Transport of citrate-coated silver nanoparticles in unsaturated sand

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ABSTRACT

Chemical factors and physical constraints lead to coupled effects during particle transport in unsaturated porous media. Studies on unsaturated transport as typical for soils are currently scarce. In unsaturated porous media, particle mobility is determined by the existence of an air–water interface in addition to a solid–water interface. To this end, we measured breakthrough curves and retention profiles of citrate-coated Ag nanoparticles in unsaturated sand at two pH values (5 and 9) and three different flow rates corresponding to different water contents with 1 mM KNO_3 as background electrolyte. The classical DLVO theory suggests unfavorable deposition conditions at the air–water and solid–water interfaces. The breakthrough curves indicate modification in curve shapes and retardation of nanoparticles compared to inert solute. Retention profiles show sensitivity to flow rate and pH and this ranged from almost no retention for the highest flow rate at pH = 9 to almost complete retention for the lowest flow rate at pH = 5. Modeling of the breakthrough curves, thus, required coupling two parallel processes: a kinetically controlled attachment process far from equilibrium, responsible for the shape modification, and an equilibrium sorption, responsible for particle retardation. The non-equilibrium process and equilibrium sorption are suggested to relate to the solid–water and air–water interfaces, respectively. This is supported by the DLVO model extended for hydrophobic interactions which suggests reversible attachment, characterized by a secondary minimum (depth 3–5 kT) and a repulsive barrier at the air–water interface. In contrast, the solid–water interface is characterized by a significant repulsive barrier and the absence of a secondary minimum suggesting kinetically controlled and non-equilibrium interaction. This study provides new insights into particle transport in unsaturated porous media and offers a model concept representing the relevant processes.

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1. Introduction

Ongoing efforts to understand mechanisms governing transport and retention of engineered nanoparticles (NPs) in porous media are motivated by their wide array of application. For instance, engineered Ag NPs are used for antibacterial (Choi et al., 2008; Yu et al., 2014), conductive (Jiang et al., 2005), diagnostic and therapeutic (Cuenca et al., 2006; Sotiriou et al., 2010), and optical (Willets and van Duyne, 2007) applications. Incidentally, NPs may be released and enriched in some compartments of the ecosystem (e.g., soils and surface waters) relative to their natural background occurrence (Aitken et al., 2006). Due to their toxic and bioaccumulative tendencies, engineered Ag NPs may pose hazard upon environmental exposure. This calls for systematic investigation into their interaction within the unsaturated zone which cushions groundwater against potential long-term contaminant sources (Schaumann et al., in this issue).

Mechanisms governing particle transport in porous media are multifaceted ranging from geometric and hydrologic to hydrogeochemical controls. Previous studies are mostly focused on transport under fully saturated conditions (e.g., Badawy et al., 2013; Liang et al., 2013a; Wang et al., 2012), while transport under unsaturated conditions (e.g., Fang et al., 2013) still requires systematic investigation to elucidate governing mechanisms. During unsaturated flow, capillary forces are expected to control colloid interaction in the vicinity of air–water interface (AWI) (e.g., Bradford and Torkzaban, 2008; Lazouskaya et al., 2006) and this tendency could be crucial for their transport. This phenomenon has not been fully investigated for engineered NPs especially with their specialized nature in terms of charge, reactivity and size. The size of engineered NPs poses challenges to directly investigate the influence of capillary forces during transport. Hence, DLVO (e.g., Fang et al., 2013; Torkzaban et al., 2008) and extended DLVO (e.g., Bradford and Torkzaban, 2008) analyses are often combined with column experiments to gain insight. The classical and extended DLVO models could

provide a priori an affinity index between NPs and potential collectors (AWI and solid–water interface, SWI) during transport.

We investigated unsaturated transport of citrate-coated Ag NPs within repacked sand as model porous media. The zeta (ζ) potential [$ML^2T^{-3}A^{-1}$] of clean quartz and glass is typically between -10 and -80 mV depending on the solution chemistry (Elimelech and O'Melia, 1990; Johnson, 1999; Elimelech et al., 2000; Redman et al., 2004). Some studies suggest that the AWI bears no charge (e.g., Mbamala and von Grünberg, 2003) while others reported charges in the range of -4 to -110 mV depending on solution composition (e.g., Bradford and Torkzaban, 2008; Cho et al., 2005; Kim et al., 2000; Li and Somasundaran, 1991; Takahashi, 2005; Yang et al., 2001). Grain surfaces which are not completely wettable may have air–water–solid (AWS) contact points. In contrast, water films may extend infinitely on completely wettable grain surfaces (Lazouskaya et al., 2006). Both cases present avenues for straining either near AWS contact points or in water films of comparable size as NPs (Schaumann et al., in this issue). Chen and Flury (2005) observed colloid retention for unsaturated flow and thermodynamic properties have been suggested to play a role. Colloid retention in porous media was observed under electrostatically unfavorable deposition conditions (e.g., Tufenkji and Elimelech, 2005; Torkzaban et al., 2008; Bradford et al., 2011) and straining has been suggested by the authors as a dominant retention mechanism. This provides a hint that physical and chemical factors may be coupled in the governing transport mechanism. Colloid transport is expected to increase for moving AWI (McCarthy and McKay, 2004) or decrease for stationary AWI (Lazouskaya et al., 2006). Fang et al. (2013) reported that decrease in water content, θ [$-$], had little impact on TiO_2 NP mobility owing to the net repulsive interaction between negatively charged AWI and TiO_2 NPs.

The limited number of studies on unsaturated transport of engineered NPs could be due to the difficulty in establishing well-defined experimental conditions (Schaumann et al., in this issue). This difficulty is further augmented by the complexity associated with the phase distribution of pore fluids (air and water) and the coupled effects of physical constraints and chemical factors. This complicates the identification of an appropriate process model. Recently, the technical problem to establish well-defined unsaturated flow conditions (i.e., constant pressure head, h_m [L], and uniform θ) has been largely solved by the newly developed multistep-flux (MS-F) approach (Weller et al., 2011; Weller and Vogel, 2012) and the related multistep-transport approach (Kumahor et al., 2015). In this study, we used the new experimental tools to explore in a systematic way and with well-controlled experimental conditions, the transport of citrate-coated Ag NPs at three different flow rates, j_w [LT^{-1}], two pH levels (5 and 9) and at a fixed pore-water ionic strength (1 mM KNO_3). Furthermore, the transport of citrate-coated Ag NPs in unsaturated sand was modeled by using a modified form of the convection–dispersion (CD) equation. The classical and extended DLVO interaction energy profiles were calculated to characterize collector–NP interaction.

2. Materials and methods

2.1. Silver nanoparticles

The citrate reduction method was used for the synthesis of Ag NPs. The synthesis procedure is detailed in Metreveli et al. (in this issue) together with the characterization of the Ag NPs. The citrate-coated Ag NPs are quasi-spherical with a hydrodynamic diameter, h_d [L], of about 40 nm. For the transport experiments, the stock of 100 mg L^{-1} Ag NP dispersion was further diluted (ratio of 1:100). The resultant dispersion was adjusted to a background electrolyte concentration of 1.0 mM KNO_3 (extra pure, MERCK) and the pH adjusted to 5 and 9 using HNO_3 (65% Suprapur, MERCK) and NaOH (pure, MERCK) respectively.

2.2. Sand medium

The sand (Co. Sand-Schulz, Berlin) used for the transport experiments has a grain size distribution of 0.1–0.3 mm with a median grain diameter, d_{50} [L], of 0.2 mm. The same sand was used by Kumahor et al. (2015) for tracer studies. A similar grain size (275 μm) is typically used in sand filters (e.g., Chowdhury et al., 2011). The sand was packed to a bulk density, ρ_b [ML^{-3}], of 1.52 g cm^{-3}. According to its industrial specifications, the cleaned sand may contain trace amounts of organics and reactive minerals. We used cleaned sand as model porous medium to: (i) exclude as much as possible the influence of organics and reactive minerals, and (ii) direct our focus towards understanding the impact of AWI on particle transport.

2.3. Water flow dynamics and transport experimental protocol

We combined studies on the experimental determination of hydraulic properties (i.e., moisture release and conductivity functions) with transport characteristic (for both inert solute and NPs), at the scale of a lab column to investigate the mobility of NP for well defined hydraulic states and delineated chemical conditions in terms of pH and pore-water ionic strength. The experimental column was a polyvinyl chloride (PVC) cylinder of dimensions 16.2 cm (inner diameter) and 10 cm (column height). The column was fitted on a porous glass plate with a higher conductivity compared to the sand. The low air entry point of this plate allowed for controlling h_m at the lower boundary (Fig. 1). The column was dry-packed while tapping gently on the sides to ensure a uniform ρ_b.

The water retention characteristic and the unsaturated hydraulic conductivity function were measured using the multistep-outflow (e.g., Hopmans et al., 2002; Zurmühl and Durner, 1998; van Dam et al., 1994) and MS-F (Weller et al., 2011; Weller and Vogel, 2012) approaches. The results (Kumahor et al., 2015) were used to design the NP transport experiments which aimed at investigating the influence of pH and flow regime (thus, structure of the flow field). Two pH values (5 and 9) and three flow rates (i.e., 2.5, 9.7 and 17.0 cm h^{-1}) corresponding to three different θ values (i.e., 0.17, 0.29 and 0.35 respectively) and pore-water velocities, v [LT^{-1}], (i.e., 14.7, 33.4 and 48.6 cm h^{-1} respectively) were investigated with a 1 mM KNO_3 background electrolyte. With a constant j_w established via a peristaltic pump (ISMATEC) such that a constant h_m and uniform θ were realized during water flow (Fig. 2), we conducted the NP transport experiments along the following steps:

(1) Prior to application of Ag NP dispersion, the column was flushed with 5 pore volumes (PVs) of the background electrolyte solution and also to establish a stationary flow field.
(2) Then, 8 PVs of the Ag NP dispersion were delivered through 19 evenly distributed hypodermic needles at the surface.
(3) This was followed by another 8 PVs of Ag NP-free solution to quantify the mass of NPs irreversibly retained.
(4) The column was then dissected into layers of 1 cm height and oven dried at 105 °C for 24 h. The sand was homogenized and a subsample (10 g) taken for leaching studies. The retention profiles (RPs) were measured as follows: (a) the sand was moistened with some Milli-Q water, (b) 5 mL of 65% suprapur HNO_3 was added, (c) the content was placed in an ultrasonic bath at about 60 °C for 10 min, (d) then topped up to 50 mL with Milli-Q water, (e) this was followed by centrifugation (f) and the supernatant diluted 1:50 with Milli-Q water for ICP-MS measurements.
(5) A mass balance was calculated from the BTCs and RPs.

This procedure was repeated for the different flow rates and pH values. Moisture content was measured using a weighing balance (Balance 1 in Fig. 1) and h_m was continuously monitored at high