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Influence of gravity on transport and retention of representative engineered nanoparticles in quartz sand

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ABSTRACT

Four types of NPs: carbon nanotubes and graphene oxide (carbon-based NPs), titanium dioxide and zinc oxide metal-oxide NPs, were utilized to systematically determine the influence of gravity on the transport of NPs in porous media. Packed column experiments for two types of carbon-based NPs were performed under unfavorable conditions in both up-flow (gravity-negative) and down-flow (gravity-positive) orientations, while for two types of metal-oxide NPs, experiments were performed under both unfavorable and favorable conditions in both up-flow and down-flow orientations. Both breakthrough curves and retained profiles of two types of carbon-based NPs in up-flow orientation were equivalent to those in down-flow orientation, indicating that gravity had negligible effect on the transport and retention of carbon-based NPs under unfavorable conditions. In contrast, under both unfavorable and favorable conditions, the breakthrough curves for two types of metal-oxide NPs in down-flow orientation were lower relative to those in up-flow orientation, indicating that gravity could decrease the transport of metal-oxide NPs in porous media. The distinct effect of gravity on the transport and retention of carbon-based and metal-oxide NPs was mainly attributed to the contribution of gravity to the force balance on the NPs in quartz sand. The contribution of gravity was determined by the interplay of the density and sizes of NP aggregates under examined solution conditions.

1. Introduction

With the rapid growth of the nanotechnology industry, different types of nanomaterials such as carbon-based nanoparticles (NPs) and metal/metal-oxide NPs have been fabricated and used increasingly in various fields. Carbon nanotubes (CNTs), graphene oxide (GO), titanium dioxide (nTiO$_2$), and zinc oxide (nZnO) NPs, have been regarded as the most important nanomaterials due to their various applications (Hu et al., 2011; Mauter and Elimelech, 2008; Soares et al., 2008). The massive applications would eventually result in the entrance of these NPs into the natural environment. To date, physicochemical factors such as fluid velocity (Lecoanet and Wiesner, 2004), solution chemistry (pH, ionic strength, and ion type) (French et al., 2009; Jiang et al., 2012; Lanphere et al., 2013; Liu et al., 2009), NP concentration (Chowdhury et al., 2011; Jaisi and Elimelech, 2009), natural organic matter (Chowdhury et al., 2012; Jones and Su, 2014), surfactant (Fang et al., 2013; Lu et al., 2013, 2014), as well as bacteria (Chowdhury et al., 2012; Jones and Su, 2014) have been shown to significantly affect the transport behavior of NPs in porous media.

A few previous studies found that gravity could also affect the transport and retention of (bio)colloids (Chen et al., 2009; Chrysikopoulos and Syngouna, 2014; Ma et al., 2011; Wan et al., 1995). For instance, by using a parallel plate flow chamber system, Chen et al. (2009) investigated the effects of gravity on

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the deposition of both bacteria and microspheres on glass surfaces under both unfavorable and favorable conditions. They found under both unfavorable and favorable conditions, gravity could increase the deposition of both bacteria and microsphere on glass collectors. By employing unit cell models, Ma et al. (2011) examined the effects of gravity on colloid transport and retention in porous media and demonstrated that gravity could also enhance the retention of colloid (in down-flow orientation). Moreover, the effect of gravity was more significant for large (>2 μm) and/or dense (>1.1 g cm^{-3}) colloids. Unlike the observation that gravity could increase the deposition of micron-sized colloids (Chen et al., 2009), Chrysikopoulos and Syngouna (2014) recently found that gravity could decrease the retention (increased transport) of clay particles in porous media. Obviously, contradicted observations on the effect of gravity on the transport and retention of (bio)colloids have been reported. Moreover, to date, the effect of gravity on the fate and transport of engineered NPs in porous media has not been studied systematically and thus requires further investigation.

Hence, this study was designed to fully investigate the role of gravity on the transport and retention of engineered NPs in quartz sand by monitoring both breakthrough curves (BTCs) and retained profiles (RPs) of NPs under various solution conditions. CNTs and GO were used as typical carbon-based nanomaterials; while, *n*TiO_2 and *n*ZnO were employed as typical metal-oxide nanomaterials. Packed column experiments were performed in both up-flow and down-flow orientations. BTCs and RPs of NPs in up-flow orientations were compared with those in down-flow orientations. Possible mechanisms by which gravity affected the transport behavior of NPs were proposed and discussed.

2. Material and methods

2.1. Preparation and characterization of NPs

Carboxyl (−COOH) functionalized multi-walled carbon nanotubes (CNTs, purity greater than 95%, in dry form) synthesized by CVD method with 0.7 wt.% metal residual (0.5% Fe and 0.2% Ni) were purchased from Chengdu Organic Chemicals Co. Ltd., China. Graphene oxide (GO) with a planar structure was prepared by a modified Hummers method (Cote et al., 2009) and the detailed synthesis method has been reported previously (Zhang et al., 2013). The oxygen contents of CNTs and GO were 7 at.% and 32 at.%, respectively. Based on previous studies (Jaisi and Elimelech, 2009; Lanphere et al., 2013; Qi et al., 2014; Tian et al., 2012), the CNTs and GO NP stock suspension were prepared by suspending 20 mg CNTs or GO powders in 200 mL Milli-Q water (Q-Gard 1, Millipore Inc., MA) and sonicated for 20 min with a sonicating probe (Ningboxinzhi Biotechnology Ltd., China) at 500 W. The resulting materials were immediately centrifuged (15 min, 5000 *g*) to remove aggregates/bundles. The supernatant was then transferred carefully into a clean bottle and then sonicated for another 20 min. The total organic carbon (TOC) of the CNTs and GO stock solution was determined to be ~50 and 60 mg L^{-1}, respectively, using a TOC-meter (TOC-V_{CPN}, Shimadzu, Japan).

Anatase titanium dioxide powders (*n*TiO_2, purity greater than 99.7%, in dry form) and zinc oxide powders (*n*ZnO, purity greater than 97%, in dry form) were purchased from Sigma-Aldrich Corp. (catalog no. 637254 for *n*TiO_2 and 677450 for *n*ZnO). Similar to many previous studies (Cai et al., 2013; Chen et al., 2012; Chowdhury et al., 2011), *n*TiO_2 and *n*ZnO NP stock suspension (1000 mg L^{-1}) was prepared by suspending *n*TiO_2 or *n*ZnO nanopowders in Milli-Q water and sonicating with a sonicating probe (Ningboxinzhi Biotechnology Ltd., China). The morphologies of the prepared CNTs, GO, *n*TiO_2, and *n*ZnO suspensions after sonication (in Milli-Q water) were determined by SEM analysis (FEI Nova Nano SEM 430) and the results were presented in Fig. S1.

For transport experiments, the influent concentrations of CNTs and GO were maintained at 10 mg L^{-1} TOC, while the influent concentration of *n*TiO_2 and *n*ZnO was set at 50 mg L^{-1}. The isoelectric point (IEP) for both CNTs and GO was not found in the wide pH range tested (from pH 3 to 11; Fig. S2). Thus, transport experiments for CNTs and GO were performed at the unadjusted pH (pH 6 and 5 for CNTs and GO, respectively), which could make the experimental conditions to be unfavorable for CNTs and GO deposition. Unlike the carbon-based nanomaterials, *n*TiO_2 and *n*ZnO had IEPs right in the midst of the environmentally relevant pH range, which could create electrostatically favorable or unfavorable conditions for their deposition. Specially, *n*TiO_2 particles used in our previous study had a near-neutral IEP value (~pH 6) (Cai et al., 2013) (Fig. S2), while, the IEP value of *n*ZnO was about pH 9.5 (Fig. S2), which was consistent with previous studies (Kim et al., 2012; Li et al., 2011, 2014). To achieve both favorable and unfavorable conditions for the deposition of NPs, the *n*TiO_2 suspension pH was set to be 5 (favorable deposition) and 7 (unfavorable deposition) by adjusting with 0.1 M HCl or NaOH. For *n*ZnO, an unadjusted solution pH (~7.5) was selected to make the experimental condition to be favorable for *n*ZnO deposition, while, the pH was set to be 10 to make unfavorable condition. It should be noted that the dissolutions of *n*ZnO NPs were quite low at these two pHs (~0.6 wt.%). The ionic strengths of the NP suspensions were 0.1 and 10 mM in NaCl solutions. After preparation, NP suspensions were sonicated at 100 W for 5 min prior to each transport experiment. The zeta potentials of the CNTs (10 mg L^{-1}), GO (10 mg L^{-1}), *n*TiO_2 (50 mg L^{-1}), and *n*ZnO (50 mg L^{-1}), under these conditions, were measured using a Zetasizer Nano ZS90 (Malvern Instruments, UK) (Table S2). Measurements were performed at room temperature (25 °C) and repeated 9–12 times. The particle sizes of CNTs, GO, *n*TiO_2, and *n*ZnO were determined by dynamic light scattering (DLS) measurement (Table S2). The resulted hydrodynamic diameters of CNTs, GO, *n*TiO_2, and *n*ZnO in Milli-Q water after sonication were 189.3 ± 15.9, 396.2 ± 11.4, 436.0 ± 9.9, and 502.4 ± 16.2 nm, respectively.

2.2. Porous media

Quartz sand (ultrapure with 99.8% SiO_2; Hebeizhensheng Mining Ltd., Shijiazhuang, China) with sizes ranging from 417 to 600 μm, commonly used as model porous media in many previous studies (Chrysikopoulos et al., 2012; Solovitch et al., 2010; Syngouna and Chrysikopoulos, 2012), was used for NP transport experiments in the present study. The procedure used for cleaning the quartz sand was provided in the Supplementary Information (Text S1). The zeta potentials of the crushed quartz sand were also measured under the experimental conditions

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