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Polymer-Capped Nanoparticle Transport in Granular Media Filtration: Deviation from the Colloidal Filtration Model

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Abstract: The single-collector removal efficiency based on the colloidal filtration model is widely used to quantify deposition of nanoparticles in porous media filtration. The validity of this theory for nanoparticles, especially at filtration rates used in water treatment, was evaluated. Granular media filtration experiments were performed under widely variant physical conditions. Chemical effects were minimized by selecting spherical branched polyethylenimine capped silver nanoparticles as a positively charged nanoparticle to avoid electrostatic repulsion with the negatively charged silica filter media. The model and experimental results agreed well for 50 and 100 nm particles, but 10 nm particles were removed to a lesser extent than the model predicted. An updated Derjaguin-Landau-Verwey-Overbeek calculation was performed for the interaction energy between polymer-capped nanoparticles and the collector surface, under constant potential, constant charge, and mixed assumptions. The effect of particle size on these calculations was dramatic, leading to far less attractive energy for the smallest particles in the mixed case, and even repulsion in the constant charge case. These revised calculations are the primary means to explain the unexpected data.

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Introduction

A major contribution of the career of Charles O'Melia was his insights about granular media filtration, with some of the key articles published in this journal (O'Melia 1985; Ramaley et al. 1981; Wiesner et al. 1987; Logan et al. 1995). He introduced the concept, now universally accepted in the environmental engineering community and beyond, that particle capture in water and wastewater filters involved two steps that could be conceptually divided: transport to the vicinity of the media surface and attachment to that surface (O'Melia and Stumm 1967). But, in the days of those writings, little concern was voiced about nanoparticles; then, we had few, if any, engineered nanoparticles, and we did not even have that word! Now, the extensive use of engineered nanoparticles (ENPs) has caused great research interest in the transport and deposition of these particles in porous media, such as granular media filters (Petosa et al. 2010). Despite the plethora of research, the question remains whether the transport of nanoparticles at the relatively high filtration velocities used in water treatment is similar to that studied in earlier times with larger particles.

Regarding the transport of nanoparticles in granular media filtration, the attachment efficiency (α) has often been estimated as a correction to the single collector contact efficiency (η_o) calculated from one of several possible colloidal filtration models (Benjamin and Lawler 2013). This approach to determine α has been adopted by many researchers because the colloidal filtration model has shown good agreement with experimental results for larger particles in general. However, considering the recent shift of research focus from supra-micrometer colloids to nanoparticles, it is worthwhile to determine whether the colloidal transport model properly describes nanoparticle transport. Though the colloidal filtration model has been updated by simulations of the detailed contact between nanoparticles and the filter media (Long and Hilpert 2009; Ma et al. 2009; Nelson and Ginn 2011; Tufenkji and Elimelech 2004), little effort has been made to verify the colloidal filtration model with experimental evidence at nano size under the conditions found in water treatment practice. In particular, though nanoparticles less than 30 nm were reported to show more distinguished properties than their larger counterparts (Auffan et al. 2009), few researchers have tested whether the effects of size within the nano range are well predicted by the existing filtration models. Because the ENPs are usually coated with polymer capping, the Hamaker constant (A), and thus the van der Waals (vdW) attraction is reduced by the capping. In addition, the favorable deposition assumption when the approaching particles and the surface are oppositely charged needs to be discussed under different electrostatic boundary conditions: constant potential case (Hogg et al. 1966), constant charge case (Usui 1973), and mixed case (one surface with constant potential and the other with constant surface charge density) (Kar et al. 1973).

The objective of this study was to verify the colloidal filtration model with experimental results of the transport of nanoparticles in granular media filtration under conditions similar to those in water treatment plants. The widely accepted model of Tufenkji and Elimelech (2004) was the filtration model of choice; this model resulted from extensive trajectory simulations that specifically included nanoparticles. By using positively charged particles with negatively charged filter media, it was assumed that no energy barrier to attachment would exist, and experiments were conducted under various physical conditions and various nanoparticle sizes. The physical parameters that were varied included the velocity, media size, and media depth. To isolate the effect of physical parameters, the chemical parameters were controlled in a way to minimize their effect on the filtration experiments. An updated analytical expression for the vdW attraction was proposed to include the effect of polymer capping; and Derjaguin-Landau-Verwey-Overbeek (DLVO) energy was calculated under different electrostatic conditions. The experimental results were compared with the Tufenkji and Elimelech colloidal filtration model to evaluate the applicability of the model to nanoparticles.

Materials and Methods

Chemicals. 10, 50, and 100 nm spherical branched polyethylenimine (BPEI) silver nanoparticles (AgNPs) were purchased from Nanocomposix (San Diego, CA). The sizes of AgNPs were confirmed by transmission electron microscopy (TEM, FEI Tencai), nanoparticle tracking analysis (NTA, LM10 Nanosight), and dynamic light scattering (DLS, Malvern Zetasizer NanoZS). The electrophoretic mobility (EPM) of AgNPs was determined by electrophoretic light scattering (ELS, Malvern Zetasizer NanoZS) in 1 mM $NaNO_3$ over the pH range of 4 to 12. The EPM values were converted to ζ potentials via the Smoluchowski approximation built into the DLS software (Philippe 2015; Pokhrel and Dubey 2013). Though surface potentials of soft particles are better obtained from EPM through the Ohshima's soft particle theory (Kuznar and Elimelech 2007; Ohshima 1995), this theory has an assumption (linear structures of polymer) that does not apply to BPEI particles (branched structures of polymer). Therefore, in this study, the surface potential of BPEI AgNPs was calculated from the ζ potential using the Gouy-Chapman equation with the distance between the slipping plane and the particle surface taken as 0.5 nm (van Oss et al. 1990)

Column Tests. Spherical glass beads with diameters in the range of 300~355, 425~500, and 710~850 μm were purchased from MO-SCI (St. Louis, MO) for use as the filter media. Each group of beads was sieved on a pair of US sieves corresponding to the designated size range (#45 (354 μm) and #50 (297 μm), #35 (500 μm) and #40 (425 μm), and #20 (841 μm) and #25 (710 μm), respectively). Prior to use, the beads were washed by the following cleaning process (Darby 1988): rinsing with deionized (DI) water 10 times, sonication in 1 M HNO_3 solution overnight followed by rinsing with DI water 10 times, sonication in DI water for 10 min followed by rinsing with DI water 20 times, and complete drying in a 105°C oven.

A cylindrical column with a 3.81 cm inner diameter was employed for the filtration tests. The filtration test system was designed to keep the AgNP suspension and the background solution separate until the two solutions were mixed immediately before the filter entrance (Fig. S1). The flow rate of each solution was controlled to achieve the designated filtration velocity (2, 4, or 8 m/h) and influent AgNP concentration

(100 μg/L). A series of filtration tests was conducted under varying filter depth, filtration velocity, particle size, and filter media size. Immediately prior to each test, the flow of background water through the column was established for at least 45 pore volumes. Then, each filtration test consisted of two phases: 45 pore volumes of filtration with AgNPs followed by 45 pore volumes of filtration without AgNPs. The main purpose of each test was to obtain the removal efficiency, that is, a plateau in relative concentration (effluent Ag concentration over influent Ag concentration,c/c_0) according to the test condition, to compare with model predictions. Ionic strength was fixed at 1 mM of $NaNO_3$, and pH was controlled at 7.0 ± 0.1 using 0.025 mM bicarbonate buffer. The influent and effluent samples were acidified in 3% trace metal grade HNO_3 solution, and Ag concentration was analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Varian 710, Agilent, Santa Clara, CA).

Theoretical removal efficiency. The theoretical removal efficiency was calculated using the colloid filtration model (Benjamin and Lawler 2013)

$$\frac{C}{C_0} = exp\left[-\frac{3}{2}\frac{(1-\varepsilon)\alpha\eta_0}{d_c}L\right] \tag{1}$$

with all the variables defined in the Notation section. α is 1 under the favorable deposition assumption (no repulsive forces between the approaching particle and the collector), and η_0 is determined using the Tufenkji and Elimelech model (2004). The theoretical removal efficiency (c/c_0) calculated from Eq. 1 was compared with the experimental results of AgNPs remaining (effluent concentration over influent concentration) from ICP-OES measurement.

Particle-collector interaction. Because the molecular weight of capping BPEI is small and the steric interaction between the particle and the collector is greatly reduced without the presence of polymeric coating on the collector surface (Lin and Wiesner 2012), only the classical DLVO interaction was considered. The energy of interaction was calculated using the sum of the electrical double layer (EDL) repulsion (V_{EDL}) and the vdW attraction (V_{vdW}). An updated analytical expression for the V_{vdW} was derived between a polymer-coated particle and an uncoated collector surface. Without considering retardation effects, the plate-plate vdW attraction in medium 4 (water) between a flat surface of material 3 and another flat surface of material 2 coated by a layer of material 1 of thickness δ can be derived from the summation of vdW attraction between the collector and the polymer capping and that between the collector and the metal core.

The vdW attraction between a molecule in plate 3 and capping layer 1 is:

$$V_{143}(z) = \int_{x=0}^{\delta}\int_{y=0}^{\infty} -\frac{\rho_1 N_A}{MW_1}\frac{2\pi y C_{143}}{[(z+x)^2+y^2]^3}\,dydx = -\frac{1}{6}\frac{\rho_1 N_A C_{143}\pi}{MW_1}[z^{-3}-(z+\delta)^{-3}] \tag{2}$$

All variables were defined in the Notation section. The subscript “143” indicates interaction between capping 1 and plate 3 suspended in a medium 4. The vdW attraction between a molecule in plate 3 and plate 2 is:

$$V_{243}(z) = \int_{x=d}^{\infty}\int_{y=0}^{\infty} -\frac{\rho_2 N_A}{MW_2}\frac{2\pi y C_{243}}{[(z+x)^2+y^2]^3}\,dydx = -\frac{1}{6}\frac{\rho_2 N_A C_{243}\pi}{MW_2}(z+\delta)^{-3} \tag{3}$$

The plate-plate interaction between plate 3 and plate 2 coated with layer 1 is:

$$V_{pp}(H) = \int_{z=H}^{\infty}[V_{143}(z)+V_{243}(z)]\frac{\rho_3 N_A}{MW_3}\,dz = -\frac{A_{143}}{12\pi}[H^{-2}-(H+\delta)^{-2}] - \frac{A_{243}}{12\pi}(H+\delta)^{-2} \tag{4}$$

Where A_{143} and A_{243} is the overall Hamaker constant for the interaction between capping 1 or plate 2 and plate 3 in medium 4. A_{143} can be calculated by (Petosa et al. 2010)

$$A_{143} = \left(\sqrt{A_{11}}-\sqrt{A_{44}}\right)\left(\sqrt{A_{33}}-\sqrt{A_{44}}\right) \tag{5}$$

and the Hamaker constants of silver, water, and glass in vacuum (e.g., A_{33}, etc.) are available from literature. The Hamaker constant of capping 1 can be calculated as a composite of polymer and medium 4 (Vincent 1973), with a segment density ϕ assumed to be 0.1 throughout the capping layer (Lin et al. 2012).

$$A_{11} = \left[\phi\left(A_{polymer}\right)^{0.5} + (1-\phi)(A_{44})^{0.5}\right]^2 \tag{6}$$

From Lin and Wiesner (2010), the plate-plate interaction can be converted to the sphere-plate interaction by

$$V_{sp}(h) = 2\pi\left[(a+h)\int_{h}^{h+2a} V_{pp}(H)dH - \int_{h}^{h+2a} V_{pp}(H)HdH\right] \tag{7}$$

Therefore, the vdW interaction between plate 3 and particle 2 coated by layer 1 is:

$$V_{sp}(h) = -\frac{A_{143}}{6}\left[\frac{a+h}{h} - \frac{a}{h+a} - \frac{a+h}{h+2a} - \frac{a}{h+2a+\delta} + ln\frac{(h+2a+\delta)h}{(h+2a)(h+\delta)}\right] - \frac{A_{243}}{6}\left[\frac{a}{h+\delta} + \frac{a}{h+2a+\delta} + ln\frac{h+\delta}{(h+2a+\delta)}\right] \tag{8}$$

When there is no capping layer around sphere 2 ($\delta = 0$), Eq. 8 becomes (Hunter 2001)

$$V_{sp}(h) = -\frac{A_{243}}{6}\frac{a}{h}\left[1 + \frac{h}{h+2a} + \frac{h}{a}ln\frac{h}{h+2a}\right] \tag{9}$$

Analytical expressions for the electrical double layer (EDL) interaction based on constant potential (Hogg et al. 1966), constant charge (Usui 1973) and mixed (constant potential for the collector and constant charge for the particle) (Kar et al. 1973) assumptions were used to quantify the electrostatic interaction between two oppositely charged surfaces: the positively charged particle and the negatively charged collector. These expressions are summarized in Table 1. The DLVO interaction between the approaching BPEI AgNPs and the silica collector was calculated with the equations in Table 1 to interpret experimental results.

Results and Discussion

Characterization of BPEI AgNPs. The size of BPEI AgNPs determined by TEM images through ImageJ software (Fig. S2, Table 2) was close to the size reported by the manufacturer. The hydrodynamic diameter (HDD) measured by NTA and DLS (Fig. S3, Table 2) was considered to include the thickness of the capping agent (MacCuspie et al. 2011). The TEM measurements appear to indicate a more nearly monodisperse particle size than was found from NTA and DLS, an apparent artifact of the latter systems. The surface charge of BPEI AgNPs was positive (Fig. S4) because BPEI includes amine groups that would be protonated at the pH of these experiments (pH 7) (Stumm and Morgan 1996). However, the surface charge decreased as particle size decreased, probably due to decreased H^+ density on the particle surface (Barisik et al. 2014) or greater degree of hydroxylation (Chae et al. 2010). Nevertheless, the point of zero charge of BPEI AgNPs was somewhat higher than pH 11 regardless of particle size, proving that the surface charge of BPEI AgNPs in the filtration test was positive. The molecular weight of the BPEI was reported by Nanocomposix, Inc. to be approximately 2500 Daltons. Using the method from Yang et al. (2014), the capping layer thickness was estimated to be approximately 8 nm. This value is smaller than but in the same range as the difference between the TEM radius and the HDD radius and was used as the capping layer thickness to calculate the energy of interaction.

Particle aggregation. Aggregation of BPEI AgNPs was negligible at I=1 mM of $NaNO_3$ and pH 7 (Fig. S5). This result was consistent with previous reports that the stability of BPEI AgNP would be greatest near pH 7 (El Badawy et al. 2010) and the aggregation of BPEI AgNP would be insignificant even at I=1000 mM (El Badawy et al. 2012). Therefore, the stability of BPEI AgNPs was assured in the filtration condition.

Effect of filter depth. For the contact efficiency (η_0) estimation from the experimental results, the stabilized relative concentrations of 10, 50, and 100 nm BPEI AgNPs were examined at three different filter depths (2, 4, and 8 cm) with 4 m/h filtration velocity and 325 μm filter media size. The overall result qualitatively followed the general expectation that deeper filter depth results in greater particle deposition (Fig. S6). The time to reach a stabilized relative concentration was slightly increased as the filter depth became shallower. The removal trend as a function of particle size indicates the greater AgNP capture of smaller AgNPs due to their more vigorous Brownian motion; that is, the diffusion coefficients, calculated from the measured average hydrodynamic diameters, of the 10 nm, 50 nm and 100 nm AgNPs under the experimental condition are 1.3×10^{-9} cm^2/s, 5.2×10^{-10} cm^2/s and 3.7×10^{-10} cm^2/s, respectively. The number of potential collisions between particles and media grains as the water flowed through the filter would be inversely proportional to these values. Note that the relative concentration was nearly constant after a short period. Even though the tests were conducted at the low range of the ratio of filter depth to filter media size (L/d_c) (62, at the lowest), a constant level of AgNP deposition was maintained for a sufficient period to obtain an apparent steady state relative concentration. This result might be due to slow ripening as a consequence of low influent AgNP concentration.

Effect of filtration velocity. To investigate the effect of filtration velocity, three filtration velocities (2, 4, and 8 m/h) were applied to the filtration of 10, 50, and 100 nm BPEI AgNPs with 4 cm filter depth and 325 μm filter media size. Particles have less time to contact the filter media with increased filtration velocity, leading to less particle deposition. The effect of increased velocity on deposition is expected to be greater for particles whose capture is by sedimentation than for particles captured by Brownian motion (Tufenkji and Elimelech 2004). Although Ag has a relatively high density (10.49 g/cm^3), sedimentation of these small nanoparticles onto the filter media was calculated to be negligible in comparison to deposition by Brownian motion. The single collector contact efficiency calculated by Tufenkji and Elimelech model revealed that, even for the largest particle (100 nm) under the highest filtration velocity (8 m/h), the contact efficiency due to sedimentation was only 1.9×10^{-5}, much smaller than the contact efficiency from Brownian motion which was 3.1×10^{-3} (by two orders of magnitude). The velocity effect was apparent in all particle sizes tested (Fig. S7). The results from these experiments show a moderate change in AgNP deposition caused by the velocity variation (i.e., an increase of approximately 0.3 in the relative concentration at the plateau with the four-fold increase in filtration velocity).

Effect of filter media size. Three different filter media sizes (325, 463, and 776 μm) were employed to study the effect of filter media size on the filtration of 10, 50, and 100 nm BPEI AgNPs. The filtration tests were conducted with 4 cm filter depth and 4 m/h filtration velocity. With regard to the three sizes of AgNPs, the AgNP deposition increased as filter media size decreased (Fig. S8) due to the decreased pore sizes, the increased number of media layers for the same depth, and the increased surface area of the filter media. As the size of AgNPs increased from 10 nm to 100 nm, the AgNP deposition decreased for all filter media sizes. Specifically, when the filter media size was 776 μm, the fraction removed for the 10, 50, and 100 nm particles was 54%, 38% and 19% of the corresponding values for the 325 μm media. In particular, only 8% of the 100 nm AgNPs were captured in 776 μm filter media even under favorable attachment conditions. If nanoparticles are to be removed using granular media filtration, small filter media size would be necessary.

Effect of particle size. All of the tests followed the general knowledge that the filtration efficiency is lowered at less filter depth, higher velocity, and greater media size, but the objective in this research was to test whether these trends fit the predictions of the Tufenkji and Elimelech model. In Fig. 1, the model predictions and the experimental results are compared, using both the mean diameter and the hydrodynamic diameter determined by TEM and NTA, respectively, in the model predictions. Recall from Table 2 that these two values for each particle size were substantially different, with the hydrodynamic diameter being 30 to 40 nm larger than the mean diameter. The hydrodynamic diameter includes the solvent and macromolecules that adhere to particle surface in a liquid medium; using this measure in the predictions accounts for the fact that the added layer on the core particle decreases the diffusivity of the particle. In virtually all cases shown in Fig. 1, the two sets of model predictions bracket the experimental results, but in some cases, one of the predictions fits much better.

Considering the predictions using the mean (TEM) diameter, the experimental results were quite consistent with the colloidal filtration model expectation in the case of the 50 and 100 nm BPEI AgNPs (parts (d) to (i) of Fig. 1). Of the 18 experiments shown for these two larger particles, only three have results that were closer to the model predictions using the hydrodynamic diameter, and several results were predicted quite precisely by using the mean diameter. However, the removal efficiency of 10 nm BPEI AgNPs (parts (a) to (c) of Fig. 1) was approximately 20~30% less than the model prediction using the mean diameter for the model particle size, and most of the results were predicted somewhat better (but not precisely) using the hydrodynamic diameter. Taken together, these results suggest that the colloidal filtration model is generally quite valid, but the effect of particle size is not accounted for quite properly. One way to describe these results is to say that the assumption of favorable deposition is accurate for larger size particles, but as particle size becomes smaller, the favorable deposition assumption tends to be questionable.

1) Explanation from the energy of interaction

The energy of interaction between the approaching AgNPs and the silica media grains was calculated using equations in Table 1, and values of the parameters are summarized in Table S1. Because the BPEI polymer capping layer gives a lower Hamaker constant when interacting with the silica collector surface, the vdW attraction between the coated particle and the surface is lower (i.e., less negative) than that between an uncoated particle and the surface; these results are shown in Fig. 2. The separation distance in this and subsequent Fig.s is from the outside of the capping layer to the edge of the filter media. Although particles of different sizes have the same capping layer thickness, the smallest particles (10 nm) are affected most by the reduced vdW attraction from the polymer capping because the capping layer represents a greater fraction of the particle as the particle size decreases.

Three different assumptions for the EDL interactions (constant surface potential, constant surface charge, and mixed charge and potential) were employed, and the results are shown in Fig. 2. Constant surface potential assumes that the electrochemical equilibrium exists in the double layer during the course of particle interaction; therefore, the surface potential remains constant (Derjaguin and Landau 1941; Hogg et al. 1966). The constant surface charge approach accepts that the equilibrium is unrealistic during a Brownian collision; hence, the surface charge remains constant (Frens and Overbeek 1972; Usui 1973; Verwey and Overbeek 1948). The constant surface potential and charge assumptions are considered two extremes to the possible EDL energy of interaction; and the mixed approach lies between the two extremes (Kar et al. 1973). As the particle size decreases, Brownian motion increases and the assumption of the constant potential case that electrochemical equilibrium is maintained at all times becomes increasingly unrealistic; video clips from the NTA measurements of the 10 and 100 nm particles are shown in Fig. S9, and the much higher particle velocities of the smaller particles are obvious. Imagining that ions can rearrange themselves at that speed to always maintain equilibrium is clearly unrealistic.

Under the constant potential assumption, the interaction remains attractive if the particle and the collector surface are oppositely charged. However, under the mixed approach, the EDL attraction became much smaller for all the particle sizes; the EDL attraction for the 10 nm particle (which has less negative ζ potential) even became negligible. When the constant charge assumption was applied, the EDL interaction between the 10 nm particle and the collector surface became repulsive. Therefore, as the particle size gets smaller, the EDL interaction becomes less attractive and even repulsive as the electrochemical equilibrium assumption becomes less valid.

When the total DLVO interaction was calculated (Fig. 4), the results for the constant potential case (Fig. 4a) were consistent with the original hypothesis of the experimental work that the oppositely charged particles and media grains would lead to an attractive condition at all separation distances. On the contrary, the reduced vdW attraction and the repulsive EDL interaction under the constant charge assumption (Fig. 4b) caused a net repulsive interaction for the 10 nm particle. Under the mixed case (Fig. 4c), though no repulsive energy exists for the 10 nm particle, the attraction was nevertheless negligible and any external repulsion would cause hindrance between the particle and the collector. As a result, the assumption of favorable deposition was not valid for the filtration of 10 nm BPEI-AgNPs, even though the particle and the silica collector are oppositely charged. The deposition attachment efficiency (α) was less than unity, thus leading to a reduced deposition than that calculated from the Tufenkji and Elimelech model.

2) Other explanations

The 10 nm AgNPs showed a much greater degree of deviation between the experimental results and the model predictions, suggesting a possible alteration of nanoparticle properties as the size gets smaller than 50 nm. Others have suggested that some size dependent properties are more likely to appear below 10 nm (Bian et al. 2011), but, little is known about the details. For example, the vigorous Brownian motion of nanoparticles, especially at extremely small size, could change the deposition of nanoparticles. Either increased or decreased removal can be anticipated by an increased number of collisions with filter media. An increase would be consistent with standard filtration theory. A decrease could possibly occur because of the vigorous Brownian motion of nanoparticles 10 nm or less. The greater Brownian motion means that the 10 nm particles have a far higher velocity than the larger nanoparticles used in this study (Bhatt et al. 2013). In aerosol filtration, Wang and Kasper (Wang and Kasper 1991) proposed that nanoparticles below 10 nm could rebound off collector surfaces because the time of interaction was so short; while this phenomenon is less likely in water where the mean free path is far smaller than in air, we note the possibility. Further research would be necessary to investigate this possible explanation.

The smallest particles could also display the greatest hydrophilicity because, as the particle size decreases, the increased curvature allows a greater surface density of bound water molecules. Chae et al. (2010) reported decreased fullerene deposition onto silica surfaces as the size decreased and ascribed this result to the more hydrophilic nature of smaller nanoparticles; in their case, this phenomenon made their particles more negative and caused greater stabilization, but in our case, it makes the surface charge less positive, and therefore diminishes the attraction to the negatively charged filter media. This phenomenon also explains the difference in measured potentials of the different particle sizes reported in Table 2.

Another possible reason for variation in removal efficiency of smaller nanoparticles than predicted by the model is the stronger steric stabilization by the capping agent. As with water, a greater density of organic molecules, and therefore a greater abundance of the edge and corner sites (Grassian 2008), can adsorb onto smaller particles, so that smaller BPEI AgNPs are likely to have a denser capping layer compared to the larger particles. Further estimation of the adsorbed layer thickness on AgNPs is required to support this argument.

Conclusions

The effect of physical parameters on the transport of BPEI AgNPs in granular media filtration was experimentally evaluated under favorable attachment conditions; and DLVO interaction was calculated to explain the interaction between the polymer-capped AgNPs and the bare silica collector. A stable relative concentration of the effluent was obtainable during the test period due to low influent AgNP concentration, which retarded ripening and prevented aggregation in the suspension. Brownian motion was dominant in the experimental conditions tested in this study. Deeper filter depth, lower filtration velocity, and smaller filter media size led to more AgNP deposition, as expected. With regard to the physical variables and their values tested in this study, the removal efficiency for all particle sizes was significantly enhanced by decreasing filter media size from 776 to 325 μm. This result suggests, consistent with theory, that the selection of filter media size could be a decisive factor for nanoparticle removal using granular media filtration.

When using the mean (TEM) diameter for the model predictions, the transport of 100 nm and 50 nm BPEI AgNPs in granular media filtration showed good agreement with the expectations from the colloidal filtration model of Tufenkji and Elimelech, proving the validity of the model. However, as the particles decreased to 10 nm, experimental results differed from the model predictions. The presence of the polymer capping reduced the vdW attraction, and EDL interaction was found to be repulsive under some modeling approaches, even though the particle and the collector were oppositely charged. As the particle size became smaller, the role of the polymer capping became more important in the surface interaction. The effect of the surface capping must be considered when evaluating the transport of ENPs by applying colloidal filtration models. At this small size, experimental results also tended to move toward the predictions using the (larger) hydrodynamic diameter. These results imply a variation in nanoparticle property as particles get smaller. Since size-dependent nanoparticle transport is not well understood, more experimental evidence with different types of nanoparticles is required to support the conceivable arguments in favor of such an effect.

Further investigation on the transport of the smaller-sized nanoparticles is required to obtain sufficient experimental data to update the colloidal filtration model especially in the size range less than 50 nm. The conformation of the surface capping must be included and the EDL interaction model must be carefully chosen. The updated colloidal filtration model would be beneficial for predicting contact efficiency (η_o) in such a small particle size range, which then could lead to an accurate estimation of the attachment efficiency (α) under unfavorable attachment conditions.

In his 1985 paper in this journal, O'Melia asked three questions: "What do packed bed filters remove from suspension in water treatment plants? How do they accomplish this removal? How can this knowledge be used in water treatment practice?" In this paper, we have updated his answers to account for nanoparticle removal; the quest for firm answers to his (and the field's) questions continues.

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Notation

A	Hamaker constant
a	particle radius
C	coefficient of atom-atom pair potential
c	effluent particle concentration
c_0	influent particle concentration
d_c	average collector grain diameter
H	plate-plate separation distance (from the outside of the capping layer to the edge of the filter media)
h	plate-sphere separation distance (from the outside of the capping layer to the edge of the filter media)
L	filter bed depth
MW_i	molecular weight of material i
N_A	Avogadro number

v_0	filtration velocity
V_{ijk}	Interaction between material i and material j in medium k
V_{DLVO}	total DLVO energy of interaction
V_{EDL}	electric double layer interaction
V_{pp}	plate-plate interaction
V_{sp}	plate-sphere interaction
V_{vdW}	van der Waals attraction
α	deposition attachment efficiency
δ	capping layer thickness
ε	porosity
ε_o	dielectric permittivity in vacuum
ε_r	relative dielectric permittivity of solution
η_o	single collector contact efficiency
κ	inverse Debye length
ρ_i	density of material i
ϕ	segment density of the capping layer
Ψ_{d_p}	surface potential of flat plate
Ψ_{d_s}	surface potential of spherical particle

Supplemental Data

Table S1, Figs. S1-S8, and Videos S1-S2 are available online in the ASCE Library (ascelibrary.org).

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Fig. 1. Comparison of experimental results and model predictions under different physical conditions. (The physical conditions specified in the top figure in each column also apply to the figures below. In all cases, the model results are found using both the diameter found from electron microscope (TEM) measurements and the hydrodynamic diameter (HDD) determined by NTA measurements.)

Fig. 2. Effects of particle size and BPEI capping on vdW attraction.

Fig. 3. Effects of different surface potential models on energy of interaction between AgNPs and silica media grains: a)10 nm AgNPs, b) 50 nm AgNPs and c) 100 nm AgNPs (cc: constant charge; cp: constant potential; mixed: constant potential for the collector and constant charge for the particle).

Fig. 4. Total DLVO interaction under a) constant potential, b) constant charge, and c) mixed case. (Note the difference in scales on the ordinates.)

Table 1. Analytical expression of particle-surface DLVO interaction of different types

Interaction	Analytical Expression	Reference
V_{vdW} (uncapped)	$V_{vdW} = -\frac{A_{243}}{6}\frac{a}{h}\left[1+\frac{h}{h+2a}+\frac{h}{a}ln\frac{h}{h+2a}\right]$	(Hunter 2001)
V_{vdW} (capped)	$V_{vdW} = -\frac{A_{143}}{6}\left[\frac{a+h}{h}-\frac{a}{h+a}-\frac{a+h}{h+2a}-\frac{a}{h+2a+\delta}+ln\frac{(h+2a+\delta)h}{(h+2a)(h+\delta)}\right]$ $-\frac{A_{243}}{6}\left[\frac{a}{h+\delta}+\frac{a}{h+2a+\delta}+ln\frac{h+\delta}{(h+2a+\delta)}\right]$	This study
V_{EDL} (constant potential)	$V_{EDL} = \pi\varepsilon_o\varepsilon_r a\left\{\begin{matrix}2\Psi_{d_p}\Psi_{d_s}\ln\left[\frac{1+e^{(-\kappa h)}}{1-e^{(-\kappa h)}}\right]+\\ \left(\Psi_{d_p}^2+\Psi_{d_s}^2\right)\ln\left[1-e^{(-2\kappa h)}\right]\end{matrix}\right\}$	(Hogg et al. 1966)
V_{EDL} (constant charge)	$V_{EDL} = \pi\varepsilon_o\varepsilon_r a\left\{\begin{matrix}2\Psi_{d_p}\Psi_{d_s}\ln\left[\frac{1+e^{(-\kappa h)}}{1-e^{(-\kappa h)}}\right]-\\ \left(\Psi_{d_p}^2+\Psi_{d_s}^2\right)\ln\left[1-e^{(-2\kappa h)}\right]\end{matrix}\right\}$	(Usui 1973)
V_{EDL} (mixed)	$V_{EDL} = 4\pi\varepsilon_o\varepsilon_r a\left\{\begin{matrix}\Psi_{d_p}\Psi_{d_s}\arctan(e^{-\kappa h})+\\ \frac{1}{4}\left(\Psi_{d_p}^2-\Psi_{d_s}^2\right)\ln\left[1+e^{(-2\kappa h)}\right]\end{matrix}\right\}$	(Kar et al. 1973)
V_{DLVO}	$V_{DLVO} = V_{EDL} + V_{vdW}$	

Table 2. BPEI AgNP properties used for filtration tests

Manufactured size	Mean TEM diameter (nm)	Hydrodynamic diameter (nm)		ζ potential[a] (mV)	pH_{pzc}
		NTA	DLS		
10 nm	8.3±2.6	33.3±21.3	38.0±16.7	13.0	11.3
50 nm	45.0±4.0	83.6±35.4	87.6±33.1	42.0	11.4
100 nm	93.4±9.8	119.0±66.7	130.2±38.6	47.3	11.2

[a] Measured at I=1 mM of $NaNO_3$ and pH 7.