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# Silver nanoparticle removal from drinking water: flocculation/sedimentation or filtration?

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## Abstract

Silver nanoparticles are used in a wide variety of consumer products and are therefore rapidly becoming ubiquitous in the natural environment; they can be expected to be found in the natural waters used as drinking water supplies. This research investigated whether such particles could be expected to be removed in conventional water treatment plants such as flocculation and filtration. Both flocculation and granular media filtration experiments with citrate-capped silver nanoparticles were performed at different ionic strengths and in the presence and absence of natural organic matter. The results were generally consistent with theories of particle destabilization that have been developed for larger particles (greater than 1  $\mu\text{m}$ ), suggesting that silver nanoparticles are likely to be removed in conventional treatment processes.

## Introduction

The objective of this research is to understand whether conventional unit processes in a drinking water treatment plant are capable of silver nanoparticle removal. Silver nanoparticles (AgNPs) are incorporated into a wide variety of consumer products because of their known antimicrobial properties (Sellers et al., 2009; US EPA 2007; Kim et al., 2007). The continued widespread use, small size, and unique physical properties of AgNPs tend to concern scientists that a unique class of contaminants is proliferating in the natural environment (Liu and Hurt, 2010; Petosa et al., 2010). Understanding the fate and transport of AgNPs within water treatment plants is therefore of great interest. Our research focuses specifically on investigating removal of AgNPs in flocculation and in granular media filtration. Experiments conducted under the same environmental conditions allow for a comparison of the effectiveness of each process at removing AgNPs from drinking water sources.

## Silver Nanoparticles

Spherical AgNPs with 50 nm diameter and capped with citrate were purchased from Nanocomposix (San Diego, CA, USA); the particles come in a 1 mg/mL stock suspension. The particle size distribution was measured by DLS (Malvern Zetasizer) in our laboratory; the results shown on the left side of Figure 1 confirm the average size to be very close to 50 nm with a narrow distribution. The TEM image (FEI Tencai), also obtained in our laboratory and shown on the right in Figure 1, confirms that these particles are essentially spherical, and suggests that

the distribution is even narrower than the DLS measurement indicates. These particles were used throughout the experimentation reported herein.

## Solutions

Several different solutions were used in this research, reflecting the primary influences that inhibit or promote particle interactions with each other (both flocculation and filtration) and with other surfaces (filtration). First, two different salts were used: sodium nitrate ( $\text{NaNO}_3$ ) and calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ); these were chosen both because of the singly vs. doubly charged cation that could affect the double layer interactions between particles and because calcium could be expected to have a specific chemical interaction with the citrate capping of the AgNPs. Nitrate rather than chloride salts were used to avoid any potential ligand-promoted dissolution as observed by Linnert et al. (1990) or bridging as observed by Li et al. (2012). Second, in some experiments, two different ionic strengths were used, 2 and 10 mM; note that, to maintain the same ionic strength, different concentrations of the monovalent sodium nitrate and the divalent calcium nitrate were required. The specific values were chosen based on preliminary experiments, but the concept was based on classic DLVO (Derjaguin, Landau, Verwey, Overbeek) theory that a high ionic strength would create a sufficiently small diffuse layer surrounding the particles to encourage favorable particle-particle and particle-media interactions, whereas a lower ionic strength would have unfavorable interactions and lead to particle stability (little flocculation or little removal in a filter). Third, some suspensions were made to include natural organic matter (NOM) at a concentration (as TOC) of 3.5 mg/L. The source of the NOM was Lake Austin (Austin, TX, USA) and the hydrophobic organic acid fraction had been isolated and freeze-dried in previous research (Marron, 2010); stock solutions were made from this source and used throughout the research.

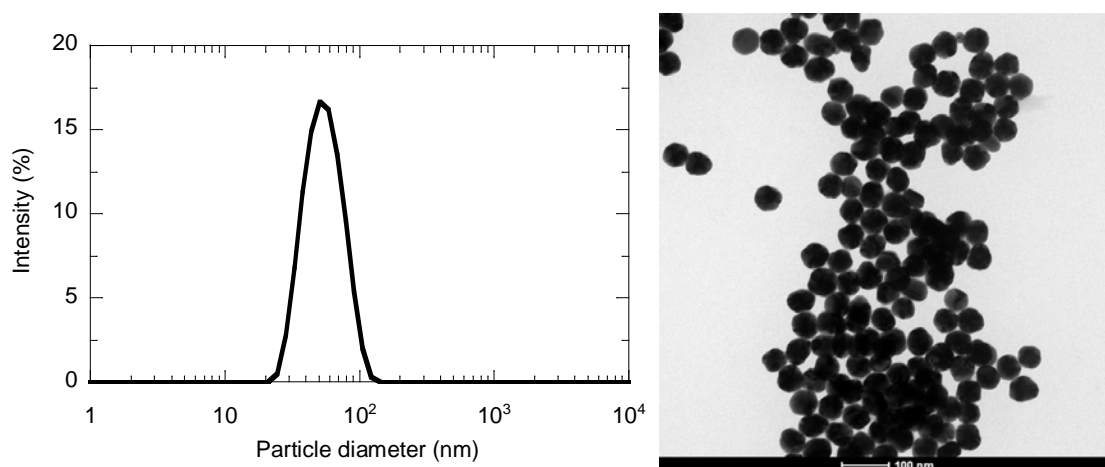


Figure 1. Particle size measurement by DLS and TEM

The silver nanoparticle suspensions were made by first diluting the stock suspension to the desired concentration for the experiments with distilled, deionized water; for different types of experiments, different silver concentrations were used as indicated below. If NOM was to be added, it was added next and allowed to interact with the particles for 24 hours to allow sufficient time for adsorption of NOM onto the AgNPs. Finally, nitrate salt stock solutions were made at a high concentration so that the desired final concentrations could be obtained with a 1:100 dilution (i.e., by adding only 10  $\mu\text{L}$  of the salt stock per 1000  $\mu\text{L}$  of the final suspension).

The nitrate salts were added immediately prior to the experiments described below (zeta potential measurements, as well as flocculation and filtration experiments).

### Zeta Potential

Solutions containing Nanocompositix citrate-capped AgNPs were prepared with and without 3.5 mg/L (as TOC) of NOM. Zeta potential was measured at different pH values using a Malvern Zetasizer nano ZS. The pH was adjusted using small amounts of concentrated nitric acid and sodium hydroxide, and appropriate amounts of concentrated salt solutions were added to the solutions to adjust the ionic strength to 10 mM for each reading. The measurements were made rapidly after the additions of these chemicals so as to not be influenced by aggregation of the particles.

The Zeta potential measurements shown in Figure 2 indicate a more negatively charged surface for the particles in the presence of  $\text{NaNO}_3$  as compared to  $\text{Ca}(\text{NO}_3)_2$ .  $\text{Ca}^{2+}$  is more efficient at neutralizing the surface charge of citrate-coated AgNPs due to its higher propensity to form complexes with citrate. The effect of NOM adsorption onto the nanoparticles is clear in the case of the  $\text{NaNO}_3$  suspensions, with the NOM increasing the negative charge of the surface at near neutral pH. Apparently, the  $\text{pK}_a$  of the NOM is higher than that of citrate, inasmuch as the point of zero charge was at a higher pH with the NOM coating than without for the sodium samples. For the calcium samples, NOM had no measurable effect on the surface charge. This lack of a surface charge change could be because the adsorption density of  $\text{Ca}^{2+}$  is greater than that of the NOM and therefore masks any subtle changes that NOM might have.

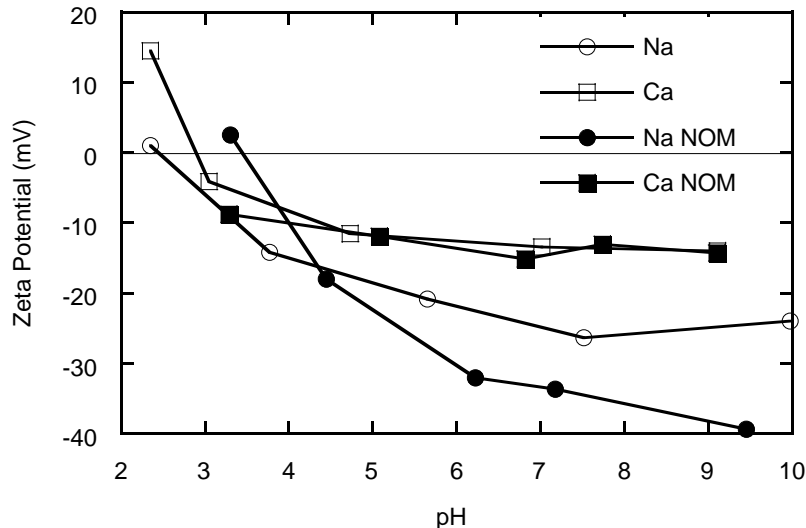


Figure 2. Zeta Potential of the silver nanoparticles: effects of pH and NOM. (All suspensions at 10 mM ionic strength)

### Energy of interaction

In the classic DLVO theory, two particles with the same sign of surface charge experience both electrostatic repulsive energy and van der Waals attractive energy that are a function of the separation distance. The sum of these interaction energies dictates the stability of the particles.

In the interaction of two identical particles, the energy of interaction can be calculated by the following equations for the attractive energy ( $V_A$ ) and the repulsive energy ( $V_R$ ) (Stumm and Morgan, 1996).

$$V_A = -\frac{A}{6} \left( \frac{2}{\bar{s}^2 - 4} + \frac{2}{s^2} + \ln \frac{\bar{s}^2 - 4}{s^2} \right)$$

$$V_R = 64\pi \frac{n_b k_B T}{\kappa^2} \frac{a_p^2}{(s + 2a_p)} \left[ \tanh \left( \frac{z \tilde{\psi}_d}{4} \right) \right]^2 \exp(-\kappa s)$$

In these equations,  $\bar{s}$  is the dimensionless separation distance,  $s$  is the true separation distance,  $A$  is the Hamaker constant,  $n_b$  is the number concentration of ions in the bulk solution,  $k_B$  is the Boltzmann's constant,  $T$  is the absolute temperature,  $a_p$  is the radius of the particles,  $\kappa^{-1}$  is the characteristic distance of the ionic diffuse layer (often called the Debye length), and  $\tilde{\psi}_d$  is the reduced (normalized) electrical potential of the surface.

For filtration, the interaction is between a particle and a much larger media grain; this situation can be modeled as the interaction between a particle and flat plate, as described by Hogg *et al.*, 1966:

$$V_A = \frac{A a_p}{6s} \left( 1 + \frac{14s}{\lambda} \right)^{-1}$$

$$V_R = \pi \epsilon_0 \epsilon_r a_p \left( 2\psi_{d_f} \psi_{d_p} \ln \left[ \frac{1 + \exp(-\kappa s)}{1 - \exp(-\kappa s)} \right] + (\psi_{d_f}^2 + \psi_{d_p}^2) \ln [1 - \exp(-2\kappa s)] \right)$$

The new variables include  $\lambda$ , the characteristic wavelength of the retarded van der Waals interaction, the product  $\epsilon_0 \epsilon_r$  is the permittivity in water, and  $\psi$  is zeta potential, with the subscripts  $p$  and  $f$  referring to the particle and the flat plate, respectively. The zeta potential of the filter media was measured to be -80 mV (at pH 8.0) by a SurPASS electrokinetic analyzer (Anton Paar GmbH, Graz, Austria). As shown in Figure 2, the AgNPs are negatively charged at pH 8.0, with somewhat different values for the different chemical conditions.

Calculations for both flocculation (particle-particle interactions) and filtration (particle-plate interactions) are shown in Figure 3(a) and 3(b), respectively; all of the calculations were made using an ionic strength of 10 mM and a pH of 8.0 (conditions used in the flocculation and filtration experiments). The Hamaker constant was assumed to be  $10^{-20}$  J for both the particles and the media. Note that the interactions are approximately an order of magnitude stronger in the filtration condition (Fig 3(b)) because the diffuse layer is essentially one-dimensional in that case and truly three-dimensional in the case of the particles. For either condition, the differences for the different solutions primarily reflect the differences in surface charge, as taken from Figure 2. As indicated above, the NOM made the particles considerably more negative in the sodium case, whereas it had essentially no effect in the calcium solutions.

The results in Figure 3 reflect the expectation that the calcium salt would have a greater effect on destabilization of the particles (i.e., reduce the repulsive energy barrier) than the sodium salt. The calculations suggest that the net energy is only very slightly repulsive at great separation distances in the particle-particle case (Figure 3(a)) for the calcium solution, suggesting that flocculation in the calcium solutions, with or without NOM, could be extensive. For the

filtration (particle-plate) case shown in Figure 3(b), all of the cases show a repulsive energy barrier to be overcome, but it is much lower for the calcium cases than the sodium cases. Results for the 2 mM ionic strength (not shown) indicated substantially higher energy barriers in all cases.

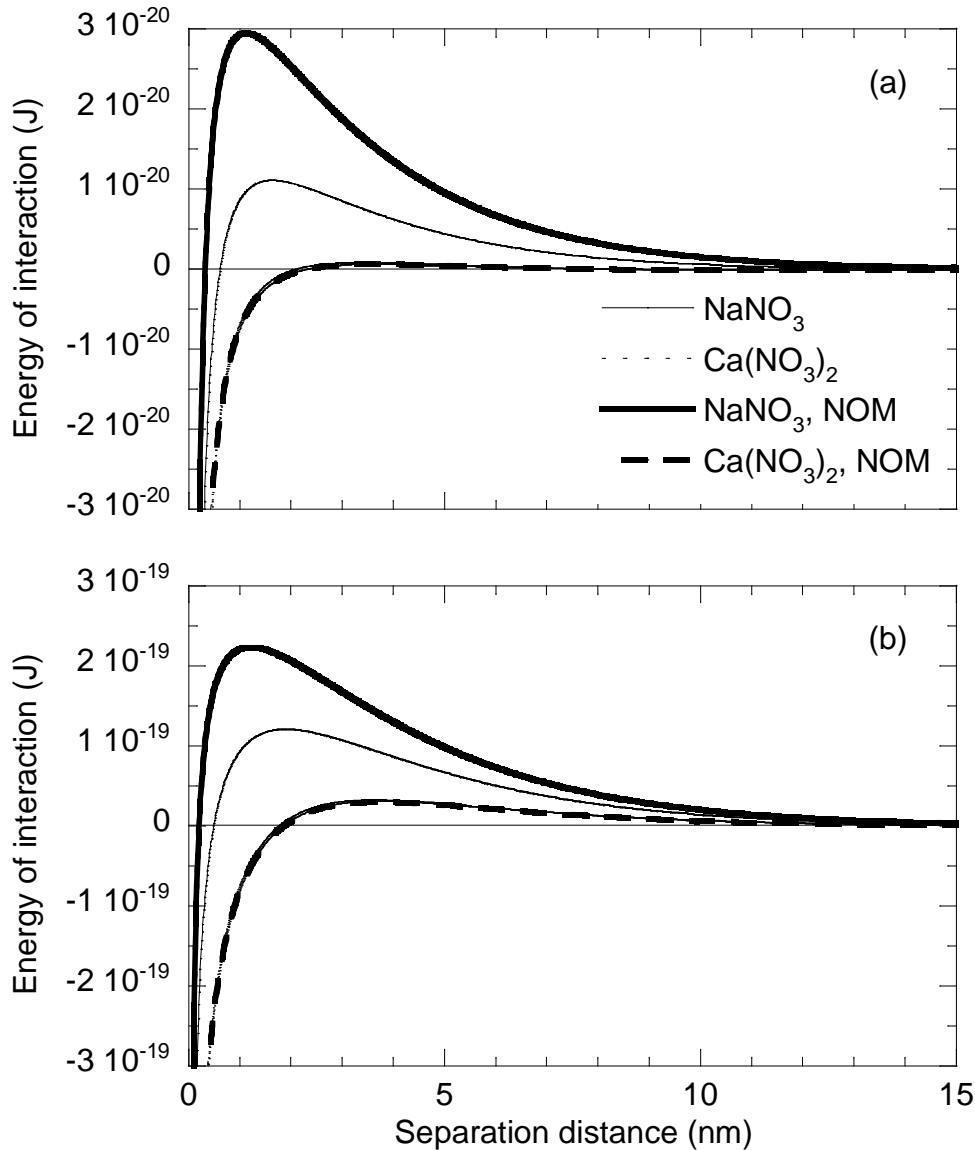


Figure 3. Energy of interaction; (a) particle-particle, (b) particle-media. (All calculations made at ionic strength of 10 mM).

### Flocculation

Flocculation of AgNPs (AgNPs) was studied in laboratory-scale. Suspensions were prepared with sodium nitrate ( $\text{NaNO}_3$ ) and calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ) at ionic strengths of 2 and 10 mM, with and without NOM. The concentration of the AgNP suspensions in these experiments was 1.67 mg/L as silver. The pH for the prepared AgNP solutions was maintained around neutral (7~8). Using a dynamic light scattering (DLS) instrument, the hydrodynamic diameter (HDD) on the basis of signal intensity of AgNPs was measured as a function of time for each

suspension. The HDD was then measured every 2 minutes for a total of 10 minutes; at the high particle concentration used in these experiments, flocculation could be expected to be rapid if the electrostatic interactions were (relatively) favorable.

The measured HDD values at two different ionic strengths without NOM are presented in Figure 4. This result shows that  $\text{NaNO}_3$  did not induce flocculation of AgNPs during the 10 minute experiment at either ionic strength; both sets of results (at the two ionic strengths) indicate no particle growth at all. Also, when the ionic strength was 2mM, the  $\text{Ca}(\text{NO}_3)_2$  suspension appeared to show a slight decrease in the measured HDD; further analysis of the raw data for the size distribution (not shown) makes it clear that the perceived decrease was insignificant. The dramatic result shown in Figure 4, however, is the increase in the HDD in the  $\text{Ca}(\text{NO}_3)_2$  suspension at the 10 mM ionic strength. In that experiment; the HDD essentially doubled during the short 10-minute experiment.

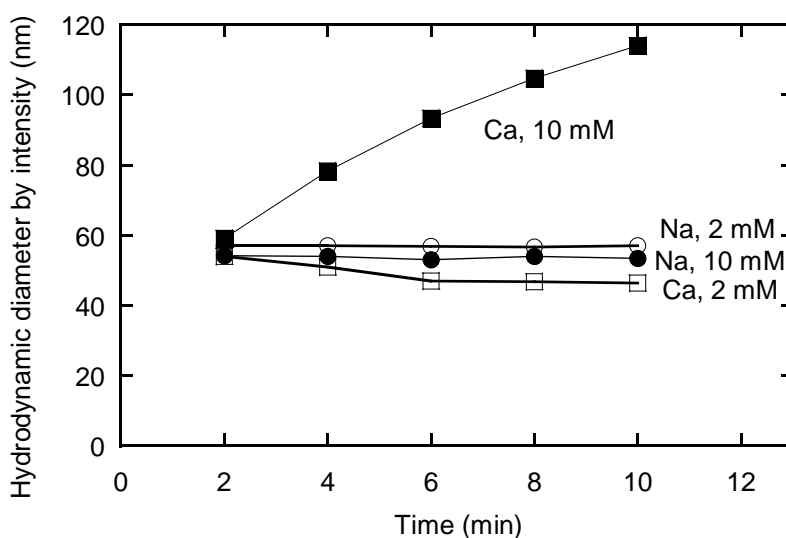


Figure 4. Flocculation in the absence of NOM.

The results of identical flocculation experiments but with the NOM included are shown in Figure 5. The results are similar to those shown in Figure 4, inasmuch as no flocculation was observed in three of the suspensions (the two sodium-based suspensions and the low ionic strength calcium-based suspension) whereas substantial flocculation was observed in the 10 mM ionic strength. However, the increase of the HDD in the high ionic strength calcium was lower than in the no NOM case; here the HDD increased by approximately 55% instead of the approximately 100% in the previous case. It should be noted that the initial values of the HDD in Figure 5 (the NOM experiment) were higher than those in shown in Figure 4 (the no NOM experiment); apparently, some flocculation occurred during the 24 hours of NOM exposure, and the samples were not sonicated prior to the salt addition and the flocculation test.

The results shown in Figures 4 and 5 are generally quite consistent with the results shown in Figures 2 and 3. The calculation shown in Figure 3(a) suggested that the suspensions in  $\text{Ca}(\text{NO}_3)_2$  (with or without NOM) would have the most dramatic flocculation because the calculated interaction energy was positive at all separation distances; the results in Figure 4 agree with this prediction. Further, the relative low repulsive energy for the Ca-NOM suspension shown in Figure 3(a) is consistent with the fact that good flocculation would occur in that

suspension, and that it would not be as extensive as in the no NOM case. Also, the results for sodium at the high ionic strength and the results for all types of solutions at the low ionic strength are consistent with the DLVO calculations. Nevertheless, the presence of NOM in the calcium-based suspensions seemed to have a greater (negative) effect on the flocculation achieved than the zeta potential measurements (Figure 2) or the calculations (Figure 3(a)) would lead one to expect. Apparently, the adsorption of NOM on the particles leads to some steric interference in the particle-particle interactions that is not captured by these measurements or calculations.

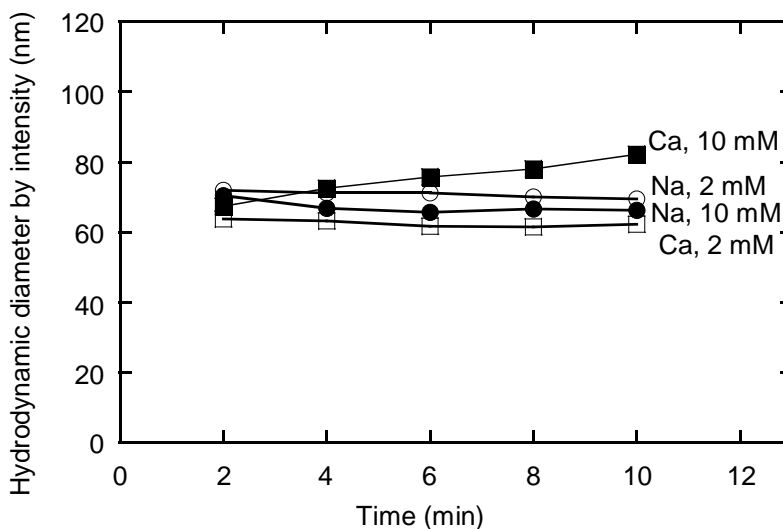


Figure 5. Flocculation in the presence of NOM.

### Granular media filtration

The filter media used in the experiments were spherical glass beads (MO-SCI Co., Missouri, USA) with diameters in the range of 300-355  $\mu\text{m}$ . Before each experiment, the beads were cleaned by sonication in a basic (0.01 M NaOH) and then an acidic (1 M HNO<sub>3</sub>) solution, and rinsed with DI water followed by drying at 105 °C.

The filter was a cylindrical acrylic column packed with the beads (3.8 cm in diameter, 10 cm in depth). A background solution and silver nanoparticle suspension were prepared separately to prevent any flocculation prior to the filter and to gauge the effect of the background solution on the removal of AgNPs. The filter bed was preconditioned with the background solution for 24 hours prior to the start of each experiment. The flow ratio of silver nanoparticle suspension to the background solution was kept to 1:20 to maintain the influent concentration less than 200  $\mu\text{g/L}$  (as Ag), and the filtration velocity was set to approximately 2 m/h, the lower limit of granular media filtration velocity in modern water treatment plants. The filtration of AgNPs was conducted at the ionic strength at 2 and 10 mM by Ca(NO<sub>3</sub>)<sub>2</sub>, and the presence of NOM was investigated at the ionic strength of 10 mM.

Filtration experiments included a flushing period with the background solution and DI water (*i.e.*, no particles) for 5 minutes prior to time zero, followed by specified period of flow with particles (0~30 minutes), and then a second 30-minute period with no particles in the influent (30~60 minutes). The samples were taken every 1 or 2 minutes during the test period, and



analyzed for total silver concentration by graphite furnace atomic absorption (Perkin Elmer) after nitric acid dissolution.

The results in Figure 6 show most obviously that the attachment was greater at the higher ionic strength. This result suggests that the electrostatic repulsion is decreased due to the reduction of double layer thickness by increased ionic strength. The effluent concentration started to increase between 1 and 2 minutes which is approximately the empty bed contact time, and the effluent concentration rapidly achieved a steady value until the particle supply was turned off at time 30 minutes. Integrating the area above the effluent curve (and below the value of  $C_{out}/C_{in} = 1$ ) for that period reveals that 30.7% (2 mM) and 95.5% (10 mM) of the particles that entered the filter were captured during that period. The results from the remaining 30 minutes (30 to 60 minutes) show that almost all of these particles remained attached to the filter, *i.e.*, that detachment was minimal.

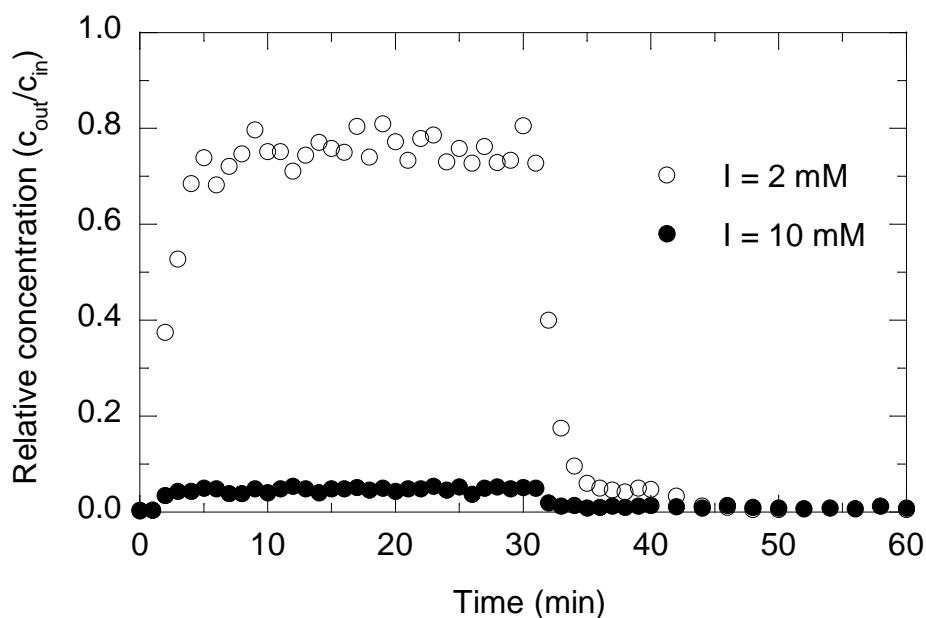


Figure 6. Effect of ionic strength (as  $\text{Ca}(\text{NO}_3)_2$ ) on the granular media filtration of silver nanoparticles in the absence of NOM.

The results in Figure 7 show that NOM coating on the AgNPs reduced their attachment in comparison to the no-NOM case. Zeta potential measurements (Figure 2) indicated that the NOM adsorption caused little or no change to the surface charge in the case of  $\text{Ca}(\text{NO}_3)_2$ , suggesting that the reduced attachment in these filtration experiments is due to steric hindrance caused by NOM. Since NOM coating can enhance both electrostatic and steric repulsion (Jaisi et al., 2008), this result suggests that  $\text{Ca}^{2+}$  adsorption to the surface might reduce the electrostatic repulsion because the surface charge is changed when the ions attach to the particle (Elimelech, 1992). Assuming the steric effect is independent of energy of interactions (Figure 3b), much less attachment of NOM-coated AgNPs can be expected at lower ionic strength than at the 10 mM in the experiment shown.

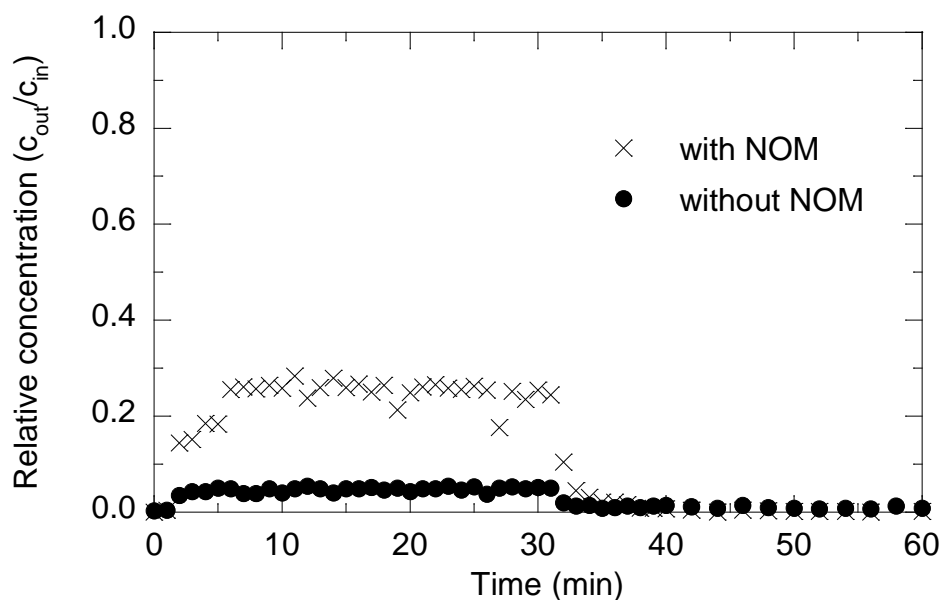


Figure 7. Effect of NOM coating on the granular media filtration of silver nanoparticles at 10 mM ionic strength (as  $\text{Ca}(\text{NO}_3)_2$ ).

### Conclusions

The results reported in this paper suggest that AgNPs can be removed from a drinking water source in essentially the same way that larger particles are removed in conventional water treatment plants. Generally, the results are consistent with standard theories of particle stability based on electrostatic repulsion and van der Waals attraction, though the presence of NOM apparently caused some steric effects on the particle-particle and particle-media interactions that are not adequately captured by these theories. The results reported herein are limited, in that particle destabilization was achieved by compression of the double layer; in real water treatment plants, this method is never used because the addition of high concentration of salt is unacceptable. Further research is planned to use particle destabilization methods that are consistent with plant practice.

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