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Effect of bacteria on the transport and deposition of multi-walled carbon nanotubes in saturated porous media☆

Peng Han [a, b, 1], Dan Zhou [a, b, 1], Meiping Tong [a, b, *], Hyunjung Kim [c, **]

[a] School of Environment and Energy, Peking University Shenzhen Graduate School, Shenzhen, 518055, China

[b] Key Laboratory of Water and Sediment Sciences, Ministry of Education, College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, 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 influence of bacteria on the transport and deposition behaviors of carbon nanotubes (CNTs) in quartz sand was examined in both NaCl (5 and 25 mM ionic strength) and $CaCl_2$ (0.3 and 1.2 mM ionic strength) solutions at unadjusted pH (5.6–5.8) by direct comparison of both breakthrough curves and retained profiles in both the presence and absence of bacteria. Two types of widely utilized CNTs, i.e., carboxyl- and hydroxyl-functionalized multi-walled carbon nanotubes (MWCNT-COOH and MWCNT-OH, respectively), were employed as model CNTs and *Escherichia coli* was utilized as the model bacterium. The results showed that, for both types of MWCNTs under all examined conditions, the breakthrough curves were higher in the presence of bacteria, while the retained profiles were lower, indicating that the co-presence of bacteria in suspension increased the transport and decreased the deposition of MWCNTs in porous media, regardless of ionic strength or ion valence. Complementary characterizations and extra column tests demonstrated that competition by bacteria for deposition sites on the quartz sand surfaces was a major (and possibly the sole) contributor to the enhanced MWCNTs transport in porous media.

1. Introduction

Due to their broad range of applications in the biomedical industry (Shen et al., 2009; Shi et al., 2009), construction (Lee et al., 2010), and the field of environmental protection (Mauter and Elimelech, 2008), carbon nanotubes (CNTs), including single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), have been regarded as the most promising carbon-based nanomaterials. The increasing utilization of CNTs will inevitably result in the release of SWCNTs and MWCNTs into natural subsurface environments during disposal processes, particularly in landfills (Klaine et al., 2008; Kohler et al., 2008). The release of CNTs into natural systems may pose a potential risk to the natural ecosystem and human health (Mauter and Elimelech, 2008; Nowack and Bucheli, 2007). Understanding the fate and distribution of CNTs in natural environments is therefore important.

The transport and deposition behaviors of CNTs under environmentally relevant conditions have been widely explored in the last few years. Various physical and chemical factors, including fluid velocity (Lecoanet and Wiesner, 2004; Lu et al., 2013), solution chemistry (ionic strength and ion types) (Tian et al., 2012a, b), the properties of individual CNTs (dimensions and surface properties) (Chowdhury et al., 2012b; O'Carroll et al., 2013; Wang et al., 2012), natural organic matter (NOM) (Wang et al., 2008; Yang et al., 2013b), clay particles (Bayat et al., 2015; Cai et al., 2014), surfactants (Lu et al., 2014; Tian et al., 2011), and the co-presence of different nanoparticles (Wang et al., 2014), have been demonstrated to affect the transport and deposition of CNTs in porous media. For example, Wang et al. (2008) found that the presence of humic acid in suspensions greatly enhanced CNTs mobility in porous media. Tian et al. (2011) showed that SWCNTs mobility in porous media can be significantly increased by three types of surfactants. Recently, Cai et al. (2013) reported that the copresence of nano-TiO_2 ($nTiO_2$) in suspensions decreased the transport of MWCNTs in quartz sand. These recent studies particularly

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

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emphasize the importance of co-transport (or co-deposition) of CNTs with other colloids that can be commonly found in subsurface or groundwater environment; no consensus reaches so far in the co-transport behavior of CNTs with other colloids because the transport behavior of CNTs is highly sensitive to the surface properties of colloids that are co-present. This clearly implies that more studies on the co-transport (or co-deposition) of CNTs with other colloids are required for better understanding of their fate in environment.

Sessile bacteria (biofilm) and suspended bacteria are ubiquitous on nearly all environmental surfaces. Previous studies have shown that biofilm could greatly affect the transport of engineered nanoparticles in porous media (Jiang et al., 2013; Lerner et al., 2012; Mitzel and Tufenkji, 2014; Morales et al., 2007; Tong et al., 2010; Tripathi et al., 2012; Xiao and Wiesner, 2013). For example, Lerner et al. (2012) found that the presence of biofilm could increase the retention of zerovalent iron nanoparticles in saturated porous media. Xiao and Wiesner (2013) also reported that biofilm significantly enhanced the retention of various engineered nanoparticles in porous media. Suspended bacteria have also been shown to influence the transport and deposition of nanoparticles (Cai et al., 2016; Chowdhury et al., 2012b). For instance, due to electrosteric and electrostatic effects, Chowdhury et al. (2012a) reported that suspended *Escherichia coli* present in nanoparticle suspensions significantly decreased $n\mathrm{TiO_2}$ deposition on glass surfaces. Very recently, Cai et al. (2016) found that the presence of both *Escherichia coli* and *Bacillus subtilis* in suspensions increased the transport of $n\mathrm{TiO_2}$ in quartz sand in 1 mM NaCl at pH 7. Similarly, bacteria present in suspensions are expected to play an important role in the fate and transport of CNTs. However, to the best of our knowledge, the influence of suspended bacteria on the transport and deposition behaviors of CNTs in porous media has never been explored. Furthermore, recent studies (Chi and Amy, 2004; Foppen et al., 2006, 2008) have reported that the competition for deposition sites on the sand surface, which normally arise from the sand chemical heterogeneity under natural conditions (i.e., unfavorable conditions), with other inorganic or organic colloids significantly influences CNTs transport. Bacteria are also expected to affect CNTs transport/retention in porous sand columns; however, no study has yet addressed this issue.

This study is therefore designed to fully investigate the influence of suspended bacteria on the transport behavior of CNTs in quartz sand by monitoring both breakthrough curves and retained profiles under various solution chemistries. Carboxyl- and hydroxyl-functionalized multi-walled CNTs (MWCNT-COOH and MWCNT-OH, respectively), two widely utilized types of carbon nanotubes, were employed as model CNTs, while *E. coli* was utilized as the model bacterium. Packed column experiments were performed both with and without bacteria in CNTs suspensions. The breakthrough curves and retained profiles obtained in the presence of bacteria were compared with those acquired in the absence of bacteria. Possible mechanisms by which bacteria influence the transport and deposition behaviors of CNTs were proposed and discussed.

2. Materials and methods

2.1. Nanoparticle suspension preparation and characterization

MWCNT-COOH and MWCNT-OH, which are widely utilized types of carbon nanotubes (Liu et al., 2009; Smith et al., 2009; Tian et al., 2012a), were employed as model CNTs. We chose these two different types of MWCNTs since they have distinctly different surface functional groups, which might cause different transport behavior with bacteria. Both types of MWCNTs were purchased from Chengdu Organic Chemicals Co. Ltd. (Chengdu, China). According to the manufacturer, the purity of both types of CNTs was over 95% by mass MWCNTs. The length and outer diameter of both types of MWCNTs were ~50 μm and 8–15 nm, respectively. The COOH and OH contents were ~2.56 wt% and ~3.7 wt%, respectively. CNTs stock suspensions were prepared by suspending 50 mg of CNTs powder in 500 mL of Milli-Q water (Q-Gard1, Millipore Inc, MA, USA) and sonicating for 20 min using an ultrasonication probe (Ningboxinzhi Biotechnology Ltd. P.R.China). The suspension was then cooled in ice water and centrifuged at 5000 *g* for 15 min to remove aggregates/bundles. The supernatant was then carefully transferred into a clean bottle and sonicated for a further 20 min to obtain stable MWCNTs suspension. The concentration of MWCNTs in the stock suspension was determined using a TOC-meter (TOC-V_{CPN}, Shimadzu, Japan). The influent concentration of both types of MWCNTs was adjusted to 10 mg L^{-1} using the stock suspension. After preparation, the MWCNTs influent suspensions were sonicated to increase the stability for 5 min prior to each transport experiment. To prepare the influent suspension containing both MWCNTs and bacteria, a known volume of bacterial stock suspension was added to the MWCNTs suspension. The preparation of the cell stock suspension is provided in the section 2.2. Salt solutions (NaCl or $CaCl_2$) were then added to the mixed MWCNTs / bacterial suspension.

The zeta potentials and sizes of MWCNTs both with and without bacteria were measured using a Zetasizer Nano ZS90 (Malvern Instruments, UK) to complement the column test results. The measurements were conducted at unadjusted pH (5.6–5.8) in both NaCl (5 or 25 mM ionic strength) and $CaCl_2$ (0.3 or 1.2 mM ionic strength) solution. In order to examine the trend of zeta potential of both MWCNTs with pH, the pH of the MWCNTs suspension was adjusted using 0.1 M HCl or 0.1 M NaOH. All measurements were carried out at least in triplicate.

2.2. Cell culture and preparation

The bacterial strain *E. coli* S17-1, labeled by green fluorescent protein (GFP) that were widely used in many previous studies (Jiang et al., 2011; Gogoi et al., 2006; Wu et al., 2010), was used as model bacterium in the transport experiments. The influent bacterial concentration in the mixed nanoparticle and cell suspension was $1.0 \times 10^7 \pm 10\%$ cells mL^{-1}. Note that this cell concentration was adopted based on many previous bacterial transport studies in sand column (Banks et al., 2003; Chowdhury et al., 2012a; Long et al., 2009; Tong et al., 2010; Upadhyayula et al., 2009; Yang et al., 2012b, 2013a) as well as reliable data analysis in terms of cell counting. The growth and harvest protocols for *E. coli*, as well as detailed information regarding the determination of bacterial concentrations, are provided in the Supplementary Information. The average size of the cells was determined to be ca. 1.1 μm via a microscopic analysis. The zeta potentials of bacteria were measured using a Zetasizer Nano ZS90 at unadjusted pH (5.6–5.8) in both NaCl (5 or 25 mM ionic strength) and $CaCl_2$ (0.3 or 1.2 mM ionic strength) solution. The detailed procedure for this measurement can be found elsewhere (Wu et al., 2016; Yang et al., 2012a).

2.3. Porous media and column experiments

Quartz sand (ultrapure with 99.80% SiO_2, Hebeizhensheng Mining Ltd., Shijiazhuang, China) with particle sizes ranging from 417 to 600 μm (with a median diameter of 510 μm) was used as the porous medium for the transport experiments. The cleaning protocol for the quartz sand as well as the column packing protocol is provided in the Supplementary Information. The porosity of the packed columns was approximately 0.42.

After packing, the columns were pre-equilibrated with at least