCl<sub>2</sub>, and AlCl<sub>3</sub> using the electrolyte concentrations in the sedimentation study (initial AgNP concentration: 1 mg/L; duration: 24 h; temperature: 25 °C).

## CONCLUSION

In summary, zeta potential of the citrate-stabilized AgNPs became less negative with increasing electrolyte concentration. As expected, multivalent cations (Ca<sup>2+</sup> and Al<sup>3+</sup>) had much stronger influence on both zeta potential and aggregation of AgNPs compared to monovalent cations (Na<sup>+</sup>), which is because multivalent cations are more effective at neutralizing the negative charge of AgNPs. The CCCs for AgNPs were determined as 0.11 M in NaCl,  $1.7 \times 10^{-3}$  M in CaCl<sub>2</sub>, and  $5.0 \times 10^{-5}$  M in AlCl<sub>3</sub> solution. Sedimentation happened in slow aggregation and fast aggregation regimes and sedimentation rate followed a particle-size-dependent manner. The result of this study suggests that aggregation of AgNPs can be influenced by the salinity in the aquatic environment. Therefore, change of salinity should be considered to predict the fate of AgNPs in aquatic systems. When AgNPs entered the water and wastewater treatment facilities, AgNPs can be removed by a conventional coagulation and aggregation process.

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