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Transport, retention, and long-term release behavior of ZnO nanoparticle aggregates in saturated quartz sand: Role of solution pH and biofilm coating

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ABSTRACT

The transport, retention, and long-term release of zinc oxide nanoparticle aggregates (denoted below as ZnO-NPs) were investigated in saturated, bare and biofilm (*Pseudomonas putida*) coated sand packed columns. Almost complete retention of ZnO-NPs occurred in bare and biofilm coated sand when the influent solution pH was 9 and the ionic strength (IS) was 0.1 or 10 mM NaCl, and the retention profiles were always hyper-exponential. Increasing the solution IS and biofilm coating produced enhanced retention of ZnO-NPs near the column inlet. The enhanced NPs retention at high IS was attributed to more favorable NP-silica and NP-NP interactions; this was consistent with the interaction energy calculations. Meanwhile, the greater NPs retention in the presence of biofilm was attributed to larger roughness heights which alter the mass transfer rate, the interaction energy profile, and lever arms associated with the torque balance; e.g., scanning electron and atomic force microscopy was used to determine roughness heights of 33.4 nm and 97.8 nm for bare sand and biofilm-coated sand, respectively. Interactions between NPs and extracellular polymeric substances may have also contributed to enhanced NP retention in biofilm-coated sand at low IS. The long-term release of retained ZnO-NPs was subsequently investigated by continuously injecting NP-free solution at pH 6, 9, or 10 and keeping the IS constant at 10 mM. The amount and rate of retained ZnO-NP removal was strongly dependent on the solution pH. Specifically, almost complete removal of retained ZnO-NPs was observed after 627 pore volumes when the solution pH was 6, whereas much less Zn was recovered when the eluting solution pH was buffered to pH = 9 and especially 10. This long-term removal was attributed to pH-dependent dissolution of retained ZnO-NPs because: (i) the solubility of ZnO-NPs increases with decreasing pH; and (ii) ZnO-NPs were not detected in the effluent. The presence of biofilm also decreased the initial rate and amount of dissolution and the subsequent transport of Zn^{2+} due to the strong Zn^{2+} re-adsorption to the biofilm. Our study indicates that dissolution will eventually lead to the complete removal of retained ZnO-NPs and the transport of toxic Zn^{2+} ions in groundwater environments with pH ranges of 5–9.

1. Introduction

Metal oxide nanomaterials have been extensively used in a variety of industrial applications. In particular, zinc oxide (ZnO) nanoparticles are widely used as raw materials for products in cosmetic, optical, and chemical industries (Wang and Song, 2006; Mu and Sprando, 2010; Wang et al., 2009). However, studies have shown that ZnO can be toxic to humans, plants, and birds (Adams et al., 2006; Brayner et al., 2006; Lin and Xing, 2007), and that it may be even more toxic when Zn^{2+} ions are released in solution (Xia et al., 2008; Miller et al., 2010; Miao et al., 2010). ZnO nanoparticles quickly dissolve in natural aquatic environments due to their solubility and large specific surface area (Mudunkotuwa et al.,

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2012). Consequently, ecosystems may be adversely affected by the transport, retention, and subsequent dissolution of ZnO nanoparticles. Information on the transport and fate behavior of ZnO nanoparticles is therefore needed to evaluate the potential environmental and health risks posed by exposure in natural environments (Wiesner et al., 2006).

A number of studies have investigated the influence of various environmental factors on the transport and retention of ZnO nanoparticles. Solution chemistry and organic matter have been identified as crucial factors affecting the transport and retention of ZnO nanoparticles (Jiang et al., 2012a; Petosa et al., 2012; Li and Schuster, 2014; Jiang et al., 2010; Jones and Su, 2014). Biofilms consisting of bacterial clusters embedded in extracellular polymeric substances (EPS) at the soil surface (Sussman et al., 1993), have also been reported to play an important role in the transport and retention of nanoparticles (Tong et al., 2010; Mitzel and Tufenkji, 2014; Lerner et al., 2012; Tripathi et al., 2012). For example, Tong et al. (2010) found that the transport behavior of fullerene (C_{60}) in a sand column decreased in the presence of biofilms. Lerner et al. (2012) investigated the transport behaviors of iron nanoparticles coated with acrylic acid (pnZVI) in porous media, and found that biofilm increase the retention of pnZVI at high ionic strength (25 mM NaCl) as a result of the polymer bridging. Tripathi et al. (2012) reported the effects of biofilms and EPS on the transport and retention of 4 types of nanoparticles in a sand column. The retention of nanoparticles was observed to be improved in the presence of the biofilm regardless of the size of the particles or the type of chemistry for the solution. Unlike the aforementioned works, Mitzel and Tufenkji (2014) measured the mobility of PVP-coated silver (Ag) nanoparticles with the age of the biofilms, and found that sand columns coated with mature biofilms have earlier breakthrough and lower retention of PVP-coated Ag nanoparticles than sand columns coated with younger biofilm or without biofilm, due to an increase of the electrosteric repulsive force between the PVP-coated Ag nanoparticles and the biofilms.

The above studies suggest that biofilms influence the transport of nanoparticles, and this is also true for ZnO nanoparticles. Jiang et al. (2013) found that the retention of bare ZnO nanoparticles in sand increased in the presence of *Escherichia coli* biofilm. However, these packed column tests were conducted at a constant pH of 8, while the pH level for actual surface water or groundwater environments varies over a wide range (e.g., 5.0–9.5) (Kim et al., 2009). Changes in pH can chemically alter ZnO nanoparticles. Indeed, ZnO nanoparticles dissolve in the pH range of groundwater environments, and their solubility increases as the pH decreases (Han et al., 2014). This information implies that retained ZnO nanoparticles may be released to the surrounding environment as dissolved Zn^{2+}, especially at a lower pH. The toxicity of dissolved Zn^{2+} may induce biofilm sloughing, which could potentially trigger additional release and transport of ZnO nanoparticles.

Although the above scenario is very plausible in natural environments, to the best of our knowledge, no study has reported on the long-term release behavior of ZnO nanoparticles under various pH conditions in sand with/without biofilm coatings. Hence, our study was designed to overcome these gaps in knowledge. The transport and retention of ZnO nanoparticle aggregates (denoted below as ZnO-NPs) was studied in packed sand columns with/without a *Pseudomonas putida* (*P. putida*) biofilm coating at a fixed pH of 9, in which almost no ZnO dissolution occurs. The post-release behavior of ZnO-NPs was then evaluated by changing the pH of the background solution. Analyses of the transport and long-term release behavior for ZnO-NPs were conducted using breakthrough curves (BTCs) and retention profiles (RPs). The collected data are needed to accurately assess the long-term risks of ZnO nanoparticles in groundwater environments.

2. Materials and methods

2.1. Porous media and electrolyte solutions

Ultra-pure quartz sand (99.8% SiO_2) with particle sizes ranging from 212 to 855 μm were sieved in U.S. standard stainless steel test sieves (Fisher Scientific), such that the average diameter of the sand particles (d_{50}) was approximately 475 μm. The quartz sand was thoroughly cleaned in order to remove any metal and organic impurities (Redman et al., 2004). The cleaned quartz sand was re-hydrated by boiling the mixture in de-ionized (DI) water (Millipore, Billerica, MA) for at least 1 h prior to wet-packing the column. The zeta potential of crushed porous medium was determined at desired conditions using an Otsuka Zetasizer ELS-Z.

Three pH (6, 9, and 10) and two ionic strength (IS) (0.1 and 10 mM) values were selected to encompass expected ranges in typical groundwater environments (Jewett et al., 1995; Kim et al., 2009). The final pH was adjusted using either 0.1 N HCl or NaOH solution (denoted as an unbuffered condition below). For some conditions, a carbonate buffer (a mixture of 9×10^{-4} M $NaHCO_3$ and 1×10^{-4} M Na_2CO_3) (Delory and King, 1945; Kim et al., 2009) was utilized to increase the pH of the solution (denoted as a buffered condition below). The IS of the solutions was adjusted using NaCl as the background electrolyte. All chemicals were reagent grade (Fisher Scientific).

2.2. ZnO nanoparticles and suspension preparation

ZnO nanoparticles were synthesized using a previously described procedure (Han et al., 2014). This protocol is used to prepare ZnO nanoparticles for commercial cosmetics in South Korea. The Supplementary Information (SI) provides details of the synthesis and characterization procedure for ZnO nanoparticles, and their physical properties under dry conditions (Fig. S1 and Table S1). The protocol used to prepare the ZnO-NP suspension has also been fully described in the SI. The influent suspension that was used in the column experiments described below consisted of 20 mg/L ZnO-NPs at a pH = 9 and IS equal to 0.1 or 10 mM NaCl. The pH 9 solution was selected for initial ZnO-NPs transport tests to minimize dissolution and complexities from Zn^{2+} ions that might have different transport characteristics. The dissolution characteristics of ZnO-NPs are presented in Fig. S2. Influent ZnO-NP suspensions were characterized by measuring their size and zeta potential using a Zetasizer (ELS-Z, Otsuka Eletronics Co., Japan). The measurements were performed right before the column experiments and were repeated 30–40 times at room temperature (25 °C).

2.3. Bacterial culture and biofilm formation in quartz sand column

P. putida (KTCT 1641), a representative soil bacterium (Jost et al., 2010), was provided by the Korea Research Institute of Bioscience and Biotechnology (KRIBB) for biofilm formation. *P. putida* was grown following the protocol provided by the KRIBB. Specifically, they were grown in a nutrient broth medium (Difco) that contained 3.0 g beef extract and 5.0 g peptone per liter, without a pH control. *P. putida* cells were inoculated into 500-ml Erlenmeyer flasks containing 200 ml of sterile medium and cultivated aerobically in an orbital rotary shaker (200 rpm) at 26 °C for 20 h. After growth, the cells were harvested by means of centrifugation (SIF-5000R, Lab companion, South Korea) at 3700 *g* for 15 min and were washed three times with 10 mL of 1 mM NaCl to remove residuals from cell surfaces. Cell pellets were then re-suspended in 5 mL of 1 mM NaCl, and this suspension was used as stock for subsequent characterization and column tests.