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Cotransport of multi-walled carbon nanotubes and titanium dioxide nanoparticles in saturated porous media

Xueting Wang [a, 1], Li Cai [a, 1], Peng Han [a], Daohui Lin [b], Hyunjung Kim [c], Meiping Tong [a, *, 1]

[a] The Key Laboratory of Water and Sediment Sciences, Ministry of Education, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, PR China
[b] Department of Environmental Sciences, Zhejiang University, Hangzhou 310058, PR China
[c] Department of Mineral Resources and Energy Engineering, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju-si, Jeollabuk-do 561-756, Republic of Korea

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ABSTRACT

The cotransport of multi-walled carbon nanotubes (MWCNTs) and nanoscaled titanium dioxide (nano-TiO_2) in porous media were investigated in 1 and 10 mM NaCl at both pH 5 and 7. Nano-TiO_2 decreased MWCNTs transport under all conditions. The increased MWCNTs deposition at pH 5 was due to MWCNTs deposition onto previously deposited nano-TiO_2 and codeposition of nano-TiO_2-MWCNTs aggregates; whereas, codeposition of nano-TiO_2-MWCNTs aggregates contributed to the increased MWCNTs deposition at pH 7. MWCNTs increased nano-TiO_2 transport under all conditions except in 10 mM NaCl at pH 5. MWCNTs facilitated transport drove to the increased nano-TiO_2 transport in 1 mM NaCl at pH 5; whereas, competition of deposition sites and stabilization of nano-TiO_2 by MWCNTs mainly caused the increased nano-TiO_2 transport at pH 7. Although MWCNTs didn't affect nano-TiO_2 breakthrough curve in 10 mM NaCl at pH 5, concurrent aggregation induced straining yet shifted nano-TiO_2 retained profile from log-linear to hyper-exponential decreases.

1. Introduction

A large variety of engineered carbon-based (e.g., carbon nanotubes and fullerene) and metal/metal oxide-based nanomaterials (e.g., Ag, Fe^0, CuO, ZnO, Al_2O_3, and TiO_2) are currently widely utilized in consumer and industrial products (Petosa et al., 2010). Among these nanomaterials, carbon nanotubes (CNTs) including single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) are considered as the most promising carbon-based nanomaterial, with wide applications in biomedical industry (Shen et al., 2009; Shi et al., 2009), construction (Lee et al., 2010) and environmental protection fields (Mauter and Elimelech, 2008). Nanoscaled titanium dioxide (nano-TiO_2) has been regarded as one of the most important metal oxide-based nanomaterials with great utilization in different products, such as cosmetics, sunscreens, paints, coatings, and photocatalysts (Chen and Mao, 2007; Guzman et al., 2006). Nanoparticles (NPs) would be inevitably released into environment during the disposal processes especially at sites for electronic waste (e-waste) disposal (Klaine et al., 2008; Koehler et al., 2008; Nowack and Bucheli, 2007; Robichaud et al., 2009). CNTs and nano-TiO_2 have been shown to contain toxic effects to organisms such as rats, algae, microbes, invertebrates, fish, as well as human cells (Lam et al., 2006; Lee et al., 2010; Liu et al., 2009; Long et al., 2006; Rodrigues et al., 2013; Warheit et al., 2007). The release of these two types of NPs into natural systems would cause potential risk to both ecosystems and human health. Information on the fate and transport of CNTs and nano-TiO_2 in natural systems, especially in the subsurface, is therefore required for the protection of human health.

In recent years, great efforts have been undertaken to investigate the transport behaviors of CNTs and nano-TiO_2 under environmentally relevant conditions. Factors such as fluid velocity (Chowdhury et al., 2011; Lecoanet and Wiesner, 2004; Lu et al., 2013), solution chemistry (pH, ionic strength (IS), and ion component) (Ben-Moshe et al., 2010; Chen et al., 2011; French et al., 2009; Tian et al., 2012b), property of porous media (e.g. size and surface heterogeneity) (Han et al., 2014; Joo et al., 2009; Kasel et al., 2013; Mattison et al., 2011), NP property (e.g. dimensions and fabrication process) (Chowdhury et al., 2012b; O'Carroll et al., 2013; Wang et al., 2012), surfactant (Godinez and Darnault, 2011; Lu et al., 2013), natural organic matter (NOM) (Aiken et al., 2011; Keller

* Corresponding author.
E-mail addresses: tongmeiping@pku.edu.cn, tongmeiping@iee.pku.edu.cn (M. Tong).
[1] These authors contributed equally to this work.

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et al., 2010; Thio et al., 2011) and bacteria (Chowdhury et al., 2012a; Tripathi et al., 2012) have been demonstrated to affect the transport behaviors of CNTs or nano-TiO_2 in porous media. For instance, Lu et al. (Lu et al., 2013) found that surfactant type, sand size, MWCNT concentration, flow velocity, pH and IS all had significant effect on MWCNT transport in quartz sand. Chowdhury et al. (2012a) reported that NOM and bacteria present in suspensions significantly increased nano-TiO_2 transport in porous media. Although the transport and retention kinetics of CNTs or nano-TiO_2 have been extensively explored, these previous studies mainly focused on understanding the fate and transport of one type of NPs (either CNTs or nano-TiO_2) in porous media. Due to their wide applications, it will be inevitable that CNTs and nano-TiO_2 will be released into natural environment simultaneously. Since they contain different surface properties, CNTs and nano-TiO_2 might interact with each other and then alter their transport behaviors in porous media. However, to date, the cotransport behaviors of CNTs and nano-TiO_2 have never been explored. It should be noted that, so far, only one study (Cai et al., 2013) has explored the cotransport behaviors of two types of engineered nanomaterials (nano-TiO_2 and nC_{60} NPs) in porous media. This study demonstrated that the cotransport behavior of nC_{60} and nano-TiO_2 was more complex than that of individual NPs. Although both CNTs and nC_{60} were carbon-based NPs, yet they contain different property (e.g. size, shape, and functional groups). The cotransport behaviors of CNTs and nano-TiO_2 in porous media might be different from those of nC_{60} and nano-TiO_2, and thus requires investigation.

Hence, this study is designed to systematically investigate the cotransport behaviors of MWCNTs and nano-TiO_2, two widely utilized and different shaped engineered NPs, in porous media under environmentally relevant conditions (pH 5 and 7, 1 and 10 mM NaCl). Carboxyl (COOH)-functionalized MWCNTs were employed as model MWCNTs in this study. Both breakthrough curves and retained profiles of MWCNTs and nano-TiO_2 in the cotransport experiments were compared with those from individual NPs transport experiments. Our results showed that the copresence of nano-TiO_2 decreased the transport (increased the retention) of MWCNTs in quartz sand under all examined conditions, while, the copresence of MWCNTs increased nano-TiO_2 transport under all examined conditions except 10 mM NaCl at pH 5. Possible mechanisms controlling the cotransport of MWCNTs and nano-TiO_2 were proposed and discussed.

2. Method and materials

2.1. Preparation of NPs suspension

Carboxyl (−COOH) functionalized multi-walled carbon nanotubes (MWCNTs, ~2.56 wt% of COOH content, purity over 95 wt%) were purchased from the Chengdu Organic Chemicals Co. Ltd, China. The length, outer diameter, specific area of MWCNTs provided by the manufacturer is ~50 μm, 8–15 nm, and more than 233 $m^2\ g^{-1}$, respectively. The MWCNT stock suspension was prepared by suspending 0.01 g MWCNT powders in 100 mL Milli-Q water (Q-Gard 1, Millipore Inc., MA) and sonicated for 20 min with a sonicating probe (Ningboxinzhi Biotechnology LTD., China), and then cooled in ice water. The resulting materials were immediately centrifuged for 15 min at 22 °C to remove aggregates/bundles. The concentration of final MWCNT solution was determined using a TOC-meter (TOC-V_{CPN}, Shimadzu, Japan). Anatase titanium dioxide powders (nano-TiO_2, purity greater than 99.7%, in dry form) were purchased from Sigma–Aldrich Corp. The diameter and specific area provided by the manufacturer is less than 25 nm and 45–55 $m^2\ g^{-1}$, respectively. Nano-TiO_2 stock suspension (1000 mg L^{-1}) was prepared by suspending 0.1 g nano-TiO_2 powder in 100 mL Milli-Q water and sonicated for 10 min with a sonicating probe.

For both individual NPs transport and mixed NPs cotransport experiments, the influent concentration of MWCNTs and nano-TiO_2 in suspension was maintained to be 10 and 50 mg L^{-1}, respectively. To prepare the mixed influent suspensions, a certain amount of MWCNTs solutions was added into nano-TiO_2 suspensions. NaCl solutions were then added into the mixed NPs suspensions. The suspension pH was set to be 5 and 7 by adjusting with 0.1M HCl or 0.1 M NaOH. The ionic strength of NPs suspension was set to be 1 and 10 mM in NaCl solutions. After preparation, the NPs suspensions were sonicated for 5 min prior to each transport experiment. The zeta potentials and sizes of NPs were measured using Zetasizer Nano ZS90 (Malvern Instruments, UK) and the results were provided in Table S1 and Fig. S1. The size distributions of the mixed suspensions under various conditions were provided in Fig. S2. The morphology and size distribution of resulted MWCNTs (10 mg L^{-1}) and nano-TiO_2 (50 mg L^{-1}) suspensions after sonication in Milli-Q water were presented in Supplementary Information (Fig. S3).

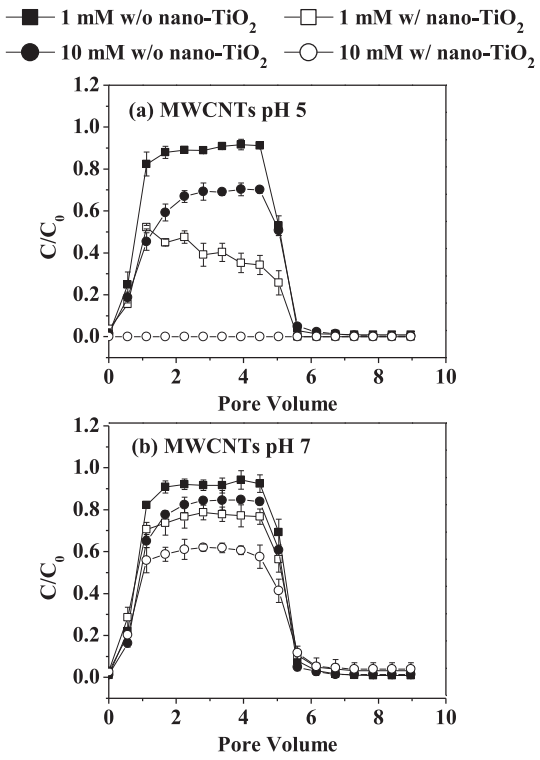

Fig. 1. Breakthrough curves for MWCNTs in quartz sand both with (open symbol) and without (solid symbol) nano-TiO_2 copresent in suspensions at 1 and 10 mM ISs in NaCl solutions at pH 5 (a) and pH 7 (b). Replicate experiments were performed under all conditions ($n \geq 2$).

2.2. Porous media

Quartz sands (ultrapure with 99.80% SiO_2) (Hebeizhensheng Mining Ltd., Shijiazhuang, China) with median diameter of 510 μm were used for all transport experiments. The procedure used for cleaning the quartz sand and is provided in the Supplementary Information (Text S1). The zeta potentials of the crushed quartz sand under the experimental conditions were measured using the Zetasizer Nano ZS90 and the measurements were repeated 9–12 times.

2.3. Column transport experiments

The cylindrical Plexiglass columns (10 cm long and 2 cm inner diameter) were wet-packed with clean quartz sand. The detailed information of column packing could be found in Tong et al. (2005) and Supplementary Information (Text S2). The porosity of packed column was approximately 0.42. After packing, columns were pre-equilibrated with at least 10 pore volumes (PVs) of NPs-free background salt solutions. Following pre-equilibration, 4.5 PVs of NPs suspension were injected into the column, followed by elution with 4.5 PVs of background salt solution (without NPs). For selected experiments, prior to the injection of individual NPs suspension (MWCNTs or nano-TiO_2), the columns were pre-equilibrated with 4.5 PVs of another individual NPs suspensions (nano-TiO_2 or MWCNTs) at desired IS and pH, which was followed by the introduction of 2 PVs of background salt solutions to release the suspended NPs (did not adsorb onto sand surfaces) present in the pore spaces from the columns. The solutions were injected into the columns in up-flow mode using a syringe pump (Harvard Apparatus Inc., Holliston, MA). During column experiments, the input NPs suspension was periodically sonicated to avoid any settlement of NPs and maintain the stability of suspension at desired solution chemistry conditions. The transport experiments were conducted at two ISs (1 and 10 mM) in NaCl solutions at two pH conditions (pH 5 and 7). The pore water velocity of all experiments was set to be 4 m day^{-1} (0.38 mL min^{-1}) to represent fluid velocities in coarse aquifer sediments, forced-gradient conditions, or engineered filtration systems (Harter et al., 1999). Samples from the column effluent were collected (~9 mL) in centrifuge tubes at desired time intervals. The influent and effluent concentrations