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1 **Polymer-capped Nanoparticle Transport in Granular Media Filtration: Deviation from** 2 **the Colloidal Filtration Model**

3 **Ijung Kim¹, Tongren Zhu², Sungmin Youn³, and Desmond F. Lawler⁴**

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

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17 **Keywords:** BPEI AgNPs, colloidal filtration model, granular media filtration, size-dependent property

18 **Introduction**

19 A major contribution of the career of Charles O'Melia was his insights about granular media filtration,
20 with some of the key articles published in this journal (O'Melia 1985; Ramaley et al. 1981; Wiesner et al.
21 1987; Logan et al. 1995). He introduced the concept, now universally accepted in the environmental
22 engineering community and beyond, that particle capture in water and wastewater filters involved two
23 steps that could be conceptually divided: transport to the vicinity of the media surface and attachment to
24 that surface (O'Melia and Stumm 1967). But, in the days of those writings, little concern was voiced
25 about nanoparticles; then, we had few, if any, engineered nanoparticles, and we did not even have that
26 word! Now, the extensive use of engineered nanoparticles (ENPs) has caused great research interest in
27 the transport and deposition of these particles in porous media, such as granular media filters (Petosa et al.
28 2010). Despite the plethora of research, the question remains whether the transport of nanoparticles at the
29 relatively high filtration velocities used in water treatment is similar to that studied in earlier times with
30 larger particles.

31 Regarding the transport of nanoparticles in granular media filtration, the attachment efficiency (α) has
32 often been estimated as a correction to the single collector contact efficiency (η_o) calculated from one of
33 several possible colloidal filtration models (Benjamin and Lawler 2013). This approach to determine α
34 has been adopted by many researchers because the colloidal filtration model has shown good agreement
35 with experimental results for larger particles in general. However, considering the recent shift of research
36 focus from supra-micrometer colloids to nanoparticles, it is worthwhile to determine whether the colloidal
37 transport model properly describes nanoparticle transport. Though the colloidal filtration model has been
38 updated by simulations of the detailed contact between nanoparticles and the filter media (Long and
39 Hilpert 2009; Ma et al. 2009; Nelson and Ginn 2011; Tufenkji and Elimelech 2004), little effort has been
40 made to verify the colloidal filtration model with experimental evidence at nano size under the conditions

41 found in water treatment practice. In particular, though nanoparticles less than 30 nm were reported to
42 show more distinguished properties than their larger counterparts (Auffan et al. 2009), few researchers
43 have tested whether the effects of size within the nano range are well predicted by the existing filtration
44 models. Because the ENPs are usually coated with polymer capping, the Hamaker constant (A), and thus
45 the van der Waals (vdW) attraction is reduced by the capping. In addition, the favorable deposition
46 assumption when the approaching particles and the surface are oppositely charged needs to be discussed
47 under different electrostatic boundary conditions: constant potential case (Hogg et al. 1966), constant
48 charge case (Usui 1973), and mixed case (one surface with constant potential and the other with constant
49 surface charge density) (Kar et al. 1973).

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

63 **Materials and Methods**

64 **Chemicals.** 10, 50, and 100 nm spherical branched polyethylenimine (BPEI) silver nanoparticles
65 (AgNPs) were purchased from Nanocomposix (San Diego, CA). The sizes of AgNPs were confirmed by
66 transmission electron microscopy (TEM, FEI Tencai), nanoparticle tracking analysis (NTA, LM10
67 Nanosight), and dynamic light scattering (DLS, Malvern Zetasizer NanoZS). The electrophoretic mobility
68 (EPM) of AgNPs was determined by electrophoretic light scattering (ELS, Malvern Zetasizer NanoZS) in
69 1 mM NaNO₃ over the pH range of 4 to 12. The EPM values were converted to ζ potentials via the
70 Smoluchowski approximation built into the DLS software (Philippe 2015; Pokhrel and Dubey 2013).
71 Though surface potentials of soft particles are better obtained from EPM through the Ohshima's soft
72 particle theory (Kuznar and Elimelech 2007; Ohshima 1995), this theory has an assumption (linear
73 structures of polymer) that does not apply to BPEI particles (branched structures of polymer). Therefore,
74 in this study, the surface potential of BPEI AgNPs was calculated from the ζ potential using the Gouy-
75 Chapman equation with the distance between the slipping plane and the particle surface taken as 0.5 nm
76 (van Oss et al. 1990)

77 **Column Tests.** Spherical glass beads with diameters in the range of 300~355, 425~500, and 710~850 μm
78 were purchased from MO-SCI (St. Louis, MO) for use as the filter media. Each group of beads was
79 sieved on a pair of US sieves corresponding to the designated size range (#45 (354 μm) and #50 (297
80 μm), #35 (500 μm) and #40 (425 μm), and #20 (841 μm) and #25 (710 μm), respectively). Prior to use,
81 the beads were washed by the following cleaning process (Darby 1988): rinsing with deionized (DI) water
82 10 times, sonication in 1 M HNO₃ solution overnight followed by rinsing with DI water 10 times,
83 sonication in DI water for 10 min followed by rinsing with DI water 20 times, and complete drying in a
84 105°C oven.

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

89 (100 µg/L). A series of filtration tests was conducted under varying filter depth, filtration velocity,
90 particle size, and filter media size. Immediately prior to each test, the flow of background water through
91 the column was established for at least 45 pore volumes. Then, each filtration test consisted of two
92 phases: 45 pore volumes of filtration with AgNPs followed by 45 pore volumes of filtration without
93 AgNPs. The main purpose of each test was to obtain the removal efficiency, that is, a plateau in relative
94 concentration (effluent Ag concentration over influent Ag concentration, c/c_0) according to the test
95 condition, to compare with model predictions. Ionic strength was fixed at 1 mM of NaNO₃, and pH was
96 controlled at 7.0 ± 0.1 using 0.025 mM bicarbonate buffer. The influent and effluent samples were
97 acidified in 3% trace metal grade HNO₃ solution, and Ag concentration was analyzed using inductively
98 coupled plasma-optical emission spectroscopy (ICP-OES) (Varian 710, Agilent, Santa Clara, CA).

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

$$101 \quad \frac{c}{c_0} = \exp \left[-\frac{3(1-\varepsilon)\alpha\eta_0}{2d_c} L \right] \quad (1)$$

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

107 **Particle-collector interaction.** Because the molecular weight of capping BPEI is small and the steric
108 interaction between the particle and the collector is greatly reduced without the presence of polymeric
109 coating on the collector surface (Lin and Wiesner 2012), only the classical DLVO interaction was
110 considered. The energy of interaction was calculated using the sum of the electrical double layer (EDL)
111 repulsion (V_{EDL}) and the vdW attraction (V_{vdW}). An updated analytical expression for the V_{vdW} was
112 derived between a polymer-coated particle and an uncoated collector surface. Without considering

113 retardation effects, the plate-plate vdW attraction in medium 4 (water) between a flat surface of material 3
 114 and another flat surface of material 2 coated by a layer of material 1 of thickness δ can be derived from
 115 the summation of vdW attraction between the collector and the polymer capping and that between the
 116 collector and the metal core.

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

$$118 \quad V_{143}(z) = \int_{x=0}^{\delta} \int_{y=0}^{\infty} -\frac{\rho_1 N_A}{MW_1} \frac{2\pi y C_{143}}{[(z+x)^2 + y^2]^3} dy dx = -\frac{1}{6} \frac{\rho_1 N_A C_{143} \pi}{MW_1} [z^{-3} - (z + \delta)^{-3}] \quad (2)$$

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

$$122 \quad V_{243}(z) = \int_{x=d}^{\infty} \int_{y=0}^{\infty} -\frac{\rho_2 N_A}{MW_2} \frac{2\pi y C_{243}}{[(z+x)^2 + y^2]^3} dy dx = -\frac{1}{6} \frac{\rho_2 N_A C_{243} \pi}{MW_2} (z + \delta)^{-3} \quad (3)$$

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

$$124 \quad V_{pp}(H) = \int_{z=H}^{\infty} [V_{143}(z) + V_{243}(z)] \frac{\rho_3 N_A}{MW_3} dz = -\frac{A_{143}}{12\pi} [H^{-2} - (H + \delta)^{-2}] - \frac{A_{243}}{12\pi} (H + \delta)^{-2} \quad (4)$$

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

$$127 \quad A_{143} = (\sqrt{A_{11}} - \sqrt{A_{44}})(\sqrt{A_{33}} - \sqrt{A_{44}}) \quad (5)$$

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

$$132 \quad A_{11} = [\phi(A_{polymer})^{0.5} + (1 - \phi)(A_{44})^{0.5}]^2 \quad (6)$$

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

$$135 \quad V_{sp}(h) = 2\pi \left[(a+h) \int_h^{h+2a} V_{pp}(H) dH - \int_h^{h+2a} V_{pp}(H) H dH \right] \quad (7)$$

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

$$137 \quad V_{sp}(h) = -\frac{A_{143}}{6} \left[\frac{a+h}{h} - \frac{a}{h+a} - \frac{a+h}{h+2a} - \frac{a}{h+2a+\delta} + \ln \frac{(h+2a+\delta)h}{(h+2a)(h+\delta)} \right] - \frac{A_{243}}{6} \left[\frac{a}{h+\delta} + \frac{a}{h+2a+\delta} + \ln \frac{h+\delta}{(h+2a+\delta)} \right] \quad (8)$$

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

$$139 \quad V_{sp}(h) = -\frac{A_{243}}{6} \frac{a}{h} \left[1 + \frac{h}{h+2a} + \frac{h}{a} \ln \frac{h}{h+2a} \right] \quad (9)$$

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

147 **Results and Discussion**

148 **Characterization of BPEI AgNPs.** The size of BPEI AgNPs determined by TEM images through
 149 ImageJ software (Fig. S2, Table 2) was close to the size reported by the manufacturer. The hydrodynamic
 150 diameter (HDD) measured by NTA and DLS (Fig. S3, Table 2) was considered to include the thickness of
 151 the capping agent (MacCusprie et al. 2011). The TEM measurements appear to indicate a more nearly
 152 monodisperse particle size than was found from NTA and DLS, an apparent artifact of the latter systems.
 153 The surface charge of BPEI AgNPs was positive (Fig. S4) because BPEI includes amine groups that
 154 would be protonated at the pH of these experiments (pH 7) (Stumm and Morgan 1996). However, the

155 surface charge decreased as particle size decreased, probably due to decreased H^+ density on the particle
156 surface (Barisik et al. 2014) or greater degree of hydroxylation (Chae et al. 2010). Nevertheless, the point
157 of zero charge of BPEI AgNPs was somewhat higher than pH 11 regardless of particle size, proving that
158 the surface charge of BPEI AgNPs in the filtration test was positive. The molecular weight of the BPEI
159 was reported by Nanocomposix, Inc. to be approximately 2500 Daltons. Using the method from Yang et
160 al. (2014), the capping layer thickness was estimated to be approximately 8 nm. This value is smaller than
161 but in the same range as the difference between the TEM radius and the HDD radius and was used as the
162 capping layer thickness to calculate the energy of interaction.

163 **Particle aggregation.** Aggregation of BPEI AgNPs was negligible at $I=1$ mM of $NaNO_3$ and pH 7 (Fig.
164 S5). This result was consistent with previous reports that the stability of BPEI AgNP would be greatest
165 near pH 7 (El Badawy et al. 2010) and the aggregation of BPEI AgNP would be insignificant even at
166 $I=1000$ mM (El Badawy et al. 2012). Therefore, the stability of BPEI AgNPs was assured in the filtration
167 condition.

168 **Effect of filter depth.** For the contact efficiency (η_0) estimation from the experimental results, the
169 stabilized relative concentrations of 10, 50, and 100 nm BPEI AgNPs were examined at three different
170 filter depths (2, 4, and 8 cm) with 4 m/h filtration velocity and 325 μm filter media size. The overall result
171 qualitatively followed the general expectation that deeper filter depth results in greater particle deposition
172 (Fig. S6). The time to reach a stabilized relative concentration was slightly increased as the filter depth
173 became shallower. The removal trend as a function of particle size indicates the greater AgNP capture of
174 smaller AgNPs due to their more vigorous Brownian motion; that is, the diffusion coefficients, calculated
175 from the measured average hydrodynamic diameters, of the 10 nm, 50 nm and 100 nm AgNPs under the
176 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
177 number of potential collisions between particles and media grains as the water flowed through the filter
178 would be inversely proportional to these values. Note that the relative concentration was nearly constant
179 after a short period. Even though the tests were conducted at the low range of the ratio of filter depth to

180 filter media size (L/d_c) (62, at the lowest), a constant level of AgNP deposition was maintained for a
181 sufficient period to obtain an apparent steady state relative concentration. This result might be due to slow
182 ripening as a consequence of low influent AgNP concentration.

183 **Effect of filtration velocity.** To investigate the effect of filtration velocity, three filtration velocities (2, 4,
184 and 8 m/h) were applied to the filtration of 10, 50, and 100 nm BPEI AgNPs with 4 cm filter depth and
185 325 μm filter media size. Particles have less time to contact the filter media with increased filtration
186 velocity, leading to less particle deposition. The effect of increased velocity on deposition is expected to
187 be greater for particles whose capture is by sedimentation than for particles captured by Brownian motion
188 (Tufenkji and Elimelech 2004). Although Ag has a relatively high density (10.49 g/cm^3), sedimentation of
189 these small nanoparticles onto the filter media was calculated to be negligible in comparison to deposition
190 by Brownian motion. The single collector contact efficiency calculated by Tufenkji and Elimelech model
191 revealed that, even for the largest particle (100 nm) under the highest filtration velocity (8 m/h), the
192 contact efficiency due to sedimentation was only 1.9×10^{-5} , much smaller than the contact efficiency from
193 Brownian motion which was 3.1×10^{-3} (by two orders of magnitude). The velocity effect was apparent in
194 all particle sizes tested (Fig. S7). The results from these experiments show a moderate change in AgNP
195 deposition caused by the velocity variation (i.e., an increase of approximately 0.3 in the relative
196 concentration at the plateau with the four-fold increase in filtration velocity).

197 **Effect of filter media size.** Three different filter media sizes (325, 463, and 776 μm) were employed to
198 study the effect of filter media size on the filtration of 10, 50, and 100 nm BPEI AgNPs. The filtration
199 tests were conducted with 4 cm filter depth and 4 m/h filtration velocity. With regard to the three sizes of
200 AgNPs, the AgNP deposition increased as filter media size decreased (Fig. S8) due to the decreased pore
201 sizes, the increased number of media layers for the same depth, and the increased surface area of the filter
202 media. As the size of AgNPs increased from 10 nm to 100 nm, the AgNP deposition decreased for all
203 filter media sizes. Specifically, when the filter media size was 776 μm , the fraction removed for the 10,
204 50, and 100 nm particles was 54%, 38% and 19% of the corresponding values for the 325 μm media. In

205 particular, only 8% of the 100 nm AgNPs were captured in 776 μm filter media even under favorable
206 attachment conditions. If nanoparticles are to be removed using granular media filtration, small filter
207 media size would be necessary.

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

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

229 larger size particles, but as particle size becomes smaller, the favorable deposition assumption tends to be
230 questionable.

231 1) Explanation from the energy of interaction

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

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

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

261 When the total DLVO interaction was calculated (Fig. 4), the results for the constant potential case (Fig.
262 4a) were consistent with the original hypothesis of the experimental work that the oppositely charged
263 particles and media grains would lead to an attractive condition at all separation distances. On the
264 contrary, the reduced vdW attraction and the repulsive EDL interaction under the constant charge
265 assumption (Fig. 4b) caused a net repulsive interaction for the 10 nm particle. Under the mixed case (Fig.
266 4c), though no repulsive energy exists for the 10 nm particle, the attraction was nevertheless negligible
267 and any external repulsion would cause hindrance between the particle and the collector. As a result, the
268 assumption of favorable deposition was not valid for the filtration of 10 nm BPEI-AgNPs, even though
269 the particle and the silica collector are oppositely charged. The deposition attachment efficiency (α) was
270 less than unity, thus leading to a reduced deposition than that calculated from the Tufenkji and Elimelech
271 model.

272 2) Other explanations

273 The 10 nm AgNPs showed a much greater degree of deviation between the experimental results and the
274 model predictions, suggesting a possible alteration of nanoparticle properties as the size gets smaller than
275 50 nm. Others have suggested that some size dependent properties are more likely to appear below 10 nm
276 (Bian et al. 2011), but, little is known about the details. For example, the vigorous Brownian motion of
277 nanoparticles, especially at extremely small size, could change the deposition of nanoparticles. Either

278 increased or decreased removal can be anticipated by an increased number of collisions with filter media.
279 An increase would be consistent with standard filtration theory. A decrease could possibly occur because
280 of the vigorous Brownian motion of nanoparticles 10 nm or less. The greater Brownian motion means that
281 the 10 nm particles have a far higher velocity than the larger nanoparticles used in this study (Bhatt et al.
282 2013). In aerosol filtration, Wang and Kasper (Wang and Kasper 1991) proposed that nanoparticles below
283 10 nm could rebound off collector surfaces because the time of interaction was so short; while this
284 phenomenon is less likely in water where the mean free path is far smaller than in air, we note the
285 possibility. Further research would be necessary to investigate this possible explanation.

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

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

299 **Conclusions**

300 The effect of physical parameters on the transport of BPEI AgNPs in granular media filtration was
301 experimentally evaluated under favorable attachment conditions; and DLVO interaction was calculated to

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

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

324 Further investigation on the transport of the smaller-sized nanoparticles is required to obtain sufficient
325 experimental data to update the colloidal filtration model especially in the size range less than 50 nm. The
326 conformation of the surface capping must be included and the EDL interaction model must be carefully

327 chosen. The updated colloidal filtration model would be beneficial for predicting contact efficiency (η_o)
328 in such a small particle size range, which then could lead to an accurate estimation of the attachment
329 efficiency (α) under unfavorable attachment conditions.

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

334 **Acknowledgements**

335 This research was provided by the US National Science Foundation (CBET-1336139).

336 **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_{dp}	surface potential of flat plate
Ψ_{ds}	surface potential of spherical particle

337 **Supplemental Data**

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

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430

431

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

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

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

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

443 **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)	$V_{EDL} = \pi \varepsilon_o \varepsilon_r a \left\{ \begin{array}{l} 2\Psi_{d_p} \Psi_{d_s} \ln \left[\frac{1+e^{(-\kappa h)}}{1-e^{(-\kappa h)}} \right] + \\ (\Psi_{d_p}^2 + \Psi_{d_s}^2) \ln [1 - e^{(-2\kappa h)}] \end{array} \right\}$	(Hogg et al. 1966)
V_{EDL} (constant charge)	$V_{EDL} = \pi \varepsilon_o \varepsilon_r a \left\{ \begin{array}{l} 2\Psi_{d_p} \Psi_{d_s} \ln \left[\frac{1+e^{(-\kappa h)}}{1-e^{(-\kappa h)}} \right] - \\ (\Psi_{d_p}^2 + \Psi_{d_s}^2) \ln [1 - e^{(-2\kappa h)}] \end{array} \right\}$	(Usui 1973)
V_{EDL} (mixed)	$V_{EDL} = 4\pi \varepsilon_o \varepsilon_r a \left\{ \begin{array}{l} \Psi_{d_p} \Psi_{d_s} \arctan(e^{-\kappa h}) + \\ \frac{1}{4} (\Psi_{d_p}^2 - \Psi_{d_s}^2) \ln [1 + e^{(-2\kappa h)}] \end{array} \right\}$	(Kar et al. 1973)
V_{DLVO}	$V_{DLVO} = V_{EDL} + V_{vdW}$	

444

445 **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

446

^aMeasured at I=1 mM of NaNO₃ and pH 7.