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Effect of different-sized colloids on the transport and deposition of titanium dioxide nanoparticles in quartz sand

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ABSTRACT

Colloids (non-biological and biological) with different sizes are ubiquitous in natural environment. The investigations regarding the influence of different-sized colloids on the transport and deposition behaviors of engineered-nanoparticles in porous media yet are still largely lacking. This study investigated the effects of different-sized non-biological and biological colloids on the transport of titanium dioxide nanoparticles ($nTiO_2$) in quartz sand under both electrostatically favorable and unfavorable conditions. Fluorescent carboxylate-modified polystyrene latex microspheres (CML) with sizes of 0.2–2 μm were utilized as model non-biological colloids, while Gram-negative *Escherichia coli* (~1 μm) and Gram-positive *Bacillus subtilis* (~2 μm) were employed as model biological colloids. Under the examined solution conditions, both breakthrough curves and retained profiles of $nTiO_2$ with different-sized CML particles/bacteria were similar as those without colloids under favorable conditions, indicating that the copresence of model colloids in suspensions had negligible effects on the transport and deposition of $nTiO_2$ under favorable conditions. In contrast, higher breakthrough curves and lower retained profiles of $nTiO_2$ with CML particles/bacteria relative to those without copresent colloids were observed under unfavorable conditions. Clearly, the copresence of model colloids increased the transport and decreased the deposition of $nTiO_2$ in quartz sand under unfavorable conditions (solution conditions examined in present study). Both competition of deposition sites on quartz sand surfaces and the enhanced stability/dispersion of $nTiO_2$ induced by copresent colloids were found to be responsible for the increased $nTiO_2$ transport with colloids under unfavorable conditions. Moreover, the smallest colloids had the highest coverage on sand surface and most significant dispersion effect on $nTiO_2$, resulting in the greatest $nTiO_2$ transport.

1. Introduction

Titanium dioxide nanoparticles ($nTiO_2$), one of the most important metal oxide nanoparticles, have been widely used in products including cosmetics, sunscreens, paints, coatings, photocatalyst, and environmental catalysts (Chen and Mao, 2007; Lorenz et al., 2010; Mueller and Nowack, 2010). The increasing applications of $nTiO_2$ will inevitably release $nTiO_2$ into natural environment (Gottschalk et al., 2009; Lin et al., 2010; Mueller and Nowack, 2008). Due to their potential risk to the natural ecosystem and human health (Baun et al., 2009; Scown et al., 2010; Wiesner et al., 2006), understanding the fate and transport of $nTiO_2$ in natural systems, especially in the subsurface, is therefore imperative for the protection of human health.

Great efforts have been devoted to investigating the transport and deposition of $nTiO_2$ under various conditions, such as pH, ionic strength, ionic composition, nanoparticle concentration and size, and flow velocity (Ben-Moshe et al., 2010; Chen et al., 2011; Chowdhury et al., 2011; Lecoanet and Wiesner, 2004; Petosa et al., 2010). Furthermore, the influence of abundant natural organic matter (NOM) on the transport of $nTiO_2$ has been highlighted by several investigations (Aiken et al., 2011; Chen et al., 2012; Domingos et al., 2009; Thio et al., 2011). In recent years, the effects of copresent colloids on the transport and deposition of

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nanoparticles have drawn attention (Abdel-Fattah et al., 2013; Cai et al., 2013; Chowdhury et al., 2012; Wang et al., 2011, 2015). For example, Chowdhury et al. (2012) reported that due to electrosteric and electrostatic effects, bacteria present in suspensions significantly decreased nTiO$_2$ deposition on glass surfaces. Very recently, Abdel-Fattah et al. (2013) reported that smectite clay particles could increase the transport of plutonium colloids in subsurface soil. Obviously, the copresence of colloidal particles in suspensions could have great effect on the transport and deposition of nTiO$_2$ in porous media. Colloids ranging from nanometer-size to micrometer-size are ubiquitous in natural environment. May and Li (2013) found that different-sized colloids could possess different deposition capacity (surface coverage) on porous media. Thus, the copresence of different-sized colloids would have different influence on the transport and deposition of nTiO$_2$ in porous media. Moreover, different-sized colloids might have different influence on the dispersion of nTiO$_2$ and thus the sizes of nTiO$_2$ might be varied with the copresence of different-sized colloids. The sizes of nanoparticles have been previously demonstrated to play an important role on the transport of nanoparticles in porous media (Darlington et al., 2009; Dunphy Guzman et al., 2006; Lecoanet et al., 2004; Phenrat et al., 2009). The general conclusion from previous studies is that decreasing the sizes of nanoparticles greatly increased the transport of nanoparticles in packed coarse sand columns (Chen et al., 2012; Li et al., 2008; Lu et al., 2013). However, the effect of copresent colloid sizes on nTiO$_2$ transport was still unknown, and thus requires investigation.

Hence, this study is designed to fully understand the role of suspended different-sized colloidal particles (including non-biological and biological ones) on the transport behavior of nTiO$_2$ in quartz sand by monitoring both breakthrough curves (BTCs) and retained profiles (RPs) of nTiO$_2$ under various solution chemistries. Spherical fluorescent carboxylate-modified polystyrene latex microspheres (CML) with diameters from 0.2 to 2 μm were employed as model non-biological colloids, while bacteria with diameters from 1 to 2 μm were employed as model biological colloids in this study. Packed column experiments were performed both with and without CML particles or bacteria in nTiO$_2$ suspensions. BTCs and RPs with copresent colloids were compared with those without copresent colloids in solutions. Possible mechanisms by which different-sized colloids affected the transport behavior of nTiO$_2$ were proposed and discussed.

2. Method and materials

2.1. Preparation of titanium dioxide, microsphere, and bacteria suspensions

Anatase titanium dioxide powders (nTiO$_2$, purity greater than 99.7%, in dry form) were purchased from Sigma–Aldrich Corp. (catalog # 637254). The diameter of nTiO$_2$ provided by the manufacturer is less than 25 nm. nTiO$_2$ nanoparticle stock suspension (1000 mg L^{-1}) was prepared by suspending nTiO$_2$ nanopowders in Milli-Q water and sonicated at 600 W for 10 min with a sonicating probe (Ningboxinzhi Biotechnology Ltd., China).

Fluoresbrite yellow-green fluorescent CML particles of three sizes with diameter of 0.2, 1, and 2 μm (with negative surface charge), purchased from Molecular Probes (Invitrogen Canada Inc.), were employed as model non-biological colloids. The 0.2, 1, and 2 μm CML stock suspensions have particle number concentrations of 4.55X10^{12}, 3.60 × 10^{10}, and 4.55 × 10^{9} particles mL^{-1}, respectively. The CML particles are hydrophilic with a density of 1.05 g cm^{-3} (reported by the manufacturer) and electrosterically stabilized. Stock solutions for 0.2–2 μm CML particles were diluted in NaCl solutions to achieve the desired target influent concentrations for CML particles. The concentrations of CML particles were analyzed by using a fluorescence spectrophotometer (CaryEclipse, Varian, Australia) with 10 mm × 10 mm quartz cuvette (Mondal and Sleep, 2013). The optimum excitation/emission wavelengths to detect the CML particles were determined to be 505/515 nm, and the excitation and emission slits of the instrument were both set at 5 nm. The calibration results confirmed a linear correlation between the CML particle concentration and the intensity of the fluorescence signals over the range of the investigated CML particle concentrations (Fig. S1). A gram-negative strain *Escherichia coli* (*E. coli*) BL21 and a gram-positive strain *Bacillus subtilis* were used as mode biological colloids in this study. The protocols for cell grown and harvest were provided in Text S1 in the Supplementary information. After harvest, the growth medium was decanted, and the cell pellets were then resuspended in Milli-Q water. The centrifugation and re-suspension process was repeated twice. The prepared stock cell concentration was determined by using a counting chamber (Buerker-Tuerk Chamber, Marienfeld Laboratory Glassware, Germany) with an inverted fluorescent Ti-E microscope (Nikon, Japan) under bright field. The stock concentration was typically at ~10^{9}–10^{10} cells mL^{-1}.

For transport experiments, the influent mass concentration of nTiO$_2$ was set to be 50 mg L^{-1} (~4.8 × 10^{10} particles mL^{-1} as spheres), the number concentrations of CML particles were maintained to be 9 × 10^{8}, 7.2 × 10^{6}, and 9 × 10^{5} ± 30% particles mL^{-1} for 0.2, 1, and 2 μm CML particles (in equal mass concentration for different-sized CML particles, ~4 mg L^{-1}), respectively, and the influent concentration of bacteria was set to be 1.0 × 10^{7} ± 30% cells mL^{-1}. The ionic strengths of experimental suspensions were 1 and 10 mM in NaCl solutions. Suspension pH was set to be 5 and 7 by adjusting with 0.1 M HCl and 0.1 M NaOH. Zeta potentials of individual nTiO$_2$, CML particles, and bacteria under examined conditions were measured using Zetasizer Nano ZS90 (Malvern Instruments, UK). Measurements were performed at room temperature (25 °C) and repeated 9–12 times. The hydrodynamic sizes (or size distribution) of individual nTiO$_2$, CML particles, bacteria and also nTiO$_2$-CML mixtures were determined by dynamic light scattering (DLS) measurement.

2.2. Porous media and column experiments

Quartz sand (ultrapure with 99.8% SiO$_2$) (Hebeizhensheng Mining Ltd., Shijiazhuang, China) with sizes ranging from 417 to 600 μm was used for individual nanoparticle transport and nanoparticle cotransport experiments in porous media. The procedure used for cleaning the quartz sand is provided in the Supplementary information (Text S2). The zeta potentials of the crushed quartz sand were also measured under the experimental conditions using the Zetasizer Nano ZS90. The electrophoretic mobility measurements were repeated 9–12 times. Cylindrical Plexiglas columns (10 cm long and 2 cm inner diameter) were wet-packed with cleaned quartz sand. Prior to packing, the cleaned quartz sand was rehydrated by boiling in Milli-Q water for at least 0.5 h. After the rehydrated quartz sand was cooled, the columns were packed by adding wet quartz sand in small increments (~1 cm) with mild vibration of the column to minimize any layering or air entrapment. One 80 mesh fabric screen was placed at each end of the column. The porosity of packed column was ~0.42.

The transport experiments were conducted at 1 and 10 mM in NaCl solutions under both electrostatically favorable (pH 5) and unfavorable (pH 7) conditions. After packing, the columns were pre-equilibrated with at least ten pore volumes (10 PV) of NaCl salt solutions at desired ionic strength and pH. Following pre-equilibration, 3 PV of nanoparticle suspensions were injected into the column, followed by elution with 5 PV of salt solution at the same ionic strength. The solutions were injected into the columns