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Mobility of nanosized cerium dioxide and polymeric capsules in quartz and loamy sands saturated with model and natural groundwaters

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ABSTRACT

The environmental and health risks posed by emerging engineered nanoparticles (ENPs) released into aquatic environments are largely dependent on their aggregation, transport, and deposition behavior. Herein, laboratory-scale columns were used to examine the mobility of polyacrylic acid (PAA)-coated cerium dioxide nanoparticles ($n\mathrm{CeO_2}$) and an analogous nanosized polymeric capsule (*n*CAP) in water saturated quartz sand or loamy sand. The influence of solution ionic strength (IS) and cation type (Na^+, Ca^{2+}, or Mg^{2+}) on the transport potential of these ENPs was examined in both granular matrices and results were also compared to measurements obtained using a natural groundwater. ENP suspensions were characterized using dynamic light scattering and nanoparticle tracking analysis to establish aggregate size, and laser Doppler electrophoresis to determine ENP electrophoretic mobility. Regardless of IS, virtually all $n\mathrm{CeO_2}$ particles suspended in $NaNO_3$ eluted from the quartz sand-packed columns. In contrast, heightened $n\mathrm{CeO_2}$ and *n*CAP particle retention and dynamic (time-dependent) transport behavior was observed with increasing concentrations of the divalent salts and in the presence of natural groundwater. Enhanced particle retention was also observed in loamy sand in comparison to the quartz sand, emphasizing the need to consider the nature of the aqueous matrix and granular medium in evaluating contamination risks associated with the release of ENPs in natural and engineered aquatic environments.

1. Introduction

Engineered nanoparticles (ENPs) exhibit appealing physicochemical properties that are absent in larger particles with equivalent chemical compositions (Auffan et al., 2009; Klaine et al., 2008). Consequently, ENPs of all types (e.g., carbon nanotubes, metals and metal oxides, semiconductors, polymers) are being incorporated into a growing number of consumer products. For example, nanosized titanium dioxide ($n\mathrm{TiO_2}$) is employed in the production of sunscreens and paint, zinc oxide (*n*ZnO) is used in cosmetics and solar cells, and iron oxides are incorporated into pigments and used in biological applications (Ju-Nam and Lead, 2008; Klaine et al., 2008). Comprehensive reviews of existing ENP types and their applications are available in the literature (Ju-Nam and Lead, 2008; Klaine et al., 2008). An inventory of consumer products containing ENPs has also been developed by the Woodrow Wilson International Center for Scholars (available at http://www.nanotechproject.org/).

Nanosized cerium dioxide ($n\mathrm{CeO_2}$) is currently employed in several applications. It can serve as a polishing agent when manufacturing glass and can serve as a capacitor and

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semiconductor (Johnson and Park, 2012). Given that $nCeO_2$ protects against the oxidative stress caused by reactive oxygen species, medical applications have also been described. These include the use of $nCeO_2$ as an antioxidant to treat retinal disorders such as glaucoma (García et al., 2011). Since $nCeO_2$ effectively absorbs ultraviolet radiation, it is used in the production of sunscreens and UV blocking agents (Cassee et al., 2011). Surface reactive properties also make $nCeO_2$ a useful exhaust gas catalyst (Cassee et al., 2011; Van Hoecke et al., 2011).

Exposure to ENPs can occur at all stages of the particle lifecycle, including fabrication and processing, product usage and disposal (Wiesner and Bottero, 2007). Many $nCeO_2$ applications are dispersive in nature, increasing the risk for exposure and heightened interactions with a variety of environmental media (Cassee et al., 2011). The release of $nCeO_2$ particles employed as UV blocking agents or diesel fuel additives may threaten aquatic and sediment dwelling organisms (Van Hoecke et al., 2011). Beyond that, ENPs entering soil environments may reach groundwater aquifers, potentially contaminating drinking water supplies and causing unknown health, safety and environmental issues (Klaine et al., 2008). Once introduced into natural subsurface environments or engineered water treatment processes, particle aggregation, transport and deposition behavior will play a major role in determining $nCeO_2$ fate, bioavailability and the likelihood for human exposure. Thus, a comprehensive understanding of $nCeO_2$ transport and deposition behavior in water saturated granular systems is required for the protection of environmental and public health.

Well-controlled laboratory experiments using columns packed with different granular matrices can be useful for drawing links between collector (grain) properties and the mobility of released ENPs in water saturated granular environments (Kretzschmar et al., 1994; Petosa et al., 2010; Quevedo and Tufenkji, 2012). A number of studies have examined the transport and deposition of ENPs in quartz sand-packed columns, providing useful insights on the effects of environmental factors such as water chemistry, grain size, particle size, and porewater velocities on ENP mobility (Petosa et al., 2010). However, little is known regarding the transport and deposition of $nCeO_2$ in water saturated granular environments (Li et al., 2011b; Liu et al., 2012).

Published $nCeO_2$ transport studies have focused on the transport of bare particles suspended in monovalent salt solutions (namely, NaCl). In considering the effect of pH and IS on $nCeO_2$ deposition on sand, Li et al. observed increased particle retention under acidic conditions (pH 3) and with increasing NaCl IS (Li et al., 2011b). Liu et al. investigated $nCeO_2$ deposition in sand-packed columns and using a quartz crystal microbalance with dissipation (QCM-D). In NaCl (pH 6.5 and 8), far more $nCeO_2$ deposition was observed in the packed columns than on silica QCM-D sensors, likely due to physical straining as a result of ENP aggregation and heterogeneities on the quartz sand collectors. Heightened $nCeO_2$ mobility in the packed columns was observed in the presence of organic matter (Liu et al., 2012). The transport of $nCeO_2$ in the presence of divalent salt solutions (e.g., $CaCl_2$ and $MgCl_2$) and natural groundwater matrices has not been reported in the literature. Furthermore, studies investigating $nCeO_2$ transport in granular matrices other than quartz sand are not available.

While the types of granular materials encountered in the natural subsurface environment can vary broadly (Kretzschmar et al., 1994), few studies have investigated the transport behavior of selected ENPs in media other than glass beads and quartz sand (Jaisi and Elimelech, 2009; Petosa et al., 2010). Previously, our group has shown that the retention of two different carboxyl-terminated quantum dots (QDs) and a carboxylated polystyrene latex nanoparticle can be enhanced by at least one order of magnitude in a loamy sand versus a quartz sand of comparable mean grain size (Quevedo and Tufenkji, 2012). Interestingly, the 3 different ENPs exhibit similar mobility in the quartz sand, but distinct transport behaviors in the loamy sand. This suggests that differences in the affinities of the polymer-coated ENPs for specific soil components can control their fate in subsurface environments. Jaisi and Elimelech investigated the transport of carboxyl-functionalized single-walled carbon nanotubes (SWCNTs) in columns packed with a complex granular matrix; namely, a sandy clay loam. Their study found SWCNT transport to be governed by physical straining, likely due to the combined effects of a very large NP aspect ratio, NP aggregation in solution and variability in soil particle size, porosity and permeability (Jaisi and Elimelech, 2009).

The purpose of this work is to systematically investigate the mobility of a polyacrylic acid (PAA)-coated $nCeO_2$ particle in water-saturated quartz sand and loamy sand matrices. Natural and artificial groundwaters are used to study the effect of electrolyte species and ionic strength (IS) on selected particle properties (i.e., aggregate size and surface potential) and transport potential. This study is the first to consider the effects of more complex granular materials and water chemistries on the transport behavior of $nCeO_2$ in water saturated porous media. Moreover, the behavior of the PAA-coated $nCeO_2$ is compared to that of analogous PAA-based nanocapsules (nCAPs) to assess whether both particle types exhibit similar transport potentials. The nCAPs employed herein were designed to serve as water dispersible polymeric nanocapsules in agricultural applications, providing a further incentive to examine their behavior in model subsurface environments.

2. Materials and methods

2.1. Natural groundwater characterization

Natural groundwater, originating from a domestic well in the township of North Glengarry, Ontario, was thoroughly characterized (methods and results are included in the Supporting Information, Table S1 and Figure S1).

2.2. Granular collector surface characterization

Quartz sand ($-50 + 70$ mesh size, $d_{50} = 256$ μm, Sigma–Aldrich) and loamy sand ($d_{50} = 225$ μm) acquired at a 35 cm depth from an Agriculture and Agri-Food Canada (AAFC) farm plot located in St-Augustin-de-Desmaures, QC, were employed as granular materials in this study. An electrokinetic analyzer (Anton Paar