



Transport and retention of surfactant- and polymer-stabilized engineered silver nanoparticles in silicate-dominated aquifer material[☆]

Yorck F. Adrian^{a, *}, Uwe Schneidewind^a, Scott A. Bradford^b, Jirka Simunek^c, Tomas M. Fernandez-Steege^d, Rafiq Azzam^a

^a Department of Engineering Geology and Hydrogeology, RWTH Aachen University, Lochnerstr. 4-20, 52064 Aachen, Germany

^b US Salinity Laboratory, USDA, ARS, Riverside, CA 92507, United States

^c Department of Environmental Sciences, University of California, Riverside, CA 92521, United States

^d Department of Engineering Geology, TU Berlin, Ernst-Reuter-Platz 1, 10587 Berlin, Germany

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ABSTRACT

Packed column experiments were conducted to investigate the transport and blocking behavior of surfactant- and polymer-stabilized engineered silver nanoparticles (Ag-ENPs) in saturated natural aquifer media with varying content of material < 0.063 mm in diameter (silt and clay fraction), background solution chemistry, and flow velocity. Breakthrough curves for Ag-ENPs exhibited blocking behavior that frequently produced a delay in arrival time in comparison to a conservative tracer that was dependent on the physicochemical conditions, and then a rapid increase in the effluent concentration of Ag-ENPs. This breakthrough behavior was accurately described using one or two irreversible retention sites that accounted for Langmuirian blocking on one site. Simulated values for the total retention rate coefficient and the maximum solid phase concentration of Ag-ENPs increased with increasing solution ionic strength, cation valence, clay and silt content, decreasing flow velocity, and for polymer-instead of surfactant-stabilized Ag-ENPs. Increased Ag-ENP retention with ionic strength occurred because of compression of the double layer and lower magnitudes in the zeta potential, whereas lower velocities increased the residence time and decreased the hydrodynamics forces. Enhanced Ag-ENP interactions with cation valence and clay were attributed to the creation of cation bridging in the presence of Ca²⁺. The delay in breakthrough was always more pronounced for polymer-than surfactant-stabilized Ag-ENPs, because of differences in the properties of the stabilizing agents and the magnitude of their zeta-potential was lower. Our results clearly indicate that the long-term transport behavior of Ag-ENPs in natural, silicate dominated aquifer material will be strongly dependent on blocking behavior that changes with the physicochemical conditions and enhanced Ag-ENP transport may occur when retention sites are filled.

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1. Introduction

Engineered silver nanoparticles (Ag-ENPs) are among the most widely used nanoparticles in consumer products due to their antimicrobial properties (Maillard and Hartemann, 2013; Zhang et al., 2016). Their use has among others been documented for textiles, paints, cleaning agents, electrical appliances, medical

technology and cosmetics (Goswami et al., 2017 for review). Ag-ENPs can be released into the environment during manufacturing processes, product distribution, product use, and disposal (Farkas et al., 2011; Kaegi et al., 2010; McGillicuddy et al., 2017). Once in the environment Ag-ENPs can become bioavailable (Navarro et al., 2008) and are potentially toxic or detrimental to a wide variety of organisms (Andrei et al., 2016; Juganson et al., 2017; Katsumiti et al., 2015; Makama et al., 2016; Malleve et al., 2014; Siller et al., 2013; Zuykov et al., 2011).

One major route for environmental release is through wastewater (Nowack and Bucheli, 2007; Nowack et al., 2012; Troester

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* Corresponding author.

E-mail address: yorck.adrian@rwth-aachen.de (Y.F. Adrian).

et al., 2016). Ag-ENPs can be retained in activated sewage sludge in wastewater treatment plants (Kaegi et al., 2011, 2013; Maier et al., 2012), which is then used as agricultural fertilizer or disposed of at landfills (Blaser et al., 2008). Ag-ENPs can subsequently be leached into the vadose zone and transported toward groundwater. Groundwater can exhibit variations in solution ionic strength (IS) because of changes in aquifer material composition, temporal variations in recharge, groundwater-surface water interactions, increased salinization, and mixing of groundwater of different age and compositions. In many countries, groundwater is a major source of drinking water serving millions of people (Danish Ministry of the Environment, 2013; Federal Statistical Office of Germany, 2013; United States Environmental Protection Agency, 2008). Thus, understanding Ag-ENP transport processes in the saturated zone is essential to the protection and future use of groundwater resources.

Colloid and nanoparticle transport studies have typically been conducted under clean bed conditions using highly idealized porous media and solution chemistries (Flory et al., 2013; Kanel et al., 2007; Lin et al., 2011; Liu et al., 2009; Mattison et al., 2011). For example, glass beads and/or coarse textured sand that have been rigorously cleaned and monovalent electrolyte solutions are commonly employed in these studies (Bradford et al., 2002; Lin et al., 2011; Liu et al., 2009). Clean bed conditions imply a constant rate of retention and an infinite retention capacity (Yao et al., 1971). Colloid filtration theory (CFT) is commonly employed to characterize colloid and nanoparticle retention under clean bed conditions (Bayat et al., 2015; Park et al., 2016). Filtration theory describes retention as a first-order process that depends on the rate of mass transfer (diffusion, interception and sedimentation) from the bulk aqueous phase to the solid surface, and a sticking or collision efficiency that is controlled by adhesive interactions between the nanoparticle and solid (Tufenkji and Elimelech, 2004a; Yao et al., 1971). Nanoparticle transport studies that apply CFT typically assume that lower effluent concentrations imply less risk of contamination (Tufenkji and Elimelech, 2004b). It is demonstrated in this work that this assumption is inaccurate in many instances for Ag-ENPs.

In contrast to the CFT assumption, soil and aquifer material always have a finite retention capacity (Johnson and Elimelech, 1995; Leij et al., 2015; Sasidharan et al., 2014; Torkzaban et al., 2012), and the retention rate coefficient, therefore, decreases over time as available retention sites fill (also referred to as blocking). Retention is completely eliminated when all of the available retention sites are filled, and the retained solid phase concentration reaches a maximum, thus enhancing the long-term potential for Ag-ENP transport (Leij et al., 2015). Langmuirian (Adamczyk et al., 2013) and random sequential adsorption blocking (Johnson and Elimelech, 1995) models assume that the retention rate coefficient decreases in a linear and nonlinear manner with increasing retention, respectively. This has been observed not only for Ag-ENPs but also for other colloids (e.g. Kuhn et al., 2000). An alternative approach to account for nonlinear blocking dynamics is to employ Langmuirian blocking on two retention sites, with separate retention and release rate coefficients and maximum retention capacities on each site (Sasidharan et al., 2014).

The rate of filling of retention sites increases with the input concentration, input pulse duration, the clean bed retention rate and decreasing values of the maximum solid phase concentration (Leij et al., 2015). In addition, the retention rate and the maximum solid phase concentration are strong functions of many physico-chemical variables (Sasidharan et al., 2014). Consequently, the selection of experimental conditions can have a large impact on whether or not blocking is apparent in transport experiments. Previous research on Ag-ENP transport has focused on the

determination of retention rate coefficients for varying physico-chemical conditions, including grain size (Liang et al., 2013b), water velocity (Braun et al., 2015), solution IS (Liang et al., 2013b; Wang et al., 2014) and pH (Flory et al., 2013), ionic composition (Liang et al., 2013a), organic matter (Hou et al., 2017; Mitzel and Tufenkji, 2014; Park et al., 2016), or stabilizing agent for the Ag-ENPs (El Badawy et al., 2013). These studies typically were not designed to investigate blocking dynamics that control the long-term potential of Ag-ENP transport. A limited number of studies have examined the transport and retention of Ag-ENPs in natural soils (Cornelis et al., 2013; Liang et al., 2013a; Sagee et al., 2012; Wang et al., 2014, 2015; Makselon et al., 2017). Some of these studies neglected the influence of blocking altogether (Cornelis et al., 2013; Sagee et al., 2012), whereas those that did consider blocking (Liang et al., 2013a; Wang et al., 2014; Wang et al., 2015) did not systematically investigate the role of stabilizing agent type, small amounts of silt and clay in silicate-dominated aquifer material, and the coupling of these factors with monovalent and divalent cations, IS, and water velocity. These gaps in knowledge are addressed in this research.

The objective of our work was to study the transport and blocking behavior of surfactant- and polymer-stabilized Ag-ENPs in silicate-dominated aquifer material, a material that can be found around the world in many unconsolidated aquifers essential to drinking water supply. To achieve this objective, we conducted laboratory column experiments and employed analytical methods (inductively coupled plasma mass spectrometry, dynamic light scattering) as well as numerical modeling techniques. During the transport experiments, we specifically focused on situations that are more representative of natural conditions than previous studies (Hou et al., 2017; Li et al., 2008; Mattison et al., 2011; Mitzel and Tufenkji, 2014), including (i) IS and major cation type (Ca^{2+} or Na^{+}); (ii) stabilizing agent (polymer or surfactant) for Ag-ENPs in the absence and presence of fine particle size fractions (<0.063 mm); and (iii) changing flow velocities in the column.

2. Materials and methods

2.1. Electrolyte solutions and aquifer material

All electrolyte solutions were prepared using ultrapure water (Merck Millipore Milli-Q 18.2 M Ω ·cm, TOC: 1–2 ppb, 0.22 μm membrane filter) that was unbuffered with a pH of 5.8–6.2. Solutions of selected IS and composition were prepared by adding NaNO_3 (Sigma Aldrich, St. Louis, Missouri, USA) or $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck KGaA, Darmstadt, Germany) to the ultrapure water.

The silicate-dominated aquifer material was collected in Dormagen-Gohr, NRW, Germany from a depth between 16 and 19.5 m below surface during the drilling of a groundwater monitoring well. The shallow unconfined aquifer at that site consists mainly of unconsolidated fine to coarse Quaternary sands and gravels deposited during the Saale glaciation (Pleistocene). A sample of the aquifer material (0–2 mm grain size) was oven-dried at 40 °C, and the mineral and clay composition were determined by means of X-ray powder diffraction (XRD) using a Siemens D5000 (Table S1). The oven-dried aquifer material was also sieved into grain size fractions of 1–2, 0.5–1, 0.025–0.5, 0.125–0.25, 0.063–0.125, and <0.063 mm to obtain a representative grain size distribution (Fig. S1) with a median grain diameter of 0.7 mm. Hydrometer analysis was carried out on the fraction <0.063 mm to determine silt (fraction of 0.002–0.063 mm) and clay (<0.002 mm) percentages, and to recover them for studies examining their influence on Ag-ENP transport. The pH of the soil solution was measured according

to the German standard DIN EN 15933 (2012) in 0.01 mol L⁻¹ CaCl₂ (Merck KGaA, Darmstadt, Germany). Brunauer-Emmett-Teller (BET) measurements were conducted in triplicates on samples of aquifer material using N₂ to determine the surface area in the presence and absence of fines.

2.2. Ag-ENPs

Two types of commercial Ag-ENPs were employed in this research, namely AgPURE™ W-10 (ras materials GmbH, Regensburg, Germany) and polyvinylpyrrolidone (PVP) coated Ag-ENPs (Getnanomaterials GNM, OOCAP SAS, France, stock number: 7023HZ). The stock suspension of the sterically stabilized AgPURE™ W-10 contained a silver nanoparticle concentration of 10.16% (weight/weight, wt/wt) and corresponds to the OECD reference material NM300K, in which the silver nanoparticles are stabilized with 4% (wt) of each polyoxyethylene glycerol trioleate and Tween 20 (Klein et al., 2011). Furthermore, AgPURE™ W-10 contains 7.5% (wt/wt) ammonium nitrate (Menzel et al., 2013). The PVP-coated Ag-ENP powder consisted of 10% (wt) silver with a purity of 99.99%, as well as of 89.8% (wt) PVP and 0.2% (w) moisture. For experiments discussed below, the stock suspension of AgPURE was diluted to 10 mg Ag/L in the desired background solution and sonicated for 15 min. Similarly, the PVP coated Ag-ENP powder was dispersed in the desired background solution and sonicated for 10 min in a sonication bath. Afterwards, the dispersion was diluted to 10 mg Ag/L and sonicated for 5 min.

AgPURE Ag-ENPs have a spherical shape and 99% of the particle size is in the range of 15–20 nm, determined by transmission electron microscopy (Klein et al., 2011). Similarly, according to the manufacturer, the size of the PVP coated Ag-ENPs was 20 nm. A Zetasizer Nano ZS (Malvern GmbH) was used to determine the electrophoretic mobility at 25 °C of the Ag-ENPs and the aquifer material that was <10 µm in size in the corresponding background solution as well as the hydrodynamic diameter of the Ag-ENPs. The electrophoretic mobility was then converted to the zeta potential [mV] using the Smoluchowski equation.

2.3. Interaction energies

Section S1 of the supporting information provides details pertaining to the calculation of the total interaction energy of Ag-ENPs upon approach to the aquifer material under the various solution chemistries. In brief, the total interaction energy was determined as the sum of electrostatic (Hogg et al., 1966), van der Waals (Gregory, 1981), and Born (Ruckenstein and Prieve, 1976) interactions. These calculations employed zeta potentials in place of surface potentials, a Hamaker constant of 5.3×10^{-20} J (Bhattacharya et al., 2007), and a collision diameter of 0.26 nm to achieve a primary minimum depth at 0.157 nm (Van Oss, 1994). All interaction energies were made dimensionless by dividing by the product of the Boltzmann constant and the absolute temperature.

2.4. Transport experiments

Borosilicate glass columns (inner diameter of 2.6 cm, length of 15 cm and volume of 79.6 mL) were wet packed with the oven dried aquifer material following the German standard DIN 19258 (2009) as described by Braun et al. (2015). Some of the transport experiments considered the influence of a 2% increase in the fine soil fraction <0.063 mm, while keeping grain diameters of the distribution (Fig. S1) greater than 0.125 mm constant. Column inlets and outlets were equipped with a 2 mm thick layer of quartz wool to prevent very fine grains from being flushed out of

the material matrix. Transport experiments were carried out in an up-flow mode at an average pore-water velocity of 4.32 or 8.64 m d⁻¹ using a peristaltic pump (ICP High Precision Multi-channel Dispenser, Ismatec). These water velocities were selected based on measurements of the saturated hydraulic conductivity from falling head permeameter tests (DIN, 18130-1, 1998).

Columns were flushed with at least 10 pore volumes (PV) of ultrapure water before conducting a NaBr (Merck KGaA, Darmstadt, Germany) tracer test. The tracer test consisted of flushing 3 PV of 200 mg Br⁻/L solution through the column, followed by continued elution with 3 PV of ultrapure water. The bromide concentration was measured using ion selective electrodes (DX280-Br, Mettler Toledo GmbH, Gießen, Germany) and a reference electrode InLab® Reference (DX280-Br, Mettler Toledo GmbH, Gießen, Germany) connected to a conductivity meter (WTW pH/Cond 340i meter, Weilheim, Germany).

Before initiating an Ag-ENP transport experiment, columns were flushed with at least 10 PV of background electrolyte solution (sodium nitrate, Sigma Aldrich, USA; calcium nitrate tetrahydrate, Merck KGaA, Darmstadt, Germany), and the Ag-ENP suspension was sonicated for 15 min in an ultrasonic bath (Retsch UR-1, Retsch Technology GmbH, Germany). At least 3 PV of Ag-ENP suspension was then injected into the columns followed by flushing with at least 3 PV of Ag-ENP free background electrolyte solution with the same IS and composition. The influent Ag-ENP suspension was placed on a magnetic stirrer during long-term experiments. Column effluent fractions were collected in borosilicate vials using a fraction collector. The total Ag concentration in effluent samples was determined using ICP-MS (Agilent 7900 ICP-MS, Agilent Technologies). In brief, 1 mL of the collected effluent samples was transferred into 15 mL polypropylene centrifuge tubes (VWR International GmbH, Germany) and acidified with 1 mL 32.5% HNO₃ (Merck KGaA, Darmstadt, Germany) to dissolve the particles and minimize sorption onto the centrifuge tubes. Samples were then diluted as needed for ICP-MS analysis. Each sample was measured three times and average values are reported here. The pH of influent and effluent solutions was monitored using a SenTix 41 pH electrode (WTW, Germany) and indicator strips for comparison.

The focus of this research is to investigate the transport and blocking behavior of Ag-ENPs under a range of physicochemical conditions that are more representative of natural aquifer material. Table 1 provides a summary of the considered experimental conditions including: (i) IS; (ii) ionic composition (Na⁺ or Ca²⁺); (iii) stabilizing agent (surfactant or PVP coating) for the Ag-ENPs; (iv) absence or presence of the fine aquifer material fraction (i.e. 2% increase in the material fraction <0.063 mm in size); and (v) pore water velocity (4.32 and 8.64 m d⁻¹). The arrival time, shape, magnitude, and effluent mass balance of the Ag-ENP breakthrough curves (BTCs) were quantified in this study. The shape of the Ag-ENP retention profiles is influenced by the extent of blocking (Leij et al., 2015). The presence of multiple retention mechanisms and sites, retention rates, and retention capacities that are dependent on various physicochemical conditions further complicates the effects of blocking on retention profiles. Similar to other published blocking studies (Sasidharan et al., 2014; Torkzaban et al., 2012), retention profiles were therefore not considered in this work.

Most Ag-ENP transport experiments were replicated, and results are shown in Table S2. Illustrative examples of replicate Ag-ENP BTCs are shown in Fig. S2. The agreement between replicate experiments can be assessed by comparison of fitted model parameters and effluent mass balance information for Ag-ENPs that are presented in Table S2. Differences in effluent mass balance for

Table 1

Summary of experimental conditions and simulated parameter values for the graphs shown in Figs. 1–6.

Figure	Ag-ENP	IS	Ion	ϕ	d_{50}	d_x	q	λ	R^2	Tracer	S_{max1}/C_0	k_{sw1}	k_{sw2}	R^2	Ag-ENP Recovery	Ag-ENP
		[mM]		[-]	[mm]	[%]	$[m s^{-1}] \times 10^{-5}$	$[m] \times 10^{-2}$	[-]	recovery	$[cm^3 g^{-1}]$	$[s^{-1}] \times 10^{-4}$	$[s^{-1}] \times 10^{-4}$	[-]	[%]	[mL]
1	AgPURE	1	Na	0.38	0.7	0	3.8	0.95	1.00	100.2	0.15	1.1	—	1.00	92.6	90.3
1	PVP-AgNP	1	Na	0.37	0.7	0	3.7	0.51	0.98	99.3	0.66	31.2	1.8	0.99	51.1	299.7
1	AgPURE	1	Ca	0.37	0.7	0	1.9	0.51	0.96	109.4	11.40	40.1	1.9	0.97	25.3	3363.0
2	AgPURE	0.05	Ca	0.38	0.7	0	3.8	1.50	0.98	107.3	0.28	5.0	—	0.97	66.6	88.4
2	AgPURE	0.1	Ca	0.38	0.7	0	3.7	0.77	0.83	97.7	0.29	8.5	—	0.95	60.1	87.9
2	AgPURE	0.5	Ca	0.38	0.7	0	3.8	0.34	0.91	93.5	1.60	35.2	—	0.54	13.9	89.9
2	AgPURE	1	Ca	0.37	0.7	0	3.9	1.43	0.62	105.0	0.77	453.0	—	0.82	2.2	91.6
3	PVP-AgNP	1	Na	0.37	0.7	0	3.7	0.97	0.98	94.4	0.57	71.7	—	0.99	23.1	94.6
3	PVP-AgNP	0.1	Ca	0.38	0.7	0	3.7	0.51	0.97	104.7	0.65	151.0	—	0.96	15.6	87.7
4	PVP-AgNP	0.05	Ca	0.37	0.7	2	3.7	3.81	0.99	96.3	0.66	81.4	—	0.93	10.1	89.9
4	PVP-AgNP	0.05	Ca	0.37	0.7	0	3.7	0.85	0.79	89.7	0.44	33.1	—	0.98	34.7	89.0
5	AgPURE	1	Na	0.38	0.7	0	3.8	0.95	1.00	100.2	0.15	1.1	—	1.00	92.6	90.3
5	PVP-AgNP	1	Na	0.37	0.7	0	3.7	0.97	0.99	102.9	0.52	48.8	—	0.98	23.1	89.5
5	AgPURE	1	Na	0.37	0.7	2	3.7	1.26	0.98	105.9	0.21	3.2	—	0.97	76.1	87.8
5	PVP-AgNP	1	Na	0.37	0.7	2	3.7	1.12	0.99	94.8	1.01	117.5	—	0.93	0.4	88.4
6	AgPURE	1	Na	0.37	0.7	0	1.9	0.83	0.96	95.8	0.18	23.3	0.6	0.99	61.6	122.0
6	AgPURE	1	Na	0.37	0.7	0	3.6	0.43	1.00	95.4	0.09	31.5	0.9	1.00	78.4	122.3
6	PVP-AgNP	1	Na	0.38	0.7	0	2.5	0.41	1.00	94.1	0.81	56.1	—	0.96	12.9	62.8
6	PVP-AgNP	1	Na	0.37	0.7	0	3.7	0.97	0.99	102.9	0.52	48.8	—	0.98	23.1	89.5

IS: Ionic strength; ϕ : porosity, determined gravimetrically; d_{50} : mean grain size diameter; d_x : fraction of grains < 0.063 mm; q : Darcy velocity (discharge per unit area); λ : fitted dispersivity obtained from tracer experiments; S_{max1} : maximum solid phase concentration; k_{sw1} : first-order retention coefficient for the first sorption site; k_{sw2} : first-order retention coefficient for the second sorption site; and R^2 : Coefficient of determination.

replicate experiments (<22.7%) were controlled by the physico-chemical conditions and the uncleaned aquifer material which determine variations in the retention capacity that influence the amount and extent of blocking.

2.5. Mathematical and numerical modeling

Bromide tracer and Ag-ENP transport experiments were modeled using the numerical finite element code HYDRUS 1D, version 4.16 (Šimůnek et al., 2008, 2016). The Ag-ENP transport was modeled using one or two kinetic retention sites with Langmuirian blocking on site 1 as:

$$\frac{\partial(\theta_w C)}{\partial t} = \frac{\partial}{\partial z} \left(D \theta_w \frac{\partial C}{\partial z} \right) - \frac{\partial(qC)}{\partial z} - \theta_w (k_{sw1} \psi_1 + k_{sw2}) C \quad (1)$$

$$\frac{\partial(\rho_b S_1)}{\partial t} = \theta_w k_{sw1} \psi_1 C \quad (2)$$

$$\frac{\partial(\rho_b S_2)}{\partial t} = \theta_w k_{sw2} C \quad (3)$$

where θ_w [$L^3 L^{-3}$] is the volumetric water content, ρ_b [ML^{-3}] is the material bulk density, t [T] is the time, z [L] is the distance, D [$L^2 T^{-1}$] is the hydrodynamic dispersion coefficient, q [LT^{-1}] is the Darcy flux, C [ML^{-3}] is the aqueous phase concentration of Ag-ENP, S [MM^{-1}] is the solid phase concentration of Ag-ENP, k_{sw} [T^{-1}] is the first order Ag-ENP retention coefficient for the solid-water interface, ψ [-] is a dimensionless Langmuirian blocking function, and the subscripts 1 and 2 on parameters indicate sites 1 and 2, respectively.

The value of ψ_1 is given as (Adamczyk et al., 1992, 1994):

$$\psi_1 = 1 - \frac{S_1}{S_{max1}} \quad (4)$$

where S_{max1} [$M M^{-1}$] is the maximum solid phase concentration of Ag-ENPs on site 1. The fraction of the solid surface area that is available for retention (S_{f1}) on site 1 was calculated from S_{max1} as (Kim et al., 2009):

$$S_{f1} = \frac{A_c \rho_b S_{max1}}{(1 - \gamma) A_s} \quad (5)$$

where A_c [$L^2 N^{-1}$] is the cross sectional area of an Ag-ENP, A_s [L^{-1}] is the solid surface area per unit volume, and γ is the porosity of a monolayer packing of nanoparticles on the solid surface that was taken from the literature to be 0.5 (Johnson and Elimelech, 1995).

Transport of the conservative bromide tracer was modeled using HYDRUS-1D by setting the k_{sw} terms in Eq. (1) to zero. HYDRUS-1D includes a provision for inverse parameter optimization to experimental data based on the Levenberg-Marquardt nonlinear least squares algorithm. This option was employed to determine the dispersivity and porosity from the bromide tracer data, and retention parameters (k_{sw1} , k_{sw2} and S_{max1}) from the Ag-ENP data. The parameter k_{sw2} was only fitted when Ag-ENP BTCs exhibited a delay in breakthrough, increased in concentration, and then reached a plateau concentration.

Table 2Zeta-potential of the Ag-ENPs and the material fraction <10 μm in the corresponding background solution.

Type	IS [mM]	Ion	ζ -potential [mV]	Hydrodynamic diameter [nm]	Primary minimum [-]	Energy barrier [-]	Secondary minimum [-]
Gohr	0.05	Ca	−17.4				
Gohr	0.1	Ca	−18.9				
Gohr	0.5	Ca	−19.1				
Gohr	1	Na	−35.6				
AgPURE	0.05	Ca	−25.1	53.1 $\pm$ 1.3	−248.58	11.01	0.00
AgPURE	0.1	Ca	−10.8	54.5 $\pm$ 5.2	−257.55	3.68	0.00
AgPURE	0.5	Ca	−7.8	56.3 $\pm$ 1.2	−261.89	0.93	−0.03
AgPURE	1	Ca	−6.5	56.4 $\pm$ 1.5	−289.34	0.69	−0.07
AgPURE	1	Na	−14.0	51.0 $\pm$ 3.1	−263.09	5.18	−0.05
PVP-Ag-ENP	0.05	Ca	−7.1	64.0 $\pm$ 1.2	−380.27	2.82	0.00
PVP-AgNP	0.1	Ca	−6.8	61.8 $\pm$ 0.9	−382.56	2.33	0.00
PVP-AgNP	1	Na	−3.6	66.9 $\pm$ 4.4	−434.37	−0.11	−0.15

IS: ionic strength.

3. Results and discussion

3.1. Characterization of Ag-ENPs and porous media

The zeta-potential and hydrodynamic diameter of the Ag-ENPs in the considered background solutions are presented in Table 2. Measurements show that PVP-coated Ag-ENPs are less negatively charged compared to AgPURE. The sterically stabilized PVP-coated Ag-ENPs showed only little changes in their zeta potential even under varying IS. This was also encountered by El Badawy et al. (2010) for PVP-coated Ag-ENP from the same manufacturer. In general, the zeta potential becomes less negative for both Ag-ENP types with increasing IS and ion valence. Hydrodynamic diameters for PVP-coated Ag-ENPs and AgPURE were found to be 61.79–66.89 nm and 51.03–56.41 nm, respectively. Additional size measurements taken over several days show that both Ag-ENP suspensions were stable (see Figs. S3 and S4). Similarly, Liang et al. (2013b) reported a hydrodynamic diameter of 45.1 ± 4.5 nm in a 1 mM KNO_3 background solution for AgPURE that was stable over a period of 24 h. Furthermore, they found Ag^+ release to be less than 1% of the total mass within three days.

The average surface area of the aquifer material was determined to be 2.69 and $3.26 \text{ m}^2 \text{ g}^{-1}$ in the absence and presence of fines, respectively. The pH of the soil solution was determined to be 6.6. Hydrometer analysis results showed that the fraction <0.063 mm consisted of 90% silt and 10% clay-sized particles. The electrophoretic mobility of the aquifer material that was <10 μm in size was measured at ISs of 0.05, 0.1, and 0.5 mM Ca^{2+} , and 1 mM Na^+ . The zeta potential of the aquifer material was more negative than that of the Ag-ENPs at a given IS (Table 2). X-ray diffraction analysis indicated that quartz was the dominant mineral by weight (see Table S1) for all experiments. Quartz and feldspar are negatively charged in groundwater environments, making them less favorable for Ag-ENP attachment than minerals with positively charged sites such as clays, iron oxides and iron hydroxides (Johnson et al., 1996; Liang et al., 2013b; Molnar et al., 2015). However, patch-wise geochemical surface heterogeneity may also be found on quartz surfaces in groundwater environments due to the presence of Fe, Al and Mn-oxides that have contrasting isoelectric points (Johnson et al., 1996). For example, ferric and aluminum oxyhydroxides are positively charged minerals that are often found on grain surfaces. Consequently, iron-containing soil colloids (Liang et al., 2013b) or subsurface material with locally high iron oxide/hydroxide content (Neukum et al., 2014) are expected to form regions that are electrostatically favorable for the attachment of negatively charged Ag-ENPs and thus contribute to their retention. Indeed, iron oxides, as well as the clay minerals muscovite and kaolinite, were detected

with X-ray diffraction analysis and a patch-wise iron-oxide coating on the quartz sand surfaces was visible even to the naked eye.

3.2. Interaction energies

Table 2 presents a summary of calculated interaction parameters for AgPURE and PVP coated Ag-ENPs with the aquifer material under selected solution chemistry conditions. Interaction energy calculations predict the presence of a negligible secondary minimum (>-0.15), a small energy barrier (<11.0), and a deep primary minimum (<-248.6). These parameters indicate that Ag-ENPs will interact with the aquifer material in a deep primary minimum. A decrease in the energy barrier height increases the probability for Ag-ENPs to diffuse over the energy barrier into the primary minimum (Shen et al., 2007; Simoni et al., 1998). Consequently, calculated energy barriers predict increasing Ag-ENP retention with increasing IS and for PVP coated Ag-ENPs in comparison with AgPURE.

The XDLVO calculations in Table 2 assume that the Ag-ENPs and aquifer material are perfectly smooth and chemically homogeneous, and neglect the potential influence of electrosteric interactions. Electrosteric repulsion has commonly been employed to explain the enhanced stability of PVP or surfactant coated Ag-ENPs (Grasso et al., 2002). Indeed, XDLVO calculations can be modified to consider the influence of electrosteric repulsion using information about the adsorbed polymer or surfactant layer thickness and density (Fritz et al., 2002; Phenrat et al., 2007; Song et al., 2011; Vincent et al., 1986). For example, Liang (2014) considered the influence of electrosteric repulsion on interaction energies between AgPURE and quartz sand, and reported that adsorbed surfactant increased the dimensionless energy barrier by around 1000 for similar solution chemistry conditions to this work. In this case, no Ag-ENP retention is expected on the aquifer material. Consequently, steric interactions cannot explain retention of Ag-ENPs on the aquifer material, and other explanations need to be considered. In particular, we discuss the roles of XDLVO interactions shown in Table 2, charge and roughness heterogeneity, and cation bridging below.

3.3. Ag-ENP blocking

Table 1 provides a summary of the considered physicochemical conditions, measured and/or fitted model parameters and mass balance information for bromide tracer and Ag-ENP transport experiments, and the coefficient of determination for the goodness of fit (R^2) for Ag-ENP BTCs. The pH of influent and effluent solutions was determined to be between 5.8 and 6.2. Fitted values of $S_{\text{max}1}$

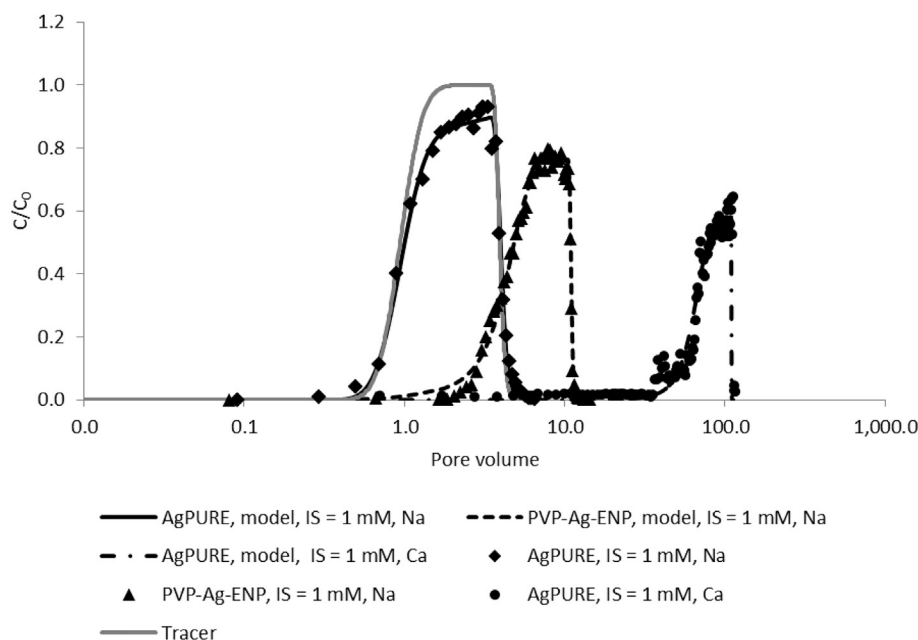


Fig. 1. Illustrative examples of long term transport behavior for Ag-ENPs under various physicochemical conditions, including varying stabilizing agent (surfactant and polymer coating) and background solution.

were used to calculate S_{f1} (Table S3) according to Eq. (5) when using measured values of the aquifer material surface area and Ag-ENP hydrodynamic diameters. Consistent with previous literature (Sasidharan et al., 2014), calculated values of S_{f1} were very small ($<5.4 \times 10^{-5}$). This indicates that only a minor fraction of the solid surface area contributed to Ag-ENP retention in these studies.

Fig. 1 presents observed and simulated Ag-ENP BTCs for different physicochemical conditions and an example BTC for the bromide tracer. Relative effluent concentrations (C/C_0 , where C_0 is the influent concentration) are plotted as a function of the number of PV flushed through the columns on a log scale. Bromide tracer tests showed nearly complete recovery (89.7–109.4%), and breakthrough occurred at 1 PV. All of the Ag-ENPs BTCs were well described ($R^2 > 0.97$) using either a one- or two-site retention model that neglected detachment and accounted for Langmuirian blocking on site 1. Blocking always produced an increase in the effluent concentration with continued Ag-ENP injection due to filling of a limited number of retention sites, and this behavior is manifested in several ways. In the AgPURE (IS = 1 mM, Na) experiment the value of k_{sw1} is small enough that breakthrough occurs at 1 PV, and then the relative concentration rapidly increases to 0.94 as S_{max1} is reached due to continued Ag-ENP injection. In contrast, k_{sw1} is larger in the other two experiments and this causes a delay in breakthrough that depends on the values of S_{max1} , C_0 , and the input pulse duration (Leij et al., 2015). Here, breakthrough of Ag-ENPs in the PVP-Ag-ENP (IS = 1 mM, Na) and AgPURE (IS = 1 mM, Ca) experiments occurred after about 4 and 76 PV, respectively, and a corresponding increase in the input pulse duration was needed to observe blocking. Larger values of S_{max1} and smaller values of C_0 cause a longer delay in breakthrough. If the input pulse duration is too small, breakthrough will not occur. If blocking occurs only on one retention site, the relative effluent concentrations will rapidly approach a C/C_0 of 1 following breakthrough due to filling of the retention sites. Conversely, the modeled relative effluent concentrations approach a plateau concentration of 0.76 in the PVP-Ag-ENP (IS = 1 mM, Na) experiment and 0.58 in the AgPURE (IS = 1 mM, Ca) experiment with continued injection. This is indicative of a second retention site with a lower k_{sw2} and higher

S_{max2} than on site 1. Note that it was not possible to accurately determine the values of S_{max2} in PVP-Ag-ENP (IS = 1 mM, Na) and AgPURE (IS = 1 mM, Ca) experiments because of the slow rate of filling.

Fig. 1 clearly demonstrates that temporal changes in the breakthrough time and the peak effluent concentration will occur due to blocking that is a strong function of the physicochemical conditions. Below, we systematically study the influence of Ag-ENP blocking under different physicochemical conditions that are more representative of natural environments than previous studies, including: the role of stabilizing agent type, small amounts of silt and clay in silicate-dominated aquifer material, and the coupling of these factors with monovalent and divalent cations, IS, and water velocity.

3.4. Ionic strength

Soil solution and groundwater can exhibit variations in IS because of changes in aquifer material composition, temporal variations in recharge, groundwater-surface water interactions, increased salinization, and mixing of groundwater of different age and compositions. Fig. 2 presents observed and simulated BTCs for AgPURE when the calcium concentration was varied such that the IS equaled 0.05, 0.1, 0.5, and 1 mM Ca^{2+} . An increase in IS produced an increase in Ag-ENP retention, and a corresponding increase in k_{sw1} and S_{max1} (Table 1). Similar to Fig. 1, blocking is evident in all BTCs and a greater delay in breakthrough occurs with higher values of k_{sw1} and S_{max1} . An explanation for this behavior can be obtained by considering factors that influence the adhesive interaction between the Ag-ENPs and the porous medium. In particular, the magnitude of the zeta potential of the Ag-ENPs decreases with an increase in IS (Table 2). Furthermore, the double layer thickness decreases with an increase in IS (Elimelech et al., 1998). Both of these factors reduce the energy barrier between the Ag-ENPs and the porous medium (Table 2) and cause greater retention. Also, spatial variations in nanoscale roughness and chemical heterogeneity can locally reduce or eliminate the energy barrier to Ag-ENP retention under otherwise electrostatically unfavorable

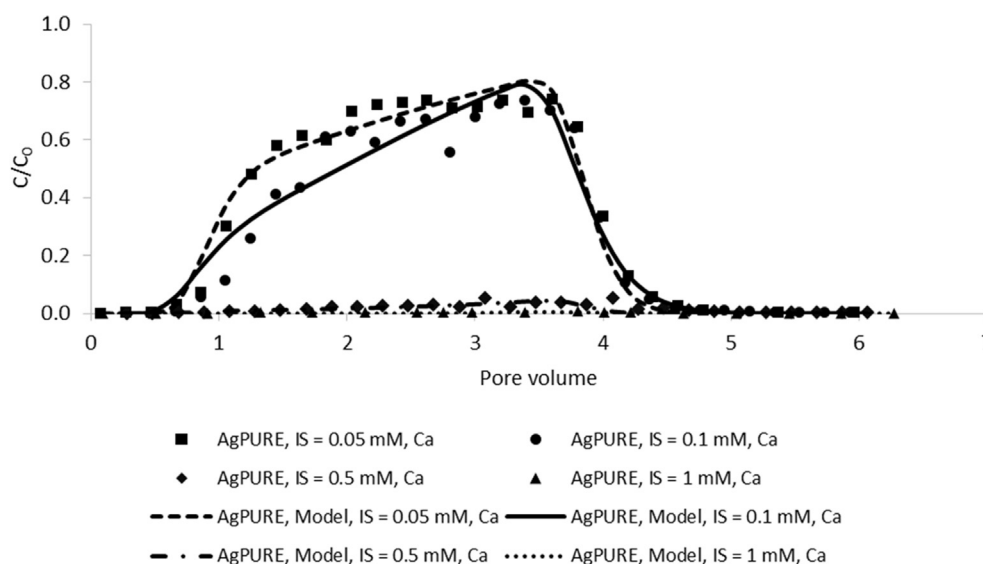


Fig. 2. Effect of ionic strength on AgPURE transport in the absence of fines. Pore water velocity = 8.64 m d^{-1} , $d_{50} = 0.7 \text{ mm}$.

conditions (Elimelech et al., 2000; Song et al., 1994). It should be mentioned that adsorption of calcium is known to produce charge neutralization and/or reversal on the solid phase (Israelachvili, 2011). Consequently, increased amounts of calcium sorption can enhance the apparent amount of nanoscale chemical heterogeneity on the solid surface. Nanoparticle retention can also be enhanced by calcium bridging between negatively charged Ag-ENPs and the porous medium. Huynh and Chen (2011) and Hoppe et al. (2014) indicated that calcium can bridge soil organic matter and the capping agent of Ag-ENPs. In addition, Liang et al. (2013a) suggested that Ca^{2+} can induce bridging between AgPURE surfactants and collector surfaces. Bridging complexation is also suggested by Torkzaban et al. (2012) who studied the transport behavior of carboxylic ligand-modified latex particles.

3.5. Cation type

Many Ag-ENP transport studies have been conducted using

monovalent electrolyte solutions (El Badawy et al., 2013; Lin et al., 2011). Conversely, groundwater can be dominated by divalent ions such as calcium. Fig. 3 presents observed and simulated BTCs for PVP-coated Ag-ENPs when the solution IS was 1 mM Na^+ or 0.1 mM Ca^{2+} . In contrast to Fig. 2, greater Ag-ENP retention occurred in the lower IS solution that contained 0.1 mM Ca^{2+} in comparison to 1 mM Na^+ . Blocking was observed for both 1 mM Na^+ and 0.1 mM Ca^{2+} systems, but greater delay in breakthrough occurred for the 0.1 mM Ca^{2+} data because of higher values of k_{sw1} and S_{max1} (Table 1). Other researchers have similarly observed greater nanoparticle retention in the presence of divalent compared to monovalent cations (Sasidharan et al., 2014; Wang et al., 2016). In contrast to Na^+ , Ca^{2+} produces a larger reduction in the magnitude of the zeta potential and double layer thickness (Elimelech et al., 1998; Israelachvili, 2011). These effects were accounted for in the interaction energy calculations and predicted a larger energy barrier in 0.1 mM Ca^{2+} than 1 mM Na^+ (Table 2). However, these interaction energy calculations do not consider

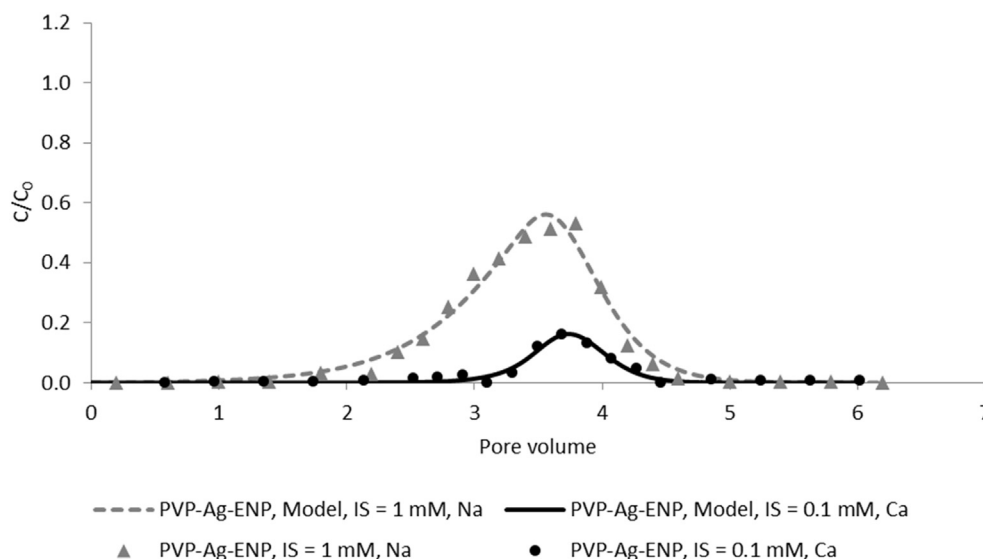


Fig. 3. Effect of $\text{Ca} = 0.1 \text{ mM}$ (solid) and $\text{Na} = 1 \text{ mM}$ (dashed) on PVP-Ag-ENP transport in absence of fines. Pore water velocity = 8.64 m d^{-1} , $d_{50} = 0.7 \text{ mm}$.

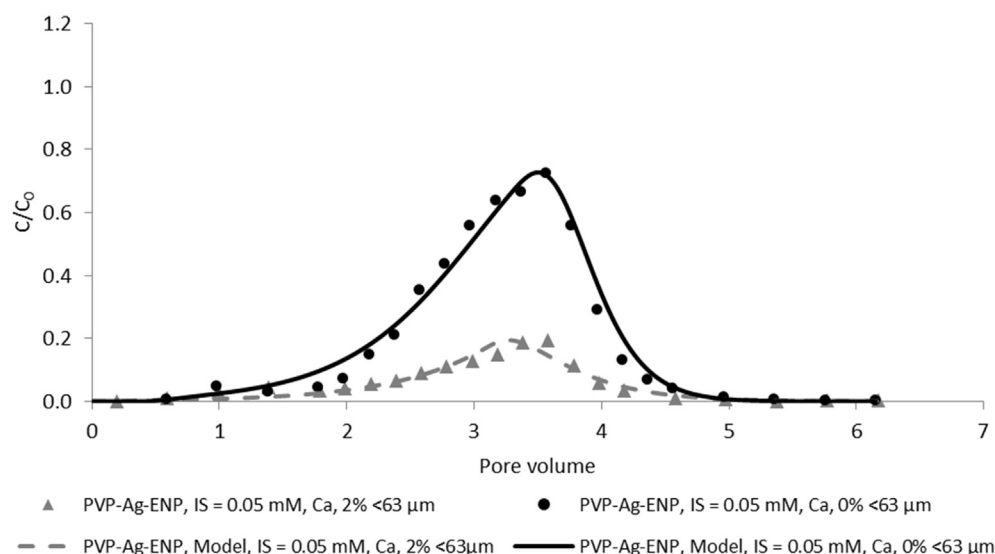


Fig. 4. Effect of presence (dashed line) and absence (solid) of fines (<0.063 mm) on PVP-Ag-ENP transport when Ca = 0.05 mM. Pore water velocity = 8.64 m d^{-1} , $d_{50} = 0.7 \text{ mm}$.

the potential influence of Ca^{2+} on charge neutralization or reversal (Israelachvili, 2011) and cation bridging (Liang et al., 2013a) which all contribute to an increased retention of Ag-ENPs, even at a lower IS.

3.6. Fine grain fraction

Clay and silt particles are a result of chemical weathering in soils and aquifer materials (Blume et al., 2010). Additional transport experiments were therefore conducted to assess the influence of clay and silt particles on Ag-ENP transport. Fig. 4 presents observed and simulated BTCs for PVP-coated Ag-ENPs in the absence and presence (2%) of fine grained particles (<0.063 mm) when the solution IS was 0.05 mM Ca^{2+} . Similar to Figs. 1–3, a delay in Ag-ENP breakthrough was observed as a result of blocking. However, the presence of a small amount of fines significantly enhanced the retention of the Ag-ENPs and produced larger values of k_{sw1} and S_{max1} (Table 1).

Enhanced retention of Ag-ENPs in the presence of fines can be caused by several effects. In general, the presence of fine material increases the reactive surface area (see also section 3.1) and potentially the number of sites for Ag-ENP retention. Cabal et al. (2010) and Cornelis et al. (2013) reported that Ag-ENPs preferentially attach to positively charged edges of clay minerals, the number of which can increase with an increasing amount of fine grains. Furthermore, cation bridging between the stabilizing agent of nanoparticles and the solid phase has been reported to be enhanced by clay particles (Cabal et al., 2010; Han et al., 2008). This is especially the case for background solutions containing increased amounts (increased IS) of Ca^{2+} leading to a decrease of the size of the diffuse electrical double layer and increased possibility for charge reversal so that Ag-ENPs are more likely to attach also to the previously negatively charged clay layers. When fine grains are heterogeneously coated with positively charged minerals such as iron oxides, Ag-ENP attachment also becomes more favorable and retention capacity increases (Cabal et al., 2010). Furthermore, the inter-particle structure can influence nanoparticle retention. For example, the possibility of the presence of dead pore volumes and small pore spaces increases with increasing silt and clay content. Water can flow through these pore structures which may be inaccessible to the nanoparticles (Sagee et al., 2012) and induce physical straining (Xin et al., 2016)

or microfiltration (Azzam, 1993).

3.7. Stabilizing agent

Suspensions of Ag-ENPs are frequently stabilized using various surfactant and/or polymer coatings (El Badawy et al., 2010; El Badawy et al., 2012). Additional experiments were carried out to explore the influence of the stabilizing agent on Ag-ENP transport. Fig. 5 presents observed and simulated BTCs for AgPURE and PVP-stabilized Ag-ENPs in the absence (Fig. 5a) and presence (Fig. 5b) of fine-grained material (2% < 0.063 mm) when the solution IS was 1 mM Na^+ . Surfactant-coated Ag-ENPs always exhibited less retention and delay in BTCs than those coated with PVP. This corresponds to smaller values of k_{sw1} and S_{max1} for AgPURE than for PVP-coated Ag-ENPs. This can be explained in part by the more negative zeta potential for AgPURE (−14.0 mV) than PVP-coated Ag-ENPs (−3.55 mV) in 1 mM Na^+ solution, which produces greater amounts of electrostatic repulsion from the negatively charged aquifer material (Table 2). Similar to Fig. 4, greater amounts of retention and delay in BTCs were observed in the presence (Fig. 5b) than the absence (Fig. 5a) of fines for both AgPURE and PVP-coated Ag-ENPs. However, the influence of fines was most pronounced for the less negatively charged PVP coated Ag-ENPs.

Differences in the amount and configuration of adsorbed stabilizing agent on the Ag-ENPs and the aquifer material will also play an important role in the transport and blocking behavior of Ag-ENPs. Section 3.2 provides a discussion on why steric interactions cannot explain Ag-ENP retention on the aquifer material. An alternative explanation for the enhanced stability and low amounts of retention for polymer or surfactant coated Ag-ENPs is due to nanoscale heterogeneity (Bradford et al., 2017). All natural surfaces contain nanoscale roughness and chemical heterogeneity (Suresh and Walz, 1996; Vaidyanathan and Tien, 1991). Nanoscale roughness and chemical heterogeneity can have a controlling influence on interaction energy parameters (Bendersky and Davis, 2011; Huang et al., 2010). In particular, nanoscale roughness tends to have a greater influence on interaction energy profiles than charge heterogeneity, and can locally reduce the energy barrier height and the magnitudes of secondary and primary minima (Bradford et al., 2017; Bradford and Torkzaban, 2013), especially when roughness occurs on both the colloid and the solid-water interface (Bradford et al., 2017). In contrast to the influence of electrosteric repulsion

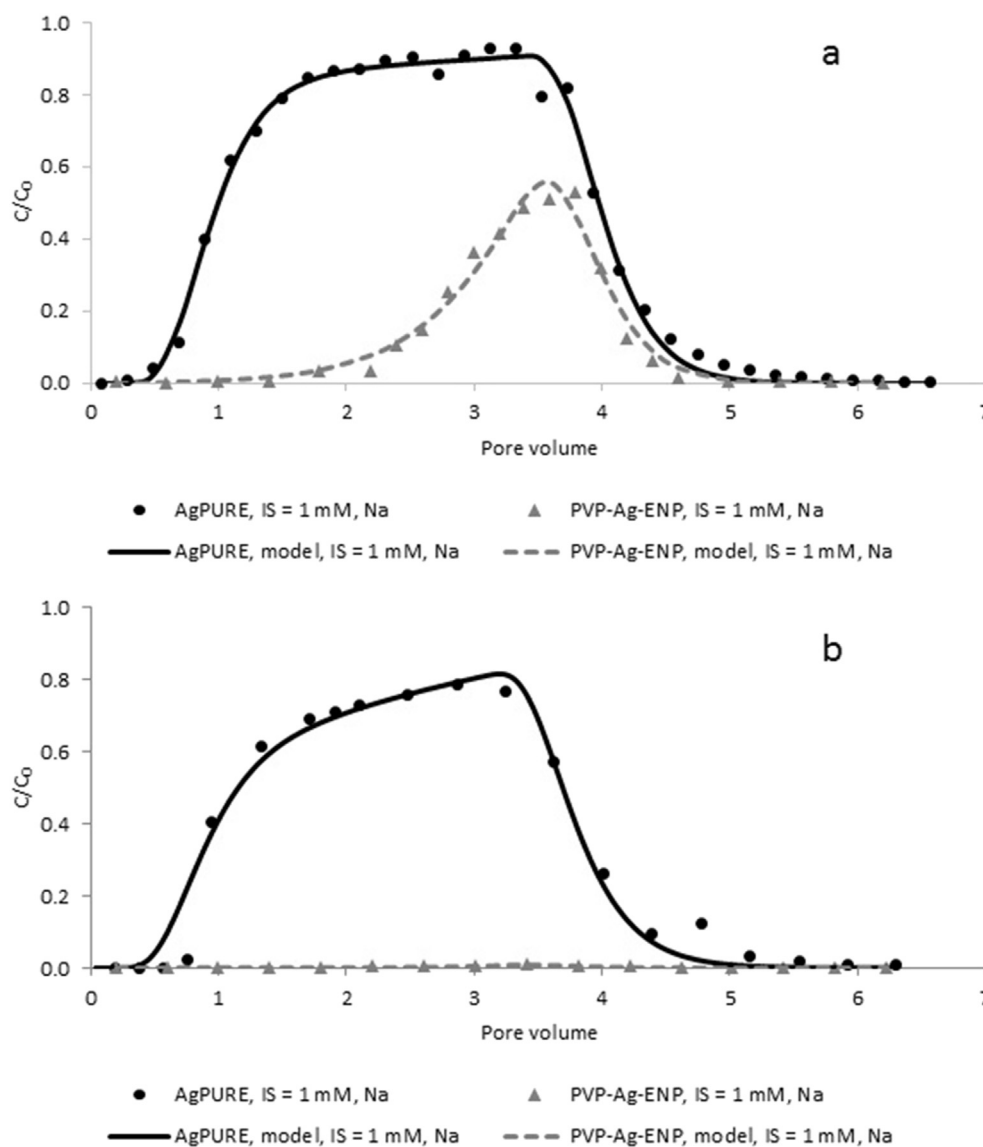


Fig. 5. Effect of stabilizing agent (solid = AgPURE; dashed = PVP) in the absence (5a) and presence (5b) of fines (<0.063 mm). Pore water velocity = 8.64 m d^{-1} , $d_{50} = 0.7 \text{ mm}$.

on the energy barrier height, nanoscale roughness creates colloid stability and low amounts of retention by producing shallow primary minima that are subject to diffusive release. Spatial differences in roughness parameters on the aquifer material will alter the depth of the primary minimum to produce Ag-ENP retention only on some locations. Consistent with this hypothesis, calculated values of S_{fl} were very small ($<5.4 \times 10^{-5}$). In addition to nanoscale roughness, Liang et al. (2013b) report that the original AgPURE solution contains 5% unbound surfactant. Similarly, PVP coated Ag-ENPs are also expected to contain a small percentage of unbound polymer (Poda et al., 2011). Unbound stabilizing agents may compete for the same positively charged (e.g., Al- and Fe-oxides) retention sites as Ag-ENPs and enhance their mobility through competitive blocking (Liang et al., 2013b; Becker et al., 2015). Consequently, differences in the amount and sorption behavior of unbound stabilizing agent can also contribute to observed differences in the AgPURE and PVP coated Ag-ENP transport and blocking. Additional research is needed to fully address issues of nanoscale roughness and competitive blocking, but is beyond the scope of this manuscript.

3.8. Flow velocity

The subsurface environment commonly exhibits variations in water velocity due to heterogeneity in hydraulic properties and temporal changes in the hydraulic gradient, e.g. because of recharge and pumping (Domenico and Schwartz, 1998). Fig. 6 presents observed and simulated BTCs for AgPURE (Fig. 6a) and PVP-coated Ag-ENPs (Fig. 6b) when the IS was 1 mM Na^+ and the pore water velocity was 4.32 or 8.64 m d^{-1} . Greater Ag-ENP retention and delay in the BTCs occurs at the lower pore water velocity. In particular, the recovery of AgPURE in the effluent decreased from around 80 to around 62% when the pore water velocity was halved. Similarly, the breakthrough of PVP-coated Ag-ENPs occurred after around 2.8 and 4.3 PV when the pore water velocity was 8.64 and 4.32 m d^{-1} , respectively. Other researchers have also previously observed greater Ag-ENP retention at lower pore water velocities (Sagee et al., 2012; Taghavy et al., 2013). Results in Fig. 6 demonstrate that the influence of velocity on Ag-ENP retention also depends on the stabilizing agent.

The influence of pore water velocity on nanoparticle retention

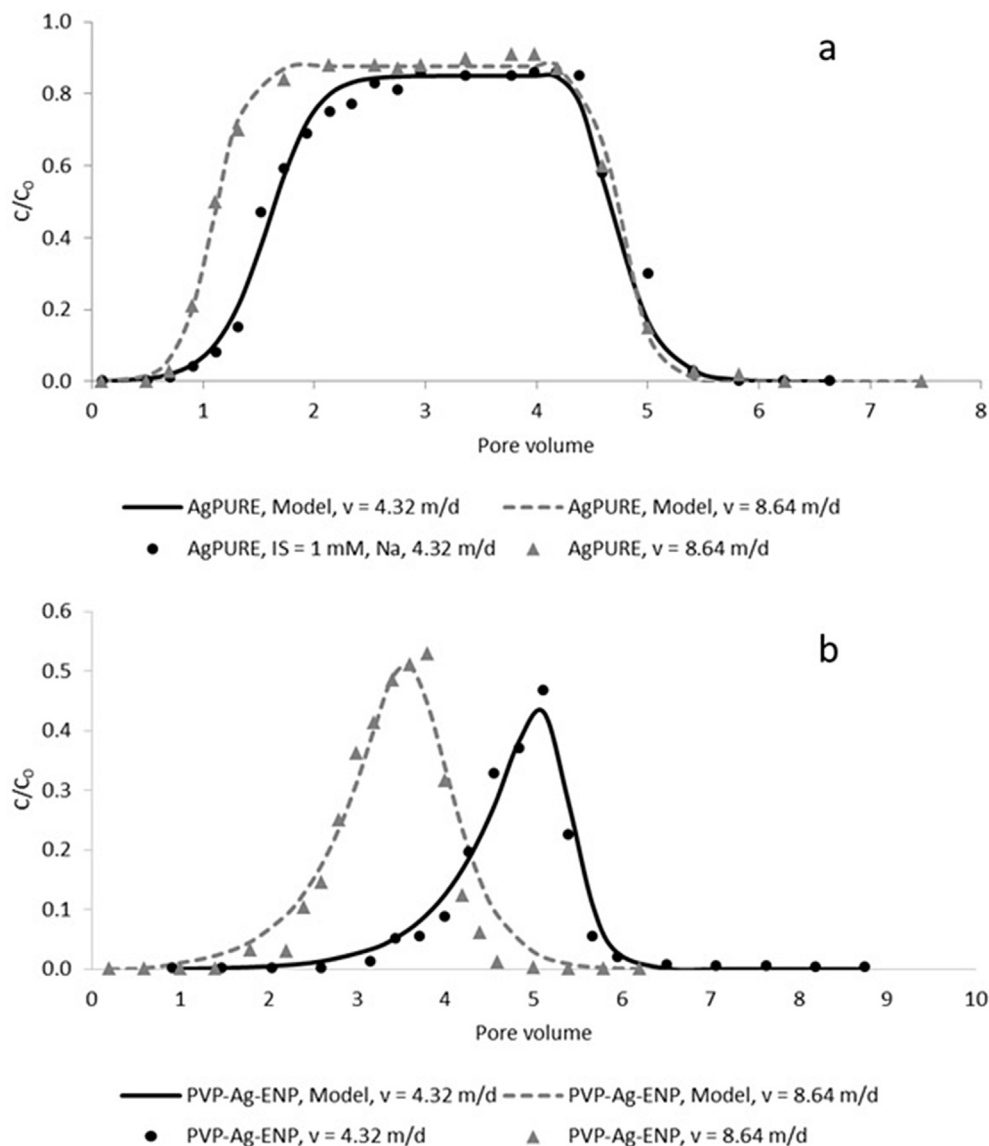


Fig. 6. Effect of velocity on transport for AgPURE (6a) and PVP-Ag-ENP (6b). All experiments were conducted at an ionic strength of 1 mM with Na^+ and for $d_{50} = 0.7$ μm .

and delay depends on a number of factors, including: (i) the resulting residence time of Ag-ENPs in the porous medium (Sharma et al., 2014); (ii) the mass transfer rate of Ag-ENPs from the bulk solution to the solid phase (Liang et al., 2013a); and (iii) the velocity dependence of the sticking efficiency and S_{max1} (Liang et al., 2013b). Similar to Fig. 6, greater Ag-ENP transport and less retention are expected at a higher pore water velocity because of a decrease in the advection controlled residence time, even though colloid filtration theory predicts that k_{sw1} increases with increased pore water velocity when the colloid sticking efficiency is constant (Yao et al., 1971). The values of the colloid sticking efficiency and S_{max1} are predicted to increase with decreasing pore water velocity because of a decrease in the hydrodynamic forces that act on the Ag-ENPs adjacent to the solid surface (Bradford and Torkzaban, 2015). Fitted values of S_{max1} are consistent with these expectations (Table 1). However, it should be noted that the influence of velocity on the BTCs is more pronounced for the PVP-coated than AgPURE Ag-ENPs (Fig. 6b). This difference is related to the velocity dependency of the colloid sticking efficiency and S_{max1} . These parameters are functions of the water velocity and the depth of the

primary minimum which is influenced by charge heterogeneity and the distribution of nanoscale roughness height and density on the surface of Ag-ENPs and aquifer material, as well as unbound stabilizing agent (see section 3.7).

4. Conclusions

The findings from this study provide important insight into the role of blocking in controlling the long-term transport behavior of Ag-ENPs in natural, saturated, silicate-dominated aquifer material under different physicochemical conditions. Observed Ag-ENP transport and blocking behavior were well described using the advection dispersion equation and irreversible kinetic retention sites that included Langmuirian blocking. Increasing retention and delay in Ag-ENP transport was observed at higher IS, in the presence of divalent cations and fine-grained particles, at lower water velocities, and for polymer-stabilized compared to surfactant-stabilized Ag-ENPs. These observations were explained by changes in double layer behavior, measured zeta potentials, interaction energies, charge reversal, cation bridging, residence time,

and hydrodynamic forces. A special focus of this research was investigating the roles of cation valence and the fine-grained material fraction on Ag-ENP transport, and enhanced retention and delay of breakthrough in the presence of Ca^{2+} and fines was attributed to cation bridging which was more pronounced for polymer- than surfactant-stabilized Ag-ENPs because of differences in stabilizing agent properties and zeta potentials.

Additional research is warranted to transfer results from this laboratory-scale study to the field. If and how Ag-ENP transport in aquifers occurs under field conditions depends partly on the parameters tested during our experiments but also on characteristics of the vadose zone overlying the aquifer, on the absence/presence of geological heterogeneity, on the absence/presence of substances (e.g. organic matter) that could induce, slow down or speed up Ag-ENP transformation, as well as on the absence/presence of substances that potentially compete with Ag-ENPs for the existing retention sites (e.g., phosphorus, surfactants, and dissolved organic matter). Additionally, the chemical composition of groundwater might differ from the background solution used in our experiments. However, our results clearly demonstrate the need for long-term injection experiments of Ag-ENPs to better understand their blocking behavior in varying background solutions and under more realistic hydrogeochemical conditions. We also show that with sufficient Ag-ENP input all retention sites are filled, and a breakthrough occurs, so in theory, even under field conditions excessive exposure to Ag-ENPs could impact the quality of groundwater used for potable water production.

Conflicts of interest

The authors declare no competing interests.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.envpol.2018.01.011>.

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