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Transport and deposition of stabilized engineered silver nanoparticles in water saturated loamy sand and silty loam

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HIGHLIGHTS

- Transport and deposition of surfactant stabilized AgNPs in glass beads and two natural soils were analyzed.
- FlFFF was implemented to determine particle size changes after soil passage.
- Mathematical modeling was used to quantify transport and deposition of the AgNPs.
- Transport of AgNPs was sensitive to flow velocity, soil composition and ionic strength/valence of cations present.

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ABSTRACT

It is considered inevitable that the increasing production and application of engineered nanoparticles will lead to their release into the environment. However, the behavior of these materials under environmentally relevant conditions is still only poorly understood. In this study the transport and deposition behavior of engineered surfactant stabilized silver nanoparticles (AgNPs) in water saturated porous media was investigated in transport experiments with glass beads as reference porous medium and in two natural soils under various hydrodynamic and hydrochemical conditions. The transport and retention processes of AgNPs in the porous media were elucidated by inverse modeling and possible particle size changes occurring during the transport through the soil matrix were analyzed with flow field-flow fractionation (FlFFF). A high mobility of AgNPs was observed in loamy sand under low ionic strength (IS) conditions and at high flow rates. The transport was inhibited at low flow rates, at higher IS, in the presence of divalent cations and in a more complex, fine-grained silty loam. The slight decrease of the mean particle size of the AgNPs in almost all experiments indicates size selective filtration processes and enables the exclusion of homoaggregation processes.

1. Introduction

As production and application of engineered nanoparticles (ENPs) are growing and the potential of their release into the environment is becoming more evident, the question of ENP mobility and fate in the environment is of increasing significance (Klaine et al., 2012). Regarding the safety of drinking water resources, it is crucial to understand transport and deposition processes of ENP in soils and aquifers. In contaminant transport studies ENPs represent a special case because the behavior of particles in the environment differs from that of conventional contaminants that usually occur in dissolved form. According to particle filtration theory, transport and deposition processes of colloids and nanoparticles in porous media are dominated by physicochemical interactions between the particle surfaces and the porous media (collector) surfaces on the one hand, but also to hydrodynamic processes on the other hand (Yao et al., 1971; Torkzaban et al., 2007).

Studies with ENP and natural colloids showed deviations of experimental observations from filtration theory, especially in environmentally relevant systems. For instance, under conditions that are generally considered as unfavorable for attachment, deposition may occur due to surface charge heterogeneities providing local favorable attachment sites (Lin et al., 2011). The occupation of these sites is eventually related to hydrodynamic drag forces allowing particles to travel along a collector surface until possibly reaching an attachment site (Bradford et al., 2011; Li et al., 2005). Moreover in natural porous media retention may occur due to mechanical straining in small pore throats and at locations of high surface roughness (Jaisi and Elimelech, 2009; Kasel et al., 2013a; Li et al., 2004; Wang et al., 2012). On the other hand, transport may be enhanced by stabilizing agents causing short range repulsive forces (El-Badawy et al., 2013; Xiao and Wiesner, 2013). The number of available attachment sites is subject to physicochemical factors and may change with the environmental conditions.

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Silver nanoparticles (AgNPs) are the most commonly used nanomaterial and they are already widely applied in consumer products because of their strong antibacterial activity (WWICS, 2014). Because of the inevitable release of AgNPs into the environment (Geranio et al., 2009; Lorenz et al., 2012) and the high toxicity potential (Reidy et al., 2013) ENP environmental implication research has been particularly focused on AgNPs.

Studies with AgNPs in artificial porous media under well-defined conditions have demonstrated that AgNP transport is sensitive to physicochemical factors such as solution ionic strength (IS), presence of divalent cations, grain size and hydrodynamics as is generally suggested by filtration theory (Liang et al., 2013a; Lin et al., 2011; Taghavy et al., 2013; Thio et al., 2011). The behavior of AgNPs has been shown to also strongly depend on the application of stabilizing agents that eventually enhance the mobility due to increased repulsion between AgNPs and AgNPs and porous media surfaces (El-Badawy et al., 2013; Liang et al., 2013a; Thio et al., 2011). Additionally, Liang et al. (2013a) observed concurrent deposition of surfactants to quartz sand surfaces, resulting in nonmonotonic deposition profiles of AgNPs in sand columns.

Experimental studies on the transport behavior of AgNPs in natural porous media are scarce. Transport experiments in natural soils (Cornelis et al., 2013; Liang et al, 2013b; Sagee et al., 2012) and sandstones (Neukum et al., 2014a) showed that Ag nanoparticle transport is not only affected by the physicochemical parameters discussed above, but also by texture or grain size of the porous medium and the mineralogical composition. Heteroaggregation of AgNPs with natural colloids (Cornelis et al., 2012, 2013), and subsequent colloid facilitated transport of the AgNPs (Liang et al., 2013b; Neukum et al., 2014b) have been observed, demonstrating an important pathway for AgNP migration in soils and aquifers.

In addition to the scarcity of studies with natural porous media, many experimental studies lack the application of adequate analytical techniques, which do not only consider the chemical but also the physical form of the nanomaterials (von der Kammer et al., 2012). The distinction between particulate and dissolved species or the characterization of transport relevant parameters such as particle size distribution and aggregation state are needed in order to understand the processes that occur during the transport of nanoparticles. While in many studies the nanoparticle samples are thoroughly characterized prior to the experiments, their physical state is not monitored during or after the experiments. Exceptions are for example Lin et al. (2011) who monitored the particle size distribution of AgNPs in the effluent of transport experiments by dynamic light scattering and found no change in particle size during transport experiments or Taghavy et al. (2013) who separated particulate Ag from dissolved Ag by centrifugation to monitor the dissolution of AgNPs and found that dissolution did occur during transport through the porous media.

The purpose of this study was to gain more insight into the transport and retention processes of AgNPs in natural porous media. Column experiments were carried out with two soils, a loamy sand and a silty loam, and furthermore with glass beads as a reference medium to investigate the effect of different transport velocities and chemical compositions of the background solution on the transport behavior of AgNPs, which was then described with mathematical models. While in comparable studies with saturated porous media AgNP transport is investigated only at relatively high flow velocities that are not necessarily relevant for natural soil or aquifer systems (e.g. Cornelis et al., 2013 (8.14 m d^{-1}); Sagee et al., 2012 (9.5 m d^{-1}); Taghavy et al., 2013 (7.6 m d^{-1})) in this study, a wider scope of expected groundwater velocities in comparable natural systems was covered ranging from 0.05 m d^{-1} to 2.88 m d^{-1}. Another step towards more realistic conditions in soil would be the investigation under unsaturated conditions, which has partly been implemented for AgNPs by Liang et al. (2013b), who applied a water saturation of 90% in undisturbed loamy sand columns. Flow field-flow fractionation (FlFFF) was employed as analytical technique to characterize AgNP concentration and particle size distribution before and after the soil passage. This enabled not only the detection of changes in particle size distribution during transport through the soil but also to account only for particulate Ag in the breakthrough curves because dissolved silver is not detected in the FlFFF measurement. In the case of some selected experiments the depth profile of AgNP retention in the soil columns was also analyzed and modeled providing further insights into the respective transport and deposition processes.

2. Materials and methods

2.1. Porous media and solution chemistry

Glass beads with mean diameters between 300 and 400 μm were used as inert reference medium. In order to remove metal oxides and obtain completely hydrophilic surfaces of the glass beads they were cleaned using a procedure that was modified by Han et al. (2006) after Mehra and Jackson (1958) (see supporting information). Two soils were sampled from the upper 30 cm of agricultural field sites in Germany. The soils have already been used for other publications (Unold et al., 2009; Kasel et al., 2013b) and are therefore well characterized. Loamy sand (Gleyic Cambisol) was sampled from the test site Kaldenkirchen-Hülst (KDK), located at 51°18′22″ N 6°12′6″ E and silty loam (Orthic Luvisol) was sampled from the test site Merzenhausen (MZH) with the geographic coordinates 50°55′47‴ N and 6°17′48″ E (Unold et al., 2009). Physicochemical characteristics of the soils are given in Table 1. The clay fraction of the loamy sand soil contains the clay minerals illite, montmorillonite and kaolinite (Liang et al., 2013b). The clay fraction of the silty loam soil contains the clay minerals illite, chloride/vermiculite, kaolinite and swellable illite–smectite minerals (Burkhardt, 2003). The disturbed soil samples were oven dried at 40 °C, homogenized and sieved to <2 mm.

2.2. AgNPs

A stock suspension of stabilized AgNPs with a concentration of 10% w/w (AgPURE W-10) was purchased from ras materials, Regensburg, Germany. The product is identical to the OECD standard material NM-300 Silver, which is currently used in nanoparticle research and was already thoroughly characterized by various independent institutions. The AgNPs are stabilized with 4% w/w each of polyoxyethylene glycerol trioleate and polyoxyethylene (20) sorbitan mono-laurat (Tween 20) (Klein et al., 2011), which form sterical repulsion barriers between the AgNPs to stabilize the suspension and minimize dissolution. According to Liang et al. (2013a), the amount of free surfactant in the stock suspension is around 5% w/w. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) indicate that 99% of the AgNPs are within the size range of 15 nm to 20 nm (Liang et al., 2013a). The hydrodynamic diameter of the particles diluted in water was determined with dynamic light scattering (DLS) to be around 50 nm (Klein et al., 2011). Prior to each experiment the stock suspension was diluted to a concentration of approximately 60 mg l^{-1} with the corresponding electrolyte solution (see Section 2.3).

Table 1
Physicochemical characteristics of the loamy sand (KDK) and silty loam (MZH).

	Unit	KDK	MZH
Clay (<2 μm)[a]	% mass	4.9	15.4
Silt (2–63 μm)[a]	% mass	26.7	78.7
Sand (63–2000 μm)[a]	% mass	68.5	5.9
pH (0.01 M $CaCl_2$)[a]		5.9	6.2
Total organic matter[a]	% mass	1.1	1.3
Cation exchange capacity[a]	$cmol_c\ kg^{-1}$	7.8	11.4
Electrophoretic mobility[b]	$m^2\ V^{-1}\ s^{-1}$	−2.70E−08	−3.20E−08

[a] Data adapted from Unold et al. (2009).

[b] Data adapted from Kasel et al. (2013b).